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Titre :
Caractérisation physico-chimique de la pollution atmosphérique urbaine en Afrique de l'Ouest et étude d'impact sur la santé

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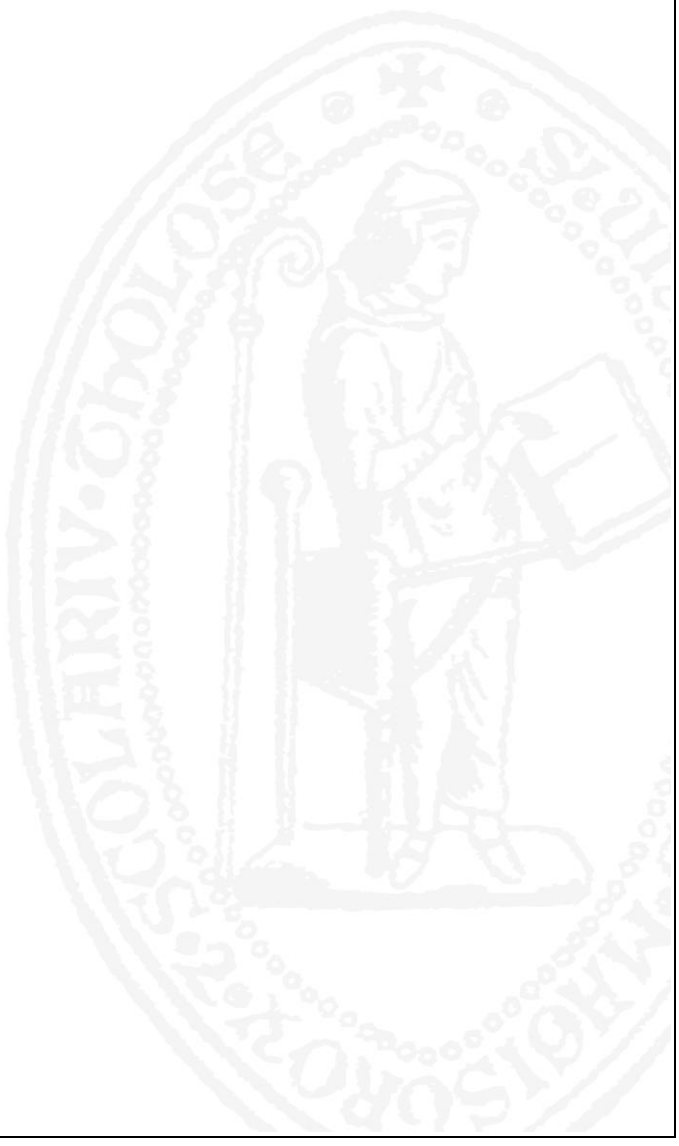

A la mémoire de mon frère,

Ndongo DOUMBIA

(14 Avril 1986 – 15 Août 2008)

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Résumé

Auteur : El Hadji Thierno DOUMBIA

Titre : Caractérisation physico-chimique de la pollution atmosphérique urbaine en Afrique de l'Ouest et étude d'impact sur la santé.

Directeurs de thèse : Catherine LIOUSSE (LA) & Alain DIDIER (CHU Larrey)

Lieu et date de soutenance : Observatoire Midi-Pyrénées, Toulouse, France, le 18/12/2012

Résumé :

Ma thèse s'inscrit dans le cadre du programme POLCA (Pollution des Capitales Africaines). Elle a pour principal objectif de caractériser la pollution particulaire sur des sites « trafic » de deux capitales africaines Dakar (Sénégal) et Bamako (Mali) et d'étudier son impact toxicologique sur l'appareil respiratoire. La pollution particulaire urbaine, bien supérieure aux normes imposées par l'organisation mondiale de la santé, est mise en exergue en lien avec un trafic automobile anarchique et d'intenses combustions domestiques. Dans ce contexte, les questionnements scientifiques suivants ont pu être abordés : - Quelle est la spéciation chimique par classes de tailles des aérosols de combustion (carbone suie, carbone organique, inorganiques, métaux traces…) pour les sites « trafic » de Dakar et Bamako ? – Quelles sont les sources prédominantes agissant sur la composition chimique en aérosols ? Quelle est la toxicité de ces aérosols et le niveau de stress oxydant ? - Quels sont les liens entre composition des aérosols différenciés en tailles et marqueurs d'inflammation pour chaque type de source ? - Quels sont les liens entre expositions aux aérosols et doses dans l'appareil respiratoire ? - Pour traiter ces questions, je me suis attaché à l'étude des résultats des campagnes intensives de 2009 à Dakar et à Bamako auxquelles j'ai participé, principalement à l'analyse chimique complète des aérosols par classes de tailles, à la caractérisation physico-chimique complète de l'aérosol pour chaque site mais également à la détermination de ses différentes sources par des modèles multivariés (ACP et PMF). Ces études ont été associées à des mesures toxicologiques in vitro effectuées sur les aérosols prélevés sur ces mêmes sites. Ce croisement mesures physcico-chimique/mesure santé a permis d'approfondir les liens sources d'émissions/chimie de l'aérosol/granulométrie et impacts biologiques associés. Enfin, en parallèle aux mesures expérimentales développées dans POLCA, la thèse a permis la mise en œuvre du modèle DEPCLUNG (DEPosition, Clearance, LUNG) afin de convertir spéciation de l'aérosol par classe de taille ou EXPOSITIONS en concentrations d'espèces par classe de taille ou DOSES dans les divers compartiments de l'appareil respiratoire (trachée, bronches, bronchioles, alvéoles).

C'est la conjonction des trois thèmes, caractérisation de la pollution urbaine particulaire en Afrique de l'Ouest et ses sources, son impact toxicologique et la modélisation des doses dans l'appareil respiratoire, qui constitue le caractère pluridisciplinaire innovant de la thèse.

***Mots-clés* :** Pollution urbaine, POLCA, carbone suie et organique, particules de poussière, trafic automobile, impact santé, sources, modèle PMF, modèle DEPCLUNG

Discipline : Physique et Chimie de l'Atmosphère

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Abstract

This thesis was a contribution to the CORUS-POLCA (French acronym for « POLlution des Capitales Africaines ») program with the aim to characterize particulate pollution on traffic sites of two West-African capitals (Bamako, Mali and Dakar, Senegal) and to study aerosol biological impacts on lung inflammation. Urban particulate pollution with levels much higher than WHO norms, are in the focus due to intense African traffic sources and domestic fires. In this context, fundamental research of this thesis is centred on the following key scientific questions:

- What is the chemical speciation of aerosols by size classes for black carbon, organic carbon, inorganic species, and trace elements for the two sites of POLCA program ?
- What is the toxicity of these combustion aerosols and the oxidative stress levels ?
- What is the link between aerosol size differentiated composition and inflammation markers for each source ?
- What is the link between aerosol exposure and aerosol dose within the respiratory tract ?

To tackle these questions, samples obtained during the intensive campaigns in Bamako (January 2009) and Dakar (December 2009) have been chemically analyzed to obtain differentiated aerosol chemical composition within size classes. All these measurements are conducted to a well physico-chemical characterization of particles in addition to source contributing determination using multivariate models (PCA, PMF). This study has been coupled to in vitro biological studies on sampled aerosols on the two sites. Such coupled studies allow to further understand the complex relationship between emissions source/aerosols chemistry/size distributions and biological health impacts.

Finally, in this study, the DEPCLUNG (DEPosition, Clearance, LUNG) model was developed to evaluate chemically/size exposures to aerosol particle size distributions and calculate their respective concentrations/doses in the different compartments (trachea, bronchial, bronchiolar, alveolar) of the human respiratory tract.

The conjunction of three themes, namely characterization of the urban particulate pollution in West Africa and its sources, its toxicological impact and dose modeling in the respiratory tract results in the multidisciplinary innovative character of the thesis.

Keywords: Urban pollution, POLCA, black and organic carbon, dust aerosol, traffic, health impact, sources, PMF model, DEPCLUNG model

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INTRODUCTION GENERALE

Contexte

La croissance démographique soutenue et le fort exode rural concentré dans de grandes métropoles en Afrique sont des éléments centraux dans l'augmentation très rapide de la pollution urbaine (**Bousquet et al., 2003**). C'est un effet général mais particulièrement fort et encore mal documenté en Afrique de l'étroite relation entre émissions de polluants et activités humaines. Estimée à 819 millions d'habitants en 2000 (13,4% de la population mondiale), la population africaine est passée en 2010 à 1033 millions (environ 15% de la population mondiale) et pourrait s'établir à 1 998 millions en 2050, soit 22% de la population mondiale (**ONU, 2008**). Cette très forte croissance démographique, combinée à une très forte urbanisation (39% de population urbaine en 2008) est associée d'une part à une augmentation forte de la demande en transports, mais aussi à une augmentation de l'activité industrielle. Ces évolutions, spécialement rapides en Afrique subsaharienne, constituent une cause majeure des émissions gazeuses et particulaires en zones urbaines (**Han and Naeher, 2006** ; **Liousse and Galy-Lacaux, 2010** ; **Assamoi and Liousse, 2010** ; **Doumbia et al., 2012a**).

La situation économique précaire et l'ouverture des pays de l'Afrique de l'Ouest à l'importation de véhicules automobiles européens « France au revoir » de seconde main ont dopé le marché de l'occasion qui a explosé. Ainsi, depuis plus de deux décennies, des centaines de milliers de véhicules d'occasion affluent dans les ports africains. Ces vielles voitures n'étant pas équipées de technologies récentes requises pour limiter les rejets des composants les plus nocifs (oxydes d'azote, dioxyde se soufre, particules fines, monoxyde carbone, plomb, etc.) constituent une sérieuse menace pour la qualité de l'air dans les villes d'Afrique de l'Ouest. A ces émissions automobiles s'ajoutent les émissions par les deux roues à moteur deux temps qui utilisent des mélanges de carburants frelatés de très mauvaise qualité (**Assamoi and Liousse, 2010**). En zones rurales et même urbaines, les feux de biomasse, les feux domestiques, ainsi que l'incinération des déchets (agricoles, domestiques) contribuent pour une très large part aussi aux émissions de polluants atmosphériques. L'ensemble de ces polluants sont des sources potentielles de maladies et d'allergies respiratoires, qu'il s'agisse de maladies chroniques telles que l'asthme ou encore, de cancers pour les populations exposées (**Ezzati et al., 2004** ; **Brunekreef, 2010**).

A cela, s'ajoutent des conditions climatiques particulières, avec des températures élevées en saison sèche qui favorisent la pollution photochimique. Egalement, les poussières sahariennes, par la fréquence et l'intensité de leurs soulèvements, constituent une

caractéristique importante de l'atmosphère en Afrique de l'Ouest (**Bertrand et al., 1974** ; **Skonieczny et al., 2011** ; **Deboudt et al., 2010**), à l'origine d'importantes quantités de particules excédant les valeurs limites préconisées par l'Union Européen et l'OMS (**Rodríguez et al., 2001** ; **Matassoni et al., 2009**). Ces poussières désertiques sont également à l'origine de certaines infections respiratoires (méningites bactériennes) (**Yaka et al., 2008**) et de maladies cardiovasculaires (**Karanasiou et al., 2012** ; **Díaz et al., 2012**).

Enjeux

Les activités humaines, comme les phénomènes naturels influent de manière conséquente sur les mécanismes et processus en œuvre dans le système atmosphérique avec par exemple une très large diversification (chimie et tailles) de l'aérosol. C'est ainsi que dans ce travail, une attention particulière est accordée aux particules d'aérosols atmosphériques dont les effets sur le climat (**Heiko Paeth, 2012** ; **Gu et al., 2012**), de même que sur la santé humaine (**Dockery and Pope, 1994** ; **Wilson et al., 2000** ; **Pope et al., 2006**) sont largement avérés. A l'heure actuelle, les effets climatiques des aérosols bénéficient d'une attention particulière de la communauté scientifique, notamment dans le cadre de grands projets internationaux tels qu'AMMA, GIEC… et ceci, en dépit de très grandes incertitudes. En revanche, la caractérisation de l'aérosol, ainsi que l'étude de son impact sanitaire en Afrique, tout particulièrement en Afrique de l'ouest sont quasi inexistants. Pourtant, cette région de l'Afrique est confrontée à des niveaux de pollution très élevés avec des populations très fortement exposées. Une connaissance largement améliorée et approfondie des caractéristiques des aérosols est donc capitale pour la prévention et la surveillance de la qualité de l'air en ces régions. Cette caractérisation passe par des investigations à long et à court terme, mais également à différentes échelles spatiales. Une fois émis, les aérosols peuvent rester en suspension dans l'air pendant plusieurs jours, voire des semaines. Par la suite, ces particules peuvent être inhalées et atteindre les différents compartiments de l'appareil respiratoire, constituant ainsi un danger pour la santé humaine (**MO, 2000**). Une des motivations premières est de mieux renseigner, les processus conduisant aux fortes concentrations de particules mesurées en zones urbaines Africaines, mais également leurs impacts sanitaires.

Objectifs

Afin d'améliorer nos connaissances sur la pollution atmosphérique et ses effets sanitaires, notre étude porte sur la caractérisation physico-chimique de l'aérosol atmosphérique, puis son lien avec la santé des populations dans deux capitales d'Afrique de l'Ouest différenciées par leur situation, aussi bien géographique et climatique que du point de vue de leur développement économique et par la diversité des sources polluantes et de leurs parcs de véhicules:

- Bamako (Mali) est une ville située dans une cuvette à l'intérieur de continent. Son parc automobile est constitué principalement de véhicules deux roues utilisant un mélange d'huile et de gasoil ;
- Dakar (Sénégal) est une ville côtière très urbanisée, en forte croissance démographique. Elle regroupe 54% de la population urbaine nationale et dispose d'un parc automobile dominé par des véhicules diesel âgés.

L'objectif de notre étude s'inscrit dans les objectifs du programme CORUS/POLCA (COopération pour la Recherche Universitaire Scientifique / POLlution des Capitales Africaines), mis en œuvre entre 2007 et 2010 pour pallier au manque de données sur la pollution en phases gazeuse et particulaire des capitales africaines et étudier leurs impacts sanitaires. A ce jour, c'est un des rares programmes qui a permis de disposer d'une base de données exhaustive sur la spéciation chimique des aérosols, leur distribution en tailles, de même que sur l'étude des polluants gazeux en zones urbaines Africaines.
Mon travail se décline autour de séries de mesures extensives (moyen terme) et intensives (court terme) de particules obtenues lors de deux campagnes de terrain à Bamako et Dakar. J'ai participé personnellement à la réalisation des campagnes, ainsi qu'aux analyses en laboratoires des échantillons collectés lors de ces campagnes. J'ai également personnellement testé et validé de nouveaux protocoles d'analyses, notamment de métaux dans les échantillons au laboratoire de Géoscience Environnement de Toulouse (GET) et de l'aérosol carboné au Laboratoire d'Aérologie (LA).

Le premier chapitre est consacré à l'étude bibliographique, en vue de faire un point sur l'état des connaissances en pollution atmosphérique en Afrique de l'Ouest. J'ai d'abord présenté un aperçu global des principales causes de pollution de l'air en Afrique, avant de me focaliser sur les projets et études menés jusqu'ici dans le cadre de la pollution particulaire en

zone urbaine Ouest Africaine. Enfin, j'ai clos ce chapitre I par la description du cadre de mon étude. Le second chapitre, constitué de l'**Article (A1)**, est consacré au premier bilan de la composante black carbon (BC) de l'aérosol, en termes de variations spatio-temporelles et de niveaux de concentrations à des sites de trafic en Afrique de l'Ouest et du centre. Le troisième chapitre présente sous forme d'un **Article (A2)** la caractérisation physico-chimique de l'aérosol et les niveaux de concentrations particulaires à Bamako et à Dakar. Les distributions en tailles, conjointement avec l'établissement de coefficients de corrélation linéaire entre éléments dans les particules ont été utilisées en tant qu'indicateurs de sources potentielles de l'aérosol urbain. La quantification de ces sources, par des techniques d'analyses multi-variées (Analyse en Composante Principale (ACP), Factorisation en Matrice Positive (PMF)) associées à des calculs de facteurs d'enrichissement (EF) fait l'objet du quatrième chapitre **(Article A3)**.

Afin d'étudier l'impact des particules sur le système respiratoire des populations Ouest africaines, nous nous sommes inspirés et avons adapté le modèle de dépôt des particules dans l'appareil respiratoire développé précédemment par la Commission Internationale pour la Protection Radiologique (**CIPR, Publication 66, 1994**) : il s'agit de notre module DEPCLUNG (DEPosition Clearance LUNG) appliqué dans notre étude aux populations ouest africaines. Les résultats obtenus avec notre modèle qui ont fait l'objet d'un article en cours de soumission, sont discutés au chapitre V **(Article A4)**. Une fois déposées dans l'organisme, les effets toxicologiques des ces particules en lien avec leur taille et leur composition chimique sont ensuite développés au chapitre VI **(Article A5)**. Dans ce chapitre, on fait état d'analyses toxicologiques en laboratoire, c'est-à-dire que les particules de tailles et de compositions chimiques différentes sont confrontées *in vitro* à des cellules épithéliales pulmonaires humaines, en vue de quantifier le stress oxydant résultant, ainsi que les réponses pro-inflammatoires induits par les mécanismes de défense de l'organisme humain (**Ayi Fanou et al., 2006 ; Ramgolam et al., 2009**).

CHAPITRE I : ETAT DE L'ART SUR LA POLLUTION ATMOSPHERIQUE URBAINE EN AFRIQUE DE L'OUEST ET ETUDE D'IMPACT SUR LA SANTE

Introduction

Les travaux sur la caractérisation de l'aérosol en milieu urbain s'inscrivent très généralement dans la compréhension des différents mécanismes à l'origine des niveaux élevés de particules observées, leurs variations spatio-temporelles, l'identification des différentes sources ainsi que leur quantification et enfin, leurs impacts environnementaux et sanitaires. L'objectif visé est celui d'une amélioration de la qualité de l'air en ville.

A cette fin, des campagnes de mesures sont effectuées sur du court terme (quelques jours, voire des semaines), du moyen terme (un à deux ans) ou du long terme (plusieurs années). Si de telles mesures exhaustives ont été menées en Europe de l'Ouest et en Amérique du Nord, il est très loin d'en être de même en Afrique, particulièrement en Afrique de l'Ouest. Seuls quelques travaux ponctuels, certains déjà anciens, sont relevés dans la littérature.

En préambule à ce chapitre, je vais présenter la situation démographique et socio économique de la région ouest africaine et les potentiels secteurs émetteurs de polluants particulaires.

I.1. Contexte démographique et socio-économique

L'Afrique de l'Ouest couvre toute la partie occidentale de l'Afrique subsaharienne. Elle regroupe approximativement 16 pays dont le Mali et le Sénégal, objet de notre étude, et couvre une superficie d'environ 6,14 millions de km^2, soit un cinquième du continent Africain. La densité de sa population est l'une des plus élevées d'Afrique, comme le montre la ***Figure I.1***. Des études récentes montrent qu'en 2020, 50% de la population africaine serait urbaine, dont plus de la moitié en Afrique de l'Ouest, soit une augmentation de 100% en moins de trente ans (**Tabutin and Schoumaker, 2004 ; UN, 2006**). Ce rapide accroissement de la population urbaine est doublé d'un étalement parfois désorganisé des villes. Elles se sont densifiées, étalées, regroupent de plus en plus la plupart des activités nationales, occupent les espaces ruraux environnants, pour former de grandes mégalopoles. Cette rapide croissance de la population n'est pas sans soulever un certain nombre de problèmes cruciaux. Ces villes ont connu une hausse de la pauvreté et une dégradation du niveau de vie des populations ces dernières années. Elles manquent d'infrastructures, se développent souvent de manière anarchique, créant d'énormes problèmes environnementaux, mais aussi sociaux et économiques.

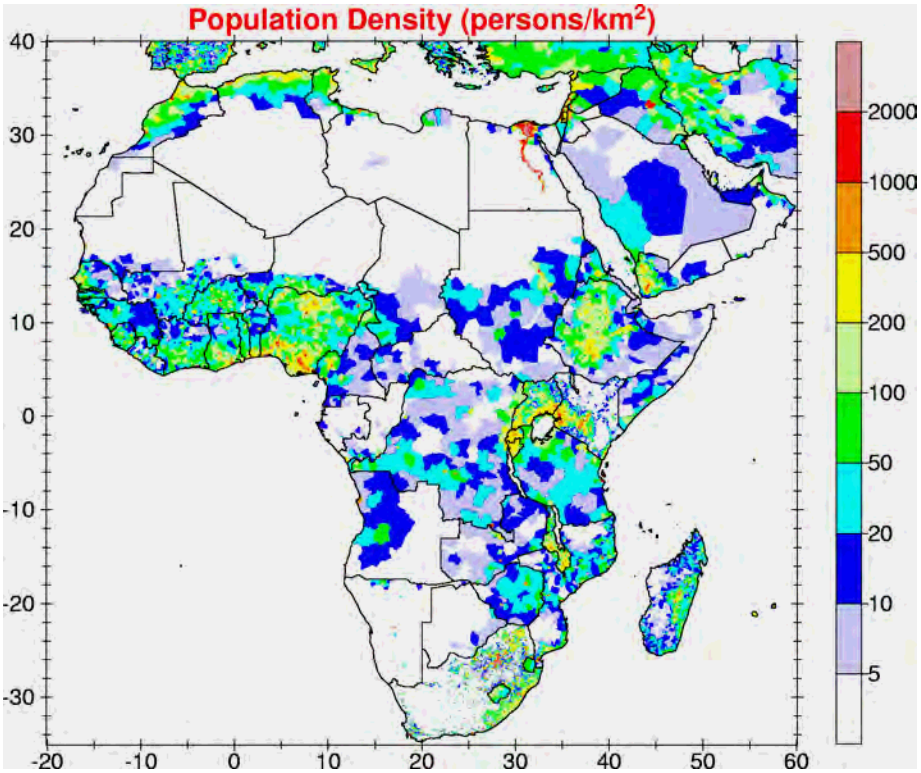

Figure I.1 : Carte de la densité de population en Afrique (nombre d'habitants par km^2) pour l'année 2000 (CIESIN, http://sedac.ciesin.columbia.edu/gpw/).

La situation économique en récession persistante fait que le consommateur africain moyen n'a pas les moyens de s'offrir un véhicule automobile neuf et moins encore, la nouvelle génération de véhicules dits «propres» qui pollue sensiblement moins. Il n'a d'autre choix que les véhicules d'occasion déclassés et importés pour 95% des pays de l'union européenne et cette situation ne cessent de perdurer. Des efforts de lutte contre cette pratique sont menés par certains pays en votant des lois limitant l'âge des véhicules importés. C'est le cas du Sénégal où l'âge des véhicules importés a été limité à 5 ans (depuis 2001), avant qu'elle ne soit portée très récemment à 8 ans (2012) pour des raisons politico-économiques. Malgré cette mesure, l'âge moyen du parc des véhicules est de plus de 18 ans en moyenne et même, de plus de 20 ans pour les poids lourds. Le parc automobile dakarois est caractérisé par une part très élevée de véhicules équipés de moteurs diesel (60%) et par un important pourcentage (11%) de poids lourds (**Wade et al., 2012**). Dakar comptait environ 230 000 voitures et minibus en 2008, soit 3/4 du parc national, alors que le réseau routier n'est que de 305 km, soit environ 670 voitures/km (**World Bank, 2005**), d'où l'importance des embouteillages. A Dakar, la majorité des voitures utilise le diesel comme carburant. Par ailleurs, dans la plupart des villes d'Afrique de l'Ouest (Ouagadougou, Bamako, Cotonou) le

transport aujourd'hui est dominé par les deux-roues, principalement avec des moteurs deux temps très polluant, mais compte également des quatre temps moins nombreux, plus chers et moins polluants. Par exemple, à Ouagadougou, on dénombrait plus de 200 000 engins deux-roues immatriculés en 2008, ce nombre augmentant chaque année de 25 000 (**Savadogo and Ouedraogo, 2009**). La pollution liée à l'utilisation du fuel comme source d'énergie constitue une autre source importante de pollution gazeuse et particulaire. Ainsi, les niveaux de pollution très élevés observés en Afrique de l'Ouest sont étroitement liés à sa situation démographique et socio-économique.

Une autre conséquence de la précarité en Afrique, est l'utilisation domestique généralisée de combustibles solides tels que le bois, le charbon de bois, la bouse de vache ou les résidus agricoles comme sources d'énergie pour la cuisine ou le chauffage. Ces combustibles génèrent une pollution supplémentaire à laquelle sont particulièrement soumis les femmes et les enfants. On estime qu'entre 50 et 75% de la population Africaine est affectée par cette pollution «interne» qui serait à l'origine de plus d'1,6 millions de morts prématurés par an, particulièrement des femmes et des enfants (**WHO, 2002a**). Ces études sont établies sur la base d'enquêtes épidémiologiques.

Enfin, une autre source significative de particules à prendre en compte est liée aux feux de biomasse. L'Afrique est en proie aux feux de végétations et de cultures qui peuvent influencer l'équilibre climatique et les concentrations atmosphériques (**Liousse et al., 2010 ; Heiko Paeth, 2012**).

A ces paramètres démographiques et socio-économiques s'ajoute une spécificité climatique de la région Ouest Africaine qui n'est pas non plus sans conséquence sur l'environnement et notamment, la pollution par les aérosols. En effet, plusieurs types de climats sont présents sur l'Afrique de l'Ouest, les plus fréquents étant le climat tropical humide, le climat tropical sec et les formes alternées, sec et humide. En période sèche, entre Novembre et Mars, la plupart des villes situées en zone Sahélienne sont confrontées, en plus de la pollution anthropique, aux vents secs du Nord Est (Harmattan), chargés de poussières Sahariennes (**Adepetu et al., 1988 ; Akeredolu, 1989 ; McTainsh et al., 1997**). Durant cette période, plusieurs villes de la région connaissent des niveaux de concentrations en particules de poussières très élevés (**Afeti and Resch, 2000**) et des températures relativement élevées le jour (**Bertrand et al., 1974**) qui inévitablement elles aussi contribuent à la pollution photochimique. Quelques études sur la caractérisation des poussières venant du Sahara existent sur quelques villes de l'Afrique de l'Ouest (**Afeti and Resch, 2000**) mais il n'en

existe pratiquement que peu qui regroupent distributions en tailles, composition chimique et impacts sur la santé. Récemment, une étude (**De Longueville et al., 2010**) a montré qu'au cours des 10 dernières années, sur 231 articles consacrés à l'étude d'impact des poussières sur la qualité de l'air, une seule concerne l'Afrique de l'Ouest.

I.2. La pollution atmosphérique en Afrique de l'Ouest

La pollution atmosphérique constitue un problème environnemental complexe et majeur qui se pose partout dans le monde. Les études associées menées en Amérique, en Europe et en Asie, montrent que cette pollution a pour cause principale les activités humaines, qu'elles soient industrielles, domestiques, agricoles, urbaines ... (**Smith and Mehta, 2003 ; Ezzati et al., 2004 ; Nweke and Sanders III, 2009 ; Brunekreef, 2010**). L'Afrique, à l'instar des autres continents, est confrontée à cette pollution, ainsi qu'à ses multiples impacts, à savoir sur le climat et sur la santé des populations. Bien que les données sur la pollution atmosphérique en Afrique soient très peu fournies, les récentes estimations de l'Organisation Mondiale de la Santé (OMS) dénombrent approximativement plus d'1 million de morts prématurés chaque année dans le monde imputables aux effets de la pollution, dont 5% pour la seule Afrique (**WHO, 2006**). Par ailleurs, les sources de cette pollution en Afrique augmentent de façon considérable, compte tenu d'une croissance urbaine galopante et soutenue des villes (**Banque Mondiale, 2003**).

Comme il apparaît sur la ***Figure I.2***, les populations d'Afrique de l'Ouest sont exposées à des niveaux de pollution de PM_{10} (particules de diamètre inférieur ou égal à 10 µm) du même ordre de grandeur que la plupart des grandes mégacités et villes industrialisées du monde, ceci notamment à cause de fortes densités de population (***Figure I.1***) soumises à des activités anthropiques de plus en plus importantes, consécutives à une urbanisation croissante très peu régulée. Un article récent du *New England Journal of Medicine* (**Patel and Burke, 2009**) soutient que l'urbanisation est un danger sanitaire pour certaines populations vulnérables et que cette évolution démographique menace de créer une catastrophe humanitaire. De même, l'impact de la pollution ambiante ne se limite pas aux seuls effets sanitaires et climatiques, mais peut influencer l'économie locale de façon significative en terme de coûts santé (**US EPA, 2012**). L'Organisation Mondiale de la Météorologie (OMM), relayée par l'OMS (Organisation Mondiale de la Santé), souligne d'ailleurs que la pollution

en milieu urbain est devenue un problème socio-économique majeur de l'ensemble de nos sociétés, quel que soit son niveau de développement. Le suivi de la qualité de l'air dans les villes africaines est pratiquement inexistant et il n'y a que peu ou même pas de texte réglementant les émissions urbaines de polluants. C'est le cas par exemple de certaines villes subsahariennes où des initiatives de réduction de l'utilisation de l'essence sans plomb viennent sous peu d'être prises. Ainsi, l'Afrique a plus que jamais besoin de trouver des solutions aux problèmes de pollution auxquels elle est confrontée : cela doit nécessairement passer par le développement de programmes de recherches bien structurés pour aborder cette problématique, particulièrement en zone tropicale et subtropicale, comme l'illustre la ***Figure I.2*** montrant les concentrations de PM_{10} (particules de diamètre aérodynamique inférieur à 10 µm) dans les principales villes du monde avec des valeurs sur l'Afrique de l'Ouest du même niveau que dans les zones très polluées d'Inde et de Chine.

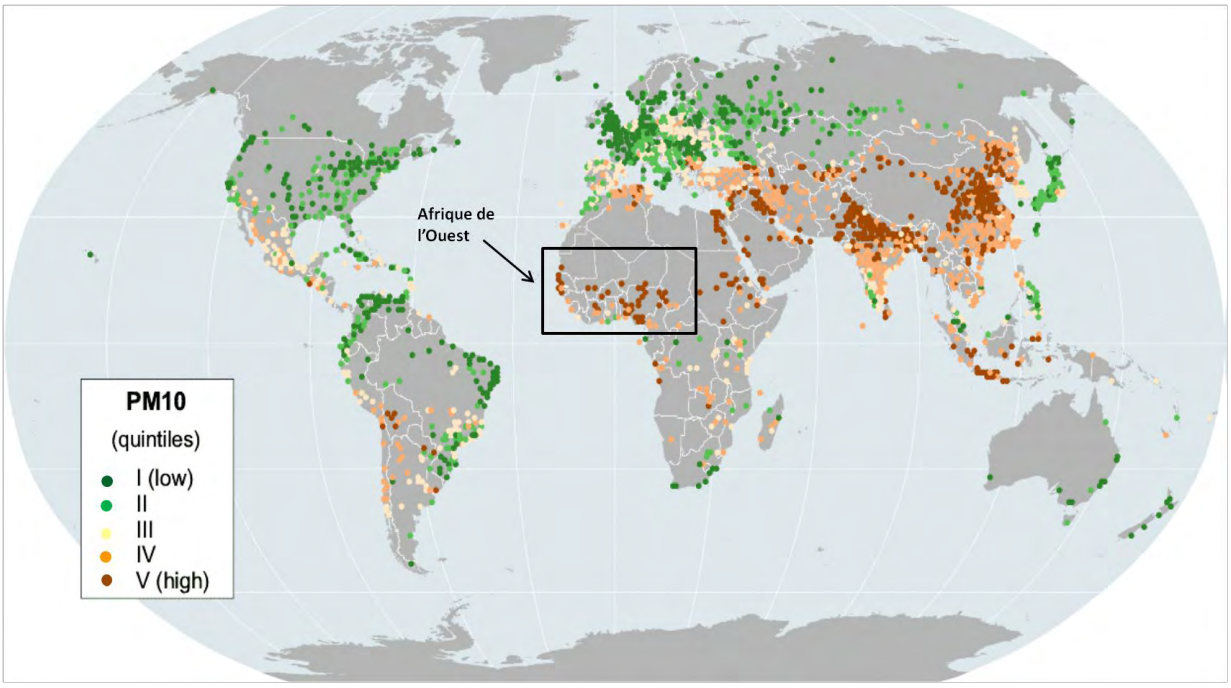

Figure I.2 : Estimation des concentrations urbaines de PM_{10} dans le monde (Pandey et al., 2002).

I.3. Initiatives sur l'étude de la pollution atmosphérique en Afrique de l'Ouest

La pollution atmosphérique en Afrique de l'Ouest a fait l'objet d'études centrées essentiellement sur les polluants gazeux, en zones rurales comme en zones urbaines (**Baumbach et al., 1995 ; Lindén et al., 2008**). De même, la composition chimique de l'air

en milieu rural intertropical africain et son impact sur les écosystèmes à échelles régionale et continentale ont fait l'objet de nombreuses études à travers divers programmes tels que DECAFE (Dynamique et Chimie de l'Atmosphère en Forêt Equatoriale, 1986-1992) et EXPRESSO (Experiment for Regional Sources and Sinks of Oxidants, 1994-1998), IDAF: IGAC/DEBITS/AFRICA (International Global Atmospheric Chemistry/ Deposition of Biogeochemical Important Trace Species/Africa, depuis 1994), AMMA (Analyse Multidisciplinaire de la Mousson Africaine, 2005-2008 (**Lacaux et al., 1993 ; Delmas et al., 1999 ; Galy-Lacaux et al., 2001 ; Liousse and Galy-Lacaux, 2010 ; Law et al., 2010 ; Ancellet et al., 2011**). Ces études ont permis de mettre en évidence des hauts niveaux de concentrations en aérosol en zones rurales ouest africaines, dues aux feux de biomasse, feux domestiques et aux événements de poussières désertiques. Par ailleurs, l'OMS (Organisation Mondiale de la santé a mis en place des projets dans le cadre de la lutte contre la pollution liée à l'utilisation de combustibles solides (**WHO, 2002b)**. Ces projets ont mis en évidence l'impact de la pollution par les feux domestiques sur la santé. Par contre, très peu d'études existent sur la pollution particulaire en milieu urbain Africain. Les campagnes d'AMMA (2005-2008) (avion, sol) ont pourtant montré des concentrations particulaires élevées à Cotonou (Bénin) et Ouagadougou (Burkina Faso), liées au trafic et aux feux domestiques.

Les particules d'aérosols, par leurs caractéristiques physiques, sont à l'origine de la plupart des problèmes de pollution en zones urbaines. Toutefois, leur impact sur la santé, de même que leurs propriétés chimiques en zones urbaines africaines, sont très mal connus. Des initiatives ont été prises, à savoir la mise en place du réseau Clean Air Initiative-Sub-Saharan Africa (CAI-SSA), une initiative conçue dans le contexte de la stratégie globale de la Banque Mondiale en vue de sensibiliser aux problèmes de la pollution atmosphérique, d'évaluer les émissions des véhicules, de mettre en œuvre et d'assurer le suivi des programmes de réduction dans les villes d'Afrique sub-saharienne. Cette initiative a contribué, par exemple, depuis 2001 à la réduction de l'utilisation de l'essence sans plomb (**Clean Air Initiative, 2003)**. Des études ponctuelles ont cependant permis d'aborder la question de l'effet des particules d'aérosols sur la qualité de l'air en Afrique de l'Ouest. Le ***Tableau I.1*** recense les principales études menées jusqu'ici en Afrique de l'Ouest sur l'évaluation de la qualité de l'air en zone urbaine. A Conakry (Guinée) en 2004, à la demande de l'ambassade des Etats-Unis, la seule étude sur la qualité de l'air a été réalisée sur un site de fond et des concentrations de PM (matière particulaire) s'élevant entre 80 et 358 $\mu g.m^{-3}$ ont été relevées, en période d'Harmattan (**Weinstein et al., 2010**). A Nouakchott (Mauritanie), une étude sur l'estimation de la dégradation de la qualité de l'air liée aux poussières du Sahara dans la zone

aéroportuaire de Nouakchott en 2000 a été menée par **Ozer et al. (2006**) qui ont mesuré des concentrations moyennes annuelles de PM_{10} et de TSP (particules en suspension totales) de 108 et 159 µg.m^{-3} respectivement. Ces auteurs ont rapporté que ces valeurs sont deux fois supérieures aux valeurs limites fixées par l'OMS ou par l'Union Européenne. Une étude similaire à Niamey (Niger) en 2003 montre également des niveaux de concentrations annuelles du même ordre de grandeur (67-103 µg.m^{-3}) (**Ozer, 2005**). Des investigations à Accra (Ghana) sur la pollution particulaire ont révélé des concentrations moyennes journalières de $PM_{2.5}$ (particules de diamètre aérodynamique inférieur à 2,5 µm) et PM_{10} entre 58 et 94 µg.m^{-3} (**Arku et al., 2008**). **Dionisio et al. (2010)** ont également montré une large variabilité des concentrations de $PM_{2.5}$ et PM_{10} à Accra, avec des valeurs variant de 25 à 400 µg/m^3 en fonction du point de mesure. Une série de mesures en temps réel des concentrations de particules dans trois villes d'Afrique (Ouagadougou, Dar es Saalam et Gaborone) ont été menées (**Eliasson et al., 2009)**. L'objectif de cette étude consiste à caractériser les variations spatio-temporelles de différentes fractions d'aérosols ($PM_{2.5}$, PM_{10}, TSP) dans ces trois villes (***Tableau I.1***). A Ouagadougou (Burkina Faso), les mesures mobiles effectuées à différents endroits de la ville révèlent des niveaux de concentrations très élevés par rapport aux valeurs obtenues lors d'études similaires à Dar es Salaam (Tanzanie) et Gaborone (Botswana), mettant en évidence le niveau élevé de pollution particulaire des capitales ouest africaines par rapport au reste de l'Afrique. Les études préliminaires sur la pollution particulaire de bruit de fond à Ouagadougou (**Cachier, communication personnelle**) font également état de hauts niveaux de concentrations de PM, avec des valeurs de l'ordre de 100 µg.m^{-3} dépassant 140 µg.m^{-3} en période de feux. Ces concentrations sont comparables à celles mesurées au Caire (Egypte) et à Pékin (Chine) et sont environ 4 fois supérieures aux valeurs obtenues à Paris (**Favez et al., 2008**). Toujours à Ouagadougou, des études récentes menées en 2007 et 2010 sur l'exposition à la pollution urbaine montrent la nécessité de tenir compte de la variabilité spatio-temporelle (**Lindén et al., 2012**). A Lagos (Nigeria), **Baumbach et al. (1995),** dans le cadre d'un projet soutenu par l'Union Européenne, ont rapporté des concentrations journalières de PM variant entre 100 et 300 µg.m^{-3} avec des valeurs atteignant 500 à 800 µg.m^{-3} en période d'Harmattan. Plusieurs autres études ont fait état de la pollution particulaire à Lagos sur des sites industriels (**Oluyemi et al., 1994 ; Adejumo et al., 1994**). Au Sénégal, les études menées à Mbour (**Flament et al., 2011**) suggèrent une large variabilité des concentrations de PM_{10}, avec des valeurs pouvant varier de 10 à 500 µg.m^{-3}. Tous ces travaux constituent des études pilotes sur la pollution urbaine en Afrique de l'Ouest mettant en

évidence la spécificité de cette région, fortement influencée par de fortes émissions de particules, qu'elles soient d'origines anthropiques ou naturelles.

Le programme POLCA (POLlution des Capitales Africaines), objet de ma thèse, constitue une étude de ce type. C'est en 2004, dans le cadre d'une coopération Franco-africaine, sous l'initiative de chercheurs français et africains que ce projet a été initié, réalisant la nécessité de renseigner les niveaux élevés de concentrations en polluants constatés, qu'ils soient gazeux ou particulaires dans deux capitales d'Afrique de l'Ouest (Bamako et Dakar). Les résultats préliminaires sur la pollution gazeuse montrent des concentrations en NO_2 supérieures aux valeurs limites imposées par l'Organisation Mondiale de la Santé **(Liousse and Galy-Lacaux, 2010**). Par ailleurs, des mesures en temps réel du black carbon (BC) ainsi que les estimations des concentrations de $PM_{2.5}$ (particules de diamètre inférieur ou égal à 2,5 µm) effectuées dans le cadre de ma thèse, révèlent également des niveaux du concentrations en $PM_{2.5}$ à Dakar quatre fois supérieurs à la norme annuelle de 10 µg/m^3 fixée par l'OMS. Ces résultats ont fait l'objet de la publication intitulée **''**Real time Black Carbon measurements in West and Central Africa urban sites**''** et qui sera présentée au chapitre II **(Article A1)**.

Tableau I.1 : Résumé de quelques études portant sur la pollution atmosphérique en zone urbaine ouest africaine.

Etude	Ville	Objectif	Principe	Espèces mesurées	Type de prélèvement
Weinstein et al. (2010)	Conakry (Guinée)	Evaluer les niveaux de $PM_{2.5}$ et PM_{10}, reconstruction sur un site de fond à Conakry en période d'Harmattan	Facteur d'enrichissement/Spéciation chimique	$PM_{2.5}$ et PM_{10} (Minivol et filtre), EC/OC (TOT méthode), ions (IC), métaux (XRF)	3 sites, mesure en temps réel de $PM_{2.5}$, PM_{10}, 1 prélèvement sur filtre par 24h pendant 1 mois
Ozer et al. (2006)	Nouakchott (Mauritanie)	Estimation des niveaux de TSP and PM_{10} à l'Aéroport de Nouakchott	Relation entre visibilité horizontale et concentrations de PM	TSP and PM_{10}	1 site, mesure en temps réel de la visibilité horizontale, pas de temps de 3h sur 1 année
Arku et al. (2008)	Accra (Ghana)	Détermination de niveaux de $PM_{2.5}$ et PM_{10}, variations spatiale et temporelle	Spéciation chimique/détermination des sources	$PM_{2.5}$, PM_{10} (TSI Inc. et filtre), EC/OC (NIOSH Protocol 5040), métaux (EDXRF), SO_4^{2-} et NO_3^- (Ogawa passive samplers)	2 sites, mesure en temps réel $PM_{2.5}$ and PM_{10}, 1 prélèvement sur filtre par 24h pendant 3 semaines
Dionisio et al. (2010)	Accra (Ghana)	Comprendre la variabilité spatiale des PM, évaluation de l'influence de la proximité des sources sur les niveaux de concentrations	Mesures mobiles, ponctuelles	$PM_{2.5}$, PM_{10} (TSI Inc.)	4 sites, mesures en temps réel $PM_{2.5}$ et PM_{10} pendant une semaine
Baumbach et al. (1995)	Lagos (Nigéria)	Mesurer les niveaux de concentration de polluants (gazeux et particulaires) sur un site trafic	Mesures en temps réel sur un site trafic sous influence des poussières sahariennes	PM et gaz (CO, NO_x, VOC)	1 site trafic, mesures en temps réel PM
Flament et al. (2011)	Mbour (Sénégal)	Détermination de la composition chimique des aérosols	Spéciation chimique/détermination des sources	PM_{10} (TEOM, filtre), nombre, BC (Aethalométre), EC/OC (Thermal), ions (IC), métaux (GFAAS),	1 site, 1 prélèvement sur filtre par 24h pendant 2 semaines
Eliasson et al. (2009)	Ouagadougou (Burkina Faso), Dar es Salaam (Tanzanie), Gaborone (Botswana)	Variation spatio-temporelle des concentrations de $PM_{2.5}$, PM_{10} et TSP	Mesures en temps réel/Compteur de particules	Masse (MetOne Aerocet 531), nombre (Grimm), $PM_{2.5}$, PM_{10}, TSP	Mesures mobiles dans les villes
Lindén et al. (2012)	Ouagadougou (Burkina Faso)	Variation spatio-temporelle des concentrations de PM_1, $PM_{2.5}$, PM_{10} et certains polluants gazeux (CO, NO_x, O_3, benzène et toluène)	Mesures en temps réel/Compteur de particules	Masse (MetOne Aerocet 531), nombre (Grimm)	Mesures ponctuelles sur différents endroits, mesures mobiles

I.4. Impact sanitaire de la pollution particulaire urbaine

I.4.1. Dépôt des particules dans le système respiratoire

Les aérosols émis en milieu urbain sont majoritairement constitués de particules de petites tailles, dites inhalables (PM_{10}). Ces particules sont la cause d'effets inflammatoires. Elles présentent des propriétés spécifiques et sont associées le plus souvent à des composés connus pour leur toxicité, tels que les métaux et certaines espèces organiques (**Huang et al., 2002 ; Happo et al., 2008 ; Seagrave et al., 2006**). Par ailleurs, les plus petites d'entre elles peuvent atteindre les cellules alvéolaires au contact de la circulation sanguine, et seraient même responsables dans certains cas de modifications de l'ADN (**Knaapen et al., 2002 ; Risom et al., 2005**).

La ***Figure I.3*** montre les divers compartiments du système respiratoire dans lesquels sont déposées les particules inhalées. Le dépôt de ces particules dépend des propriétés physico-chimiques de l'aérosol (taille, forme, surface, caractère hygroscopique et hydrosoluble et composition chimique), mais également de l'anatomie et de l'histologie de l'appareil respiratoire (**Cheng, 2003**). Les particules de tailles supérieures à 10µm (PM_{10}), telles que les poussières, se déposent majoritairement dans la région extrathoracique (pharynx et larynx). Celles de diamètres compris entre 2.5 et 10µm s'arrêtent au niveau de la zone thoracique (trachée et bronches). C'est le cas notamment de certaines espèces organiques, des ions, mais également les poussières dans cette gamme de tailles. Les particules fines et ultrafines (< $PM_{2.5}$) qui peuvent atteindre les bronchioles et les alvéoles sont essentiellement constituées de composés carbonés.

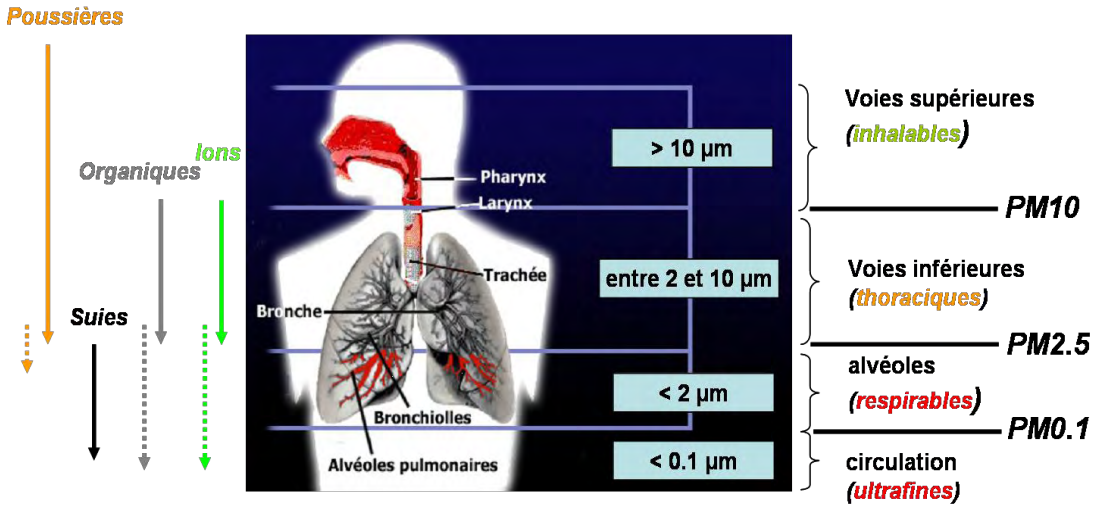

Figure I.3 : Schéma de l'appareil respiratoire et ses différents compartiments.

I.4.2. Epidémiologie/Toxicologie

Schématiquement et pour notre propos, épidémiologie et toxicologie sont deux disciplines biologiques et médicales qui traitent de l'impact santé au sens large, aux niveaux individuels et de populations, de substances (polluants) xénobiotiques tant gazeuses que particulaires. Brièvement, ces deux disciplines s'adressent à un très large spectre d'échelles spatiales (mécanismes moléculaires, cellulaires, physiologiques, comportementales, populations), comme à une gamme d'échelles temporelles (effets à très court, moyen et long termes) et s'appliquent à un très grand nombre d'affections et de maladies imputables à notre environnement et à sa dégradation. Très schématiquement encore, et de manière pratique, l'établissement de relations doses-effets et doses-réponses et les risques associés est de nature à établir le lien recherché dans cette étude entre pollution de l'air (particules notamment) et impacts sur la santé, à courtes et moyennes échéances **(Viau and Tardif, 2003 ; Brunekreef, 2010 ; Dockery and Pope, 1994)**. **Confrontée à cette très vaste thématique, comment se place plus spécifiquement notre travail** ?

a) Les études épidémiologiques et toxicologiques liées à l'inhalation des particules ont permis de mettre en évidence les risques de mortalité par maladies cardio-respiratoires associées à la pollution atmosphérique urbaine, depuis plus de deux décennies, en Amérique, en Europe et en Asie (**Dockery et al., 1993 ; Katsouyanni et al., 1997 ; Hong et al., 1999** ; **Brook, 2008 ; Pope et al., 2009**), tant « outdoor » (pollution urbaine) qu' « indoor » (pollution domestique). Notre étude, comme déjà annoncé, porte sur le domaine ouest africain, tout particulièrement dépourvu d'action couplés pollution-santé et où énormément d'analyses sont à mener, sur des populations et des individus jeunes, pris dans une démographie et une urbanisation galopantes. Cette étude va dans le sens d'une très forte émergence des maladies dues à la pollution et affections cardio-respiratoires (e.g. asthme, maladie pulmonaire obstructive chronique) en Afrique et en Afrique de l'Ouest, même comparativement aux maladies infectieuses (e.g. paludisme), essentiellement pour les populations à risques (enfants, femmes) (**Wilson et al., 2000 ; WHO, 2002a, 2006 ; Smith et al., 2000**).

b) En liaison directe avec nos mesures de pollution particulaire, les analyses toxicologiques développées ici sont effectuées *in vitro* sur des cellules épithéliales humaines avec lesquelles sont confrontées les particules collectées sur des filtres pendant les expériences POLCA à Bamako et Dakar : le lien est ainsi très direct entre pollution mesurée et effets toxicologiques résultant. De nombreuses études ont montré que l'exposition à court terme aux particules induit une inflammation locale des tissus via la production de cytokines

proinflammatoires comme le GM-CSF (Granulocyte-Macrophage Colony Stimulating Factor), l'IL-6 ou l'IL-8 (Interleukine-6 ou 8) (**Ramgolam et al., 2009 ; Lin and Yu, 2011 ; Val et al., 2009**). Les analyses effectuées ici constituent donc une étude des effets sanitaires à court terme de la pollution particulaire. Je reviendrais plus loin et plus en détail dans ce travail sur les résultats de cette approche couplée **(**chapitre VI, **Article A5)**.

Cet apport toxicologique s'inscrit dans une approche des mécanismes biologiques liés à l'exposition des cellules à des particules polluantes (***Figure I.4***) et à leurs effets, en termes de stress oxydant. En effet, certains composés comme les espèces organiques, induisent, de par leurs propriétés intrinsèques, ou suite à leur métabolisation, une surproduction d'espèces activées de l'oxygène (EAO). Ces espèces vont produire un stress oxydant, c'est-à-dire une perturbation de l'état redox «normal» de la cellule et créer un déséquilibre en faveur d'un état oxydatif qui, selon son intensité, peut induire diverses réponses biologiques. Ainsi, à un faible niveau de stress oxydant, il y a une induction de l'expression d'enzymes du métabolisme des xénobiotiques qui ont pour but de détoxifier ces composés étrangers et potentiellement dangereux pour la cellule, tels que par exemple la NADPH quinone oxydoréductase (NQO-1). Il y a aussi une induction d'enzymes antioxydantes (exemple de l'hème oxygénase) qui vont transformer les EAO en espèces non réactives afin de limiter les dégâts causés par celles-ci. Les aérosols en contact avec les cellules peuvent ainsi générer les stress oxydant responsable de la survenue d'affections cardio-respiratoires en cas d'exposition à court terme ou de maladies respiratoires chroniques (telles que l'asthme ou les bronchites chroniques) en cas d'exposition à long terme.

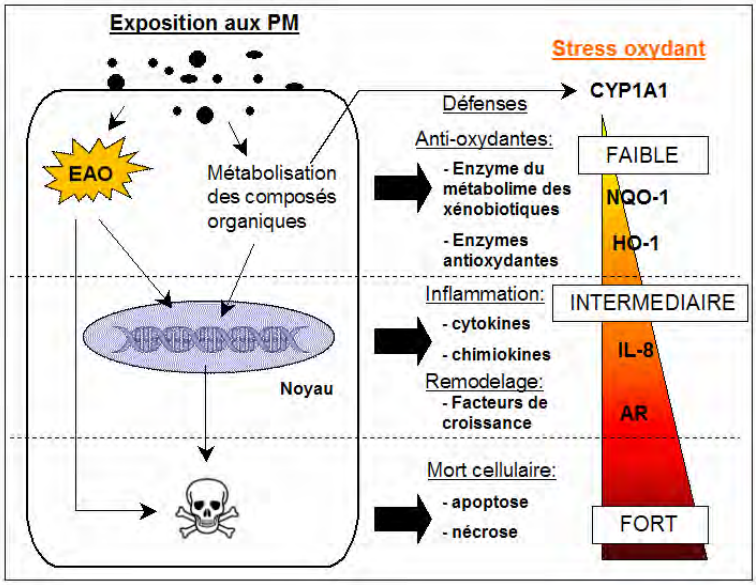

Figure I.4 : Effets cellulaires induits par une exposition aux PM en fonction de la réponse hiérarchisée au stress oxydant définie par Li et al. (2008).

c) Pour être complet, le ***Tableau I.2*** présente un résumé des quelques (rares) études recensées en Afrique de l'Ouest quant à l'impact sanitaire de la pollution urbaine. A Cotonou (Benin) une étude portant sur l'effet des particules quant à la destruction de l'ADN se basant sur l'analyse des urines de deux échantillons de population urbaine et rurale montre un effet de destruction plus important chez les populations urbaines exposées à des niveaux de concentrations de HAP (Hydrocarbure Aromatique Polycyclique) et de benzène 10 à 100 fois plus élevés comparé aux villageois (**Ayi Fanou et al., 2006**). Les tests d'exploration fonctionnelle réalisés sur 156 enfants à Cotonou révèlent que les enfants résidant à proximité d'un trafic automobile dense présentent un gros risque de perturbation des voies respiratoires (**Messan et al., 2011**). Les études menées par **Dieme et al. (2012)** sur les effets toxicologiques de particules prélevées sur des sites urbain et rural à Dakar (***Tableau I.2***) ont mis en évidence une réponse proinflammatoire plus importante des particules collectées en zone urbaine comparée aux particules prélevées en milieu rural. Par ailleurs, les auteurs ont rapporté que les HAP ainsi que certains métaux contenus dans les particules fines ($PM_{2.5}$) mesurées à Dakar (Sénégal) induisent l'expression de bio-marqueurs tels que le CYP1A1 ou CYP1B1 (Cytochrome P450 1A1 ou 1B1), TNF-α (Facteur Nécrosant de Tumeurs), IL-1β, IL-6, et/ou l'IL-8. On peut également citer les études de **Fall et al. (2008)** sur l'évaluation des effets des émissions des véhicules sur les tissus pulmonaires de rat exposés aux gaz d'échappement. Les résultats ont montré une altération du métabolisme du glutathion en présence d'émission essence. L'étude de **Kouassi et al. (2009**) à Abidjan (Cote d'Ivoire) sur la toxicité des $PM_{2.5}$ collectées sur trois sites (urbain, rural et industriel), indique la provocation de dommages oxydatifs par ces trois types d'aérosols lorsqu'ils sont mis en contact avec les cellules pulmonaires (A549).

D'autres études concernent les risques d'exposition de travailleurs dans certaines usines où sont dégagées des polluants atmosphériques (**Durosinmi et al., 1993 ; Akanle et al., 1999**). Ces nombreuses études s'articulent autour de la présence d'usines de raffinage du pétrole dans la région.

Tableau I.2 : Résumé des études recensées en Afrique de l'Ouest sur la pollution atmosphérique urbaine et son impact sanitaire.

Etude	Ville	Objectif	Principe	Type de d'échantillonnage
(Ayi Fanou et al., 2006)	Cotonou (Benin)	Evaluer la destruction des ADN suite à l'inhalation de particules atmosphérique	Dosage des ADN contenus dans les urines des deux groupes de populations	Des conducteurs de taxi non fumeurs vivant en ville et des villageois
(Messan et al., 2011)	Cotonou (Benin)	Evaluer les risques de l'exposition des enfants aux émissions automobiles	Tests d'exploration fonctionnelle respiratoire chez trois groupes d'enfants choisis en fonction de la distance entre lieu de résidence et trafic automobile dense	156 enfants
(Dieme et al., 2012)	Dakar (Sénégal)	Détermination des effets biologiques des particules fines ($PM_{2.5}$) sur les cellules BEAS-2B	Dosage des biomarqueurs : CYP1A1, CYP1B1, NQO1, TNF-α, IL-1β, IL-6, et IL-8	3 types d'aérosol (2 sites urbains et 1 site rural),
(Fall et al., 2008)	Dakar (Sénégal)	Mesurer les l'impact sanitaire des émissions de gaz d'échappement sur les tissus pulmonaires	Dosage du glutathion	Poumons de rats
(Kouassi et al., 2009)	Abidjan (Cote d'Ivoire)	Détermination des effets toxicologiques des particules fines ($PM_{2.5}$) sur les cellules A549	Mesure de la destruction des ADN	3 types d'aérosols (urbain, rural, industriel)

I.5. Cadre de l'étude : le programme POLCA

Notre étude s'inscrit dans le cadre du programme POLCA (pollution des Capitales Africaines), initié depuis 2007 et qui a pour objectif d'étudier la pollution atmosphérique urbaine tant gazeuse que particulaire pour faire le lien avec la santé des populations de deux villes d'Afrique de l'Ouest (Bamako et Dakar). Ce programme est financé par la Coopération pour la Recherche Universitaire et Scientifique (CORUS) sur une durée de 3 ans. Ma contribution dans ce projet consiste dans un premier temps à documenter la caractérisation physico-chimique des polluants particulaires à Bamako et Dakar, deux capitales d'Afrique de l'Ouest, différentes aussi bien sur le plan socio-économique que géographique et climatique. Ensuite, d'étudier l'impact sanitaire des particules mesurées. Cette partie a été réalisée en deux étapes : une étape de modélisation, consistant à modifier et à adapter le modèle de dépôt des particules dans le système respiratoire de la CIPR (Commission Internationale pour la Protection Radiologique), dédié initialement à des populations d'origines caucasiennes et asiatiques, aux populations d'Afrique de l'Ouest. La seconde étape, expérimentale, a consisté à évaluer les effets toxicologiques des aérosols sur l'organisme, en collaboration avec une équipe de toxicologues de l'université de Paris 7 (**A. Baeza**).

La stratégie expérimentale repose sur des deux campagnes de terrains (extensives et intensives) à chaque site étudié : 1) mesures à moyen terme (1 an) de certains polluants

particulaires d'intérêts (le carbone suie ou black carbon BC) et, 2) mesures à court terme (15 jours) de la spéciation chimique complète par classes de tailles de l'aérosol sur chaque site, en parallèle avec des mesures relevées pour les analyses toxicologiques.

CHAPITRE II : BILAN SUR LE BLACK CARBON (BC) : TRACEUR DE SOURCES DE COMBUSTION

II.1. Résumé de l'Article (A1)

Le carbone suie ou black carbon (BC) constitue l'un des principaux composants de l'aérosol urbain. Son étude présente un intérêt particulier pour des raisons liées à son impact sanitaire reconnu mais également son utilisation en tant que traceur de sources de combustion de fuels. Plusieurs méthodes permettent la mesure du BC dont la plus utilisée est la méthode optique (Aethalométre). L'Aethalométre est un instrument qui fournit en temps réel la concentration de BC dans l'air ambiant. Son mode opératoire est basé sur la mesure de l'atténuation optique de la transmission à une longueur d'onde donnée provoquée par l'échantillon collecté sur un filtre en fibre de quartz.

Cet article présente l'unique bilan du BC basé sur des mesures effectuées dans différentes villes d'Afrique de l'Ouest (Bamako, Dakar et Cotonou) et du centre (Yaoundé), caractérisées par des sources d'émissions variées (trafic automobile, moto à deux roues, feux domestiques, poussières, …). Les variations temporelles, spatiales et les niveaux de BC ont été déterminés pour chaque site, en particulier à Dakar.

Les résultats indiquent une nette variation intra-saisonnière des concentrations de BC à Dakar avec des valeurs maximales variant entre 11.5 et 15.5 µg/m^3 en saison sèche (Novembre-Avril) coïncidant aux pics d'émissions de BC par les feux de biomasse, suggérant ainsi une contribution de cette source aux niveaux élevés de BC constatés à Dakar.

Les évolutions diurnes des concentrations de BC montrent généralement deux pics le matin et le soir correspondant aux heures de pointes, quelque soit le site (***Figure II.1***). Ce résultat confirme la corrélation entre activités humaines et émissions de BC. Cependant, la position et la nature du pic de BC varient en fonction du site, ce qui suppose l'influence de plusieurs types de sources mais également la diversité intra-site urbain de ces sources en Afrique de l'Ouest. Par ailleurs, les variations hebdomadaires des concentrations de BC montrent une nette distinction entre jours ouvrables (Lundi à Vendredi) et week-end (Samedi et Dimanche) (***Figure II.1***), indiquant que les niveaux de BC sont modulés par l'activité des populations.

Les concentrations de BC mesurées sur nos sites sont comparables aux valeurs reportées pour les grandes mégacités et grandes villes industrialisées du monde.

Le rapport BC/$PM_{2.5}$ connu pour quelques points nous a permis d'effectuer une première estimation des concentrations de $PM_{2.5}$ sur une année à partir des données de BC collectées à Dakar. Ainsi, la concentration moyenne annuelle obtenue est quatre fois supérieure à la valeur limite annuelle de 10 µg/m^3 recommandée par l'OMS.

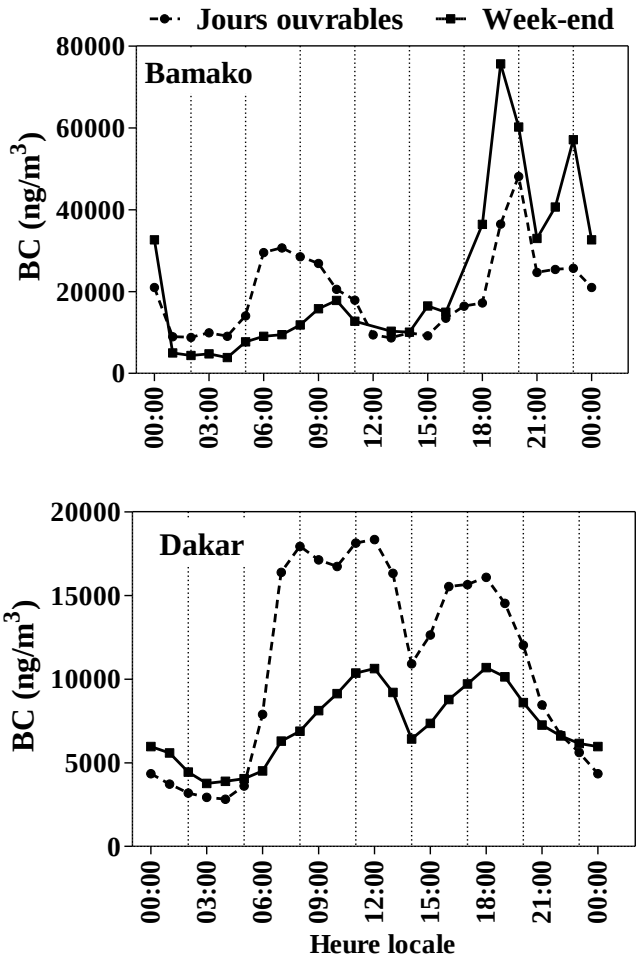

Figure II.1: Variations journalières des concentrations du BC pour les jours ouvrables (en noir), le week-end (en rouge) à Bamako (Avril 2008) et Dakar (Juin 2008-Juillet 2009).

II.2. Article A1

‘‘Real time Black Carbon measurements in West and Central Africa urban sites’’

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Abstract:

Real time measurements of Black Carbon (BC) in $PM_{2.5}$ aerosols were performed during AMMA and POLCA programs, between 2005 and 2010 in Cotonou (Benin), Dakar (Senegal), Bamako (Mali), and Yaounde (Cameroon). Indeed, BC was chosen as a metric because of its interest as an urban pollutant. The instrumented sites are representative of the traffic source. At Dakar, BC concentrations are high from November to April (13000 ± 3500 $ng.m^{-3}$) and lower from May to September (8000 ± 3200 $ng.m^{-3}$). In dry season (November-April), high BC concentrations occurred as a result of north-easterly long-range transport of polluted air masses over West Africa, in addition to local emissions. However, during wet season (May-September) reduced traffic levels, school vacations and wet deposition processes contribute to lower BC concentration levels. Measured diurnal BC peak concentrations, at all sites, mainly occur during morning and evening rush-hour periods, indicating the paramount role of traffic. Highest values are observed between 5-9 a.m. and from 5 p.m. to 9 p.m. depending on the site, while lowest are occurred at night time and middle afternoon when activities of the population are reduced. BC source apportionment from absorption measurements also confirmed the relative importance of traffic (88%) versus biomass burning (12%). Also, BC measurements were functions of days of the week, with highest values occurring on Fridays and lowest ones on Sundays. Spatial variations associated to BC levels are very different from one site to another, revealing different types of sources with strong variations at the regional scale. It appears that mean BC concentrations in Dakar are lower by a factor of two, compared to those observed in Bamako, but remain higher than in some other West African sites (e.g. Cotonou, Yaounde). Overall, BC concentrations in our different sites are comparable to reported European and Asian megacity levels.

Finally, using measured $BC/PM_{2.5}$ ratios, we have estimated $PM_{2.5}$ mass concentrations in Dakar from June 2008 to June 2009 to be 44.4 ± 14.3 $\mu g.m^{-3}$, well above the WHO (2005) threshold of 10 $\mu g.m^{-3}$. This paper clearly highlights high pollution levels in West African large cities, with potential important impacts on the health of the regional population.

Key words: Atmospheric pollution, black carbon, $PM_{2.5}$, urban site, traffic

1. Introduction

Atmospheric chemistry in West African rural areas and typical inter-tropical ecosystems has been the subject of programs such as DECAFE (1986-1992), IDAF (IGAC/DEBITS/Africa) (since 1994), EXPRESSO (1996), AMMA (2005-2006), …, (**Lacaux et al., 1993 ; Galy-lacaux et al., 2001 ; Delmas et al., 1999 ; Liousse et al., 2010**). Nevertheless, pollution and specifically, particulate emissions in urban African areas and their related health impacts have been poorly studied. There are indications that these areas are strong pollutant sources, with urban emissions quite comparable to sources in Europe, North America and Asia (**Assamoi and Liousse, 2010 ; Favez et al., 2008**). Rapid population growth, aged vehicle fleets, poor fuel quality, high per-vehicle emissions, and meteorological conditions contribute to severe atmospheric pollution in large West and Central African cities. Just visiting these regions is enough to realize the poor quality of the air. In 2004, a preliminary POLCA program (for "POLlution des Capitales Africaines") was carried out in several African capitals during 15 days. Preliminary measurements (NO_2, SO_2, O_3, HNO_3, NH_3) highlight, for example, NO_2 concentration levels well above the WHO threshold of 40 µg m^{-3} (**Liousse and Galy, 2010**). To better understand the role of atmospheric aerosols in air quality and their potential impact on health, a program dedicated to urban pollution was required. Supported by CORUS2 program (Cooperation for Academic and Scientific Research), a second POLCA program was launched in 2007 for 3 years. The objectives were to characterize atmospheric pollution including both gases and particles in some African capitals (Dakar in Senegal, Bamako in Mali and Yaounde in Cameroon) and to jointly study the impact of such pollution on human health, especially in terms of respiratory diseases. This paper deals with the first results of particulate pollution in the framework of the POLCA program presenting a focus especially on Black Carbon concentrations in $PM_{2.5}$ aerosols.

- Documentation about $PM_{2.5}$ concentrations in over developed countries has been seen to be more pertinent than PM_{10} concentrations for health purposes, particularly regarding particle penetration and deposition in the human respiratory tract. Indeed, excessive $PM_{2.5}$ concentrations have been shown to negatively affect human respiratory and cardiac health (**Pope et al., 2002**)**.** About 90% of black carbon aerosols reside in the $PM_{2.5}$ fraction, contributing to about 5 to 15% in the urban atmosphere (**Viidanoja et al., 2002**).

- Black carbon (BC) is well known to be a combustion tracer, emitted by fossil fuel combustion (traffic, domestic fires, industries...), most notably from diesel exhausts, together with various types of biomass burning (**Liousse et al., 1993**). Moreover, black

carbon aerosol particles have been seen to have a detrimental impact on human health (**Pope et al., 2002**). Atmospheric BC concentrations vary widely from a background level of 1.1 $ng.m^{-3}$ at the South Pole (**Hansen et al., 2001**), to 10000-20000 $ng.m^{-3}$ in Paris near the roadside (**Ruellan and Cachier, 2001**), to as much as 50000 $ng.m^{-3}$ in Kanpur, India (**Tripathi et al., 2005**). Moreover, since average residence times of BC aerosols are in the order of days to weeks, depending on the meteorology, they can be transported up to a few thousand kilometres far away from source regions (**Husain et al., 2007**). Thus, observed BC concentrations at a given site likely reflect both local emissions (e.g. two wheel and vehicles in Africa) and components from regional sources (e.g. biomass burning events in Africa).

In this work, we have investigated aerosol BC content within four typical source regions. Dakar is a populated area with about 70% public transport vehicles over 10 years old and mainly diesel. In Bamako, BC emissions are mainly due to traffic (two gasoline or gasoline/oil wheels) and solid fuel combustion (for example 35-50% of the populations are using wood and charcoal as their main source of domestic energy (**Assamoi and Liousse, 2010**)). In Yaounde, traffic is dominated by yellow diesel taxi with a minority of personal cars (12.6%). In Cotonou (Benin), most of the population use motorcycles as their main mode of transport. Note that all motor vehicles using fossil fuels highly emit particulate matter especially gasoline/oil engines.

Using aethalometer-collected data at Dakar for one year, and at Bamako, Yaounde and Cotonou for different periods, the objectives of this study are: (1) to analyze variations of BC concentration at the four sites with a focus on Dakar, (2) to compare BC levels with rural African sites and urban sites elsewhere, and (3) to give a first estimation of the exposure levels at Dakar to $PM_{2.5}$ aerosol.

2. Experimental method

2.1. Experimental sites

Black Carbon concentrations were automatically measured with three aethalometers (Magee Scientific, USA) with quartz fiber filter tape system with a 2-min time step. During this process the tape only moves when attenuation reaches maximum value of 100. Note that no humidity removal has been performed during measurements. The four sites (***Fig.1***) can be described as follows:

1) Dakar (14°40’20" N, 17°25’22" W, sea level), is a coastal city in west Senegal with a

population of about 3 million people (25% of the national population), and about 550 km^2 in area. Most (86%) vehicle transits in Dakar are made by rapid cars and minibuses. The sampling site is installed at Guigon pharmacy located near a crossroads at Sandaga main market: such a site is then affected by intense traffic from several nearby roads. For this study a seven-wavelength aethalometer (portable model AE-42) with $PM_{2.5}$ inlet was operated between April 2008 and July 2009 at a flow rate of 2 $L.min^{-1}$. Data were scanned with a short time-base, so as to eliminate nearby contamination peak-values which tend to increase BC concentrations by a factor of 2 to 3 (**Liousse and Cachier, 1992**).

2) Bamako (12°39'N, 8°04'W, altitude 380 m), is located in southwestern Mali. It is a city of nearly 2.2 million inhabitants (2009) and covers an area of about 267 km^2. The site is largely influenced by domestic fires and motorcycle emissions with 46% of the population owning a motorcycle (**DHS, 2006**). In Bamako, POLCA instruments including the seven-wavelengths aethalometer (model AE-42) with a $PM_{2.5}$ inlet was installed in April 2008 at the Nimaga building. The aethalometer operated at a flow rate of 4 L.min-^{1}. This studied site is located downtown, at a crossroads near the great market. BC data were also collected at different points of the city during the POLCA intensive campaign in January 2009: they will be presented too.

3) Yaounde (3.52°N, 11.31°E, altitude 750 m), political capital of Cameroon, is a city of nearly 2 million inhabitants (2002), with an area of 304 km^2. The city is characterized by a progressive rate of motorization and old vehicles (**Matcheubou et al., 2009**). A seven-wavelength aethalometer (model AE-31), with a flow rate of 5 $L.min^{-1}$, was installed in town center representative of two traffic sites near a crossroads (one at Elig-Essoma from June to august 2004 and another at Mvog-Mbi in August 2010).

4) Cotonou (6.21°N, 2.23°E, altitude 5 m), located on the coast of the Gulf of Guinea, covers a surface area of 67.5 km^2 with a population of 1.2 million inhabitants (2008). The city is polluted because of the increasing number of old second-hand cars (more than 240000) and using of two-stroke engine (with gasoline mixed to oil as a very dirty fuel) like taxis (**Assamoi and Liousse, 2010**). Moreover, gasoline is of poor quality due to the illegal import of sub-standard products from neighboring Nigeria (**Fanou et al., 2006**). The model AE-21 aethalometer (two wavelengths: 350 and 880 nm), operated at a flow rate of 4 $L.min^{-1}$, was installed in the town center on the Sogema building at Dantokpa market in May 2005 at the beginning of the wet season.

Let us precise that measurements could be longer in Bamako, Yaounde and Cotonou but some technical problems occurred with the aethalometers due to sampling conditions in Africa.

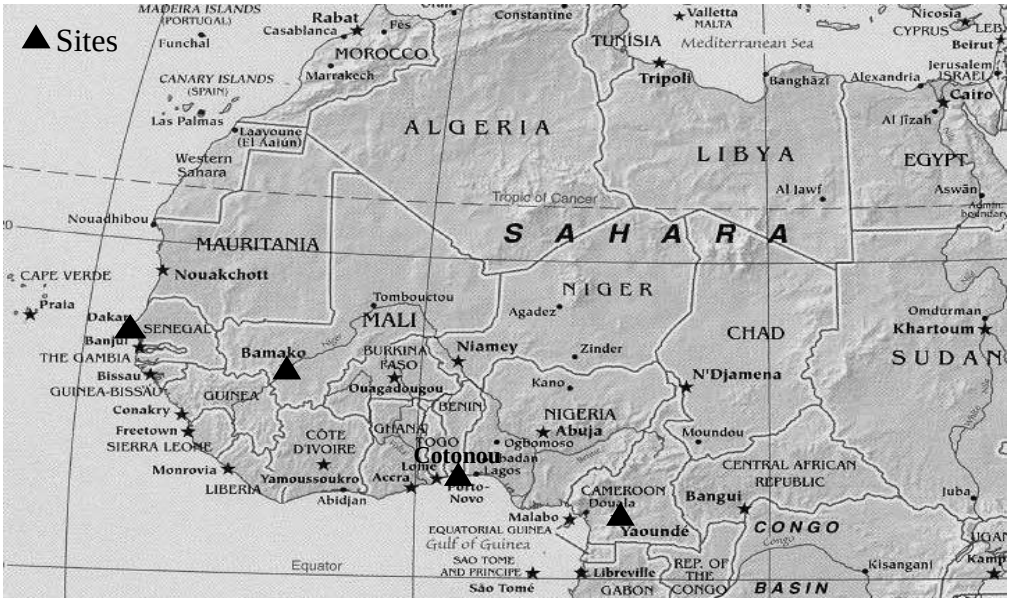

Fig. 1. Location map of the monitoring sites.

2.2. The aethalometer measurements

The operating principle of aethalometer is based on measurements of the optical attenuation of a light beam transmitted through samples on collected filters. Optical attenuation (ATN) is defined as $ATN=100 \ln(I_0/I)$, where I_0 is the intensity of transmitted light through the original filter and I, the intensity of light transmitted through the filter parts where deposited aerosols are collected (**Hansen et al., 1984**). It is assumed that ATN only increases due to light absorption by BC accumulated on the filters. Therefore, BC concentrations reported from aethalometers are calculated from the attenuation rate of change, using the specific attenuation coefficient ($m^2.g^{-1}$) that varies widely (**Petzold et al., 1997**). This variability is due to particle coating and ageing and to the chemical variability of aerosol mixtures (**Liousse et al., 1993**). Attenuation coefficients of 15.4, 16.6, 22.2, 24.8, 28.1, 31.1, and 39.5 $m^2.g^{-1}$ were used for the 950, 880, 660, 590, 520, 470 and 370 nm wavelength respectively, as recommended by the manufacturer. The 660 nm wavelength was chosen to investigate BC particles, excepted in Cotonou where values are given at 880 nm. Recent papers (**Schmid et al., 2006 ; Collaud et al., 2010**) have shown that additional corrections for instrumental artifacts and dust absorption are required.

Corrections account for the optical aerosol particles embedded in the filter. Among artifacts, there is the attenuation effect due to the filter loading, which can increase σ_{ATN} by 7

to 25% depending on the sites and the scattering artifact that takes into account the mean scattering of all aerosol embedded into the filter. Scattering correction decreases σ_{ATN} on average by 2 to 12% depending on the site measurement (**Collaud et al., 2010**). Because of lack of scattering data in parallel to our measurements, the maximum correction (12%) proposed by **Collaud et al. (2010)** for urban areas was applied to our data.

Another important artifact is the interaction of dust particles with aethalometer measurements. Two reasons can explain its importance. First, the Sahel region is subject to frequent dust events (**Klose et al., 2010**) and MODIS satellite aerosol images suggest that such dust events reach the West African area. Second, some dust (**Caquineau et al., 1998**) particles absorb light at visible wavelengths and synergistic effects can be expected to affect aerosol absorption coefficients when BC and dust are present. Note that, a "brown carbon" component is also expected to absorb light. Such phenomenon will not be considered here. **Fialho et al. (2005)** have proposed a new approach so as to decouple the contributions to attenuation data of multiple optical absorbing aerosols and especially BC and dust measured with a multi-wavelength aethalometer. Applying this method, measured BC concentrations were globally decreased by about 11% to only consider BC particles. Finally, when taking into account all of these corrections; the uncertainty on BC given by aethalometer is of the order of 30%.

Recent studies have shown that information delivered by multi-wavelength aethalometers can be used in conjunction with complementary carbon measurements, to provide source apportionment of carbonaceous aerosols: biomass burning, domestic wood combustion versus fossil fuel like traffic sources (**Sandradewi et al., 2008 ; Favez et al., 2010 ; Sciare et al., 2011**). We chose the model of **Sciare et al. (2011)** which relies on the different Angstrom Absorption Exponents for fossil fuel and biomass burning to derive concentrations of BC apportioned to fossil fuel (BC_{ff}) and biomass burning (BC_{bb}). The following equations are used:

$$b_{abs,\lambda} = b_{abs,ff,\lambda} + b_{abs,bb,\lambda} \quad (1)$$

$$\left(b_{abs,ff,470nm} / b_{abs,ff,950nm}\right) = \left(470/950\right)^{-\alpha ff} \quad (2)$$

$$\left(b_{abs,bb,470nm} / b_{abs,bb,950nm}\right) = \left(470/950\right)^{-\alpha bb} \quad (3)$$

$$BC_{ff} = b_{abs,ff,950} / MAE_{950m} \quad (4)$$

$$BC = BC_{ff} + BC_{bb} \quad (5)$$

where $b_{abs,ff,Xnm}$ is the absorption coefficient of fossil fuel at Xnm (X=470, 950); and $b_{abs,bb,Xnm}$ is the absorption coefficient of biomass burning at Xnm (X=470,950). In Eqs. (2) and (3), αff and αbb represent the Angstrom absorption exponents of fossil fuel and wood burning, respectively. In this study, values of 1.1 and 2.0 were used for αff and αbb, respectively, based on values previously reported for fossil fuel and wood burning aerosols (**Sandradewi et al., 2008 ; Favez et al., 2010**). In Eq. (4), MAE_{950nm} represents the Mass Absorption Efficiency calculated as the ratio between BC (thermo-optical method, DRI instrument) concentrations and b_{abs} at 950 nm. A mean MAE value of 15.1 ± 3.5 $m^2.g^{-1}$ was obtained from the data obtained during the intensive campaign at Dakar in December 2009 (data not presented here), with a regression coefficient of 0.53. This value is higher than in **Sciare et al., 2011**. This can be due to African sampling (**Liousse et al., 1993**). Note that in this model an assumption is made to use similar MAE values for fossil fuel and biomass burning sources. Further details of the model may be found in **Sciare et al. (2011)**.

3. Results and discussion

3.1. Seasonal BC concentration patterns at Dakar

Fig.2 displays corrected BC aethalometer measurements from June 2008 to July 2009 at Dakar, compared to biomass burning BC emissions in Senegal (**Liousse et al., 2010**). Seasonal variations show larger monthly mean BC concentrations between 15500 and 11500 $ng.m^{-3}$ during the dry season (November-April) and lower from May to September (6000 to 10000 $ng.m^{-3}$), with annual mean value of 10500 ± 3500 ng m^{-3}. The mean monthly emissions varied from 0.3 to 700 kg of BC per month, with a maximum value occurring in January. As above recalled, BC variations are influenced both by meteorological conditions, local and regional source variations: (1) in the dry season, high BC levels are most likely due to local traffic pollution. However, as shown by ***Fig. 2*** and ***Fig.3a***, biomass burning BC emissions from surrounding countries can impact Dakar. Indeed, continental aerosol is transported by trade winds (or the Harmattan) from northeast Senegal. Note that**,** the dry season is also characterized by stable atmospheric conditions in favor of high concentrations. Finally when the model described in the above paragraph is applied to aethalometer data set at Dakar to obtain BC source apportionment, fossil fuel emissions have been found to be 87% (13.04 ± 1.74 µg.m-^{3}) compared to 13% (1.88 ± 0.33 $\mu g.m^{-3}$) for biomass burning emissions; (2) During the wet season, from April/May to September, Dakar is influenced by cool and humid

maritime air masses, loaded with maritime aerosols (***Fig.3b***). This period, associated with the monsoon over the study area, is characterized by wet deposition processes. In addition, the wet season coincides with the school vacation in Dakar and thus traffic decreases. This is in agreement with BC source apportionment model which gives less fossil fuel and less biomass burning BC concentrations in the wet season than in the dry season (89% (7.87 ± 0.81 µg.m^{-3}) and 11% (0.98 ± 0.18 µg.m^{-3}), respectively). However, relative importance of fossil fuel is slightly higher than biomass burning in the wet season than in the dry season. Note that, further investigations are needed due to uncertainties on MAE and α calculations. Similar patterns may be noticed in Yaounde (***Table.1***) where BC concentrations are higher at the beginning of August than during the rest of the sampling period when the wet season is well established (May-June).

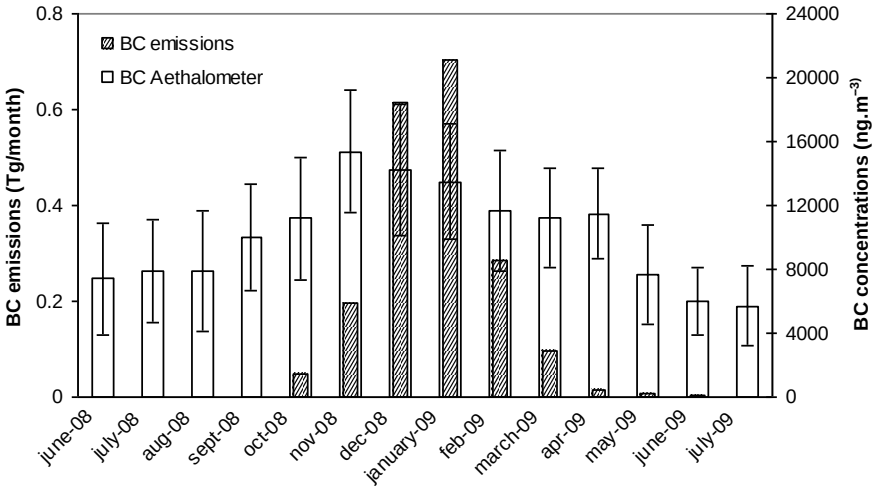

Fig. 2. Plot of corrected BC aethalometer concentrations and monthly mean biomass burning BC emissions in Senegal.

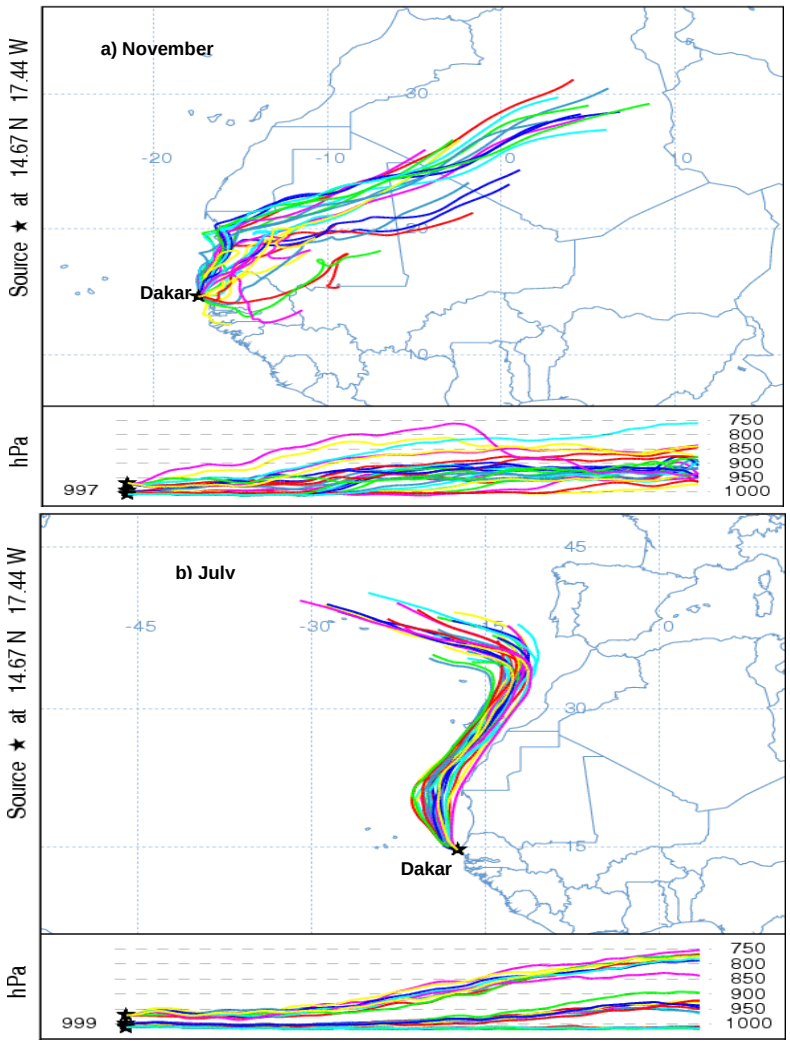

Fig. 3. Seven-day HYSPLIT air mass back trajectories for two representative months: (a) shows a set of typical trajectories during one period in the dry season, (b) shows a set of typical trajectories during one period in the wet season. Trajectory altitude is at 104 m above the Dakar sampling site.

3.2. Diurnal BC variations in different cities, with a focus on Dakar

BC diurnal variations were investigated by calculating average BC concentrations at the same time every day for each month. At Dakar, average hourly BC concentrations were found to range between 400 to 21000 ng.m^{-3}. Significant, well-defined diurnal BC variations for two representative months of the wet/summer and dry/winter periods are shown in ***Fig.4***. In July 2009, during the wet season, the average diurnal profile was relatively flat, with a discernible pre-dawn minimum in the morning and a wide peak from 7 a.m. to 2 p.m., including morning commuting. Average hourly BC concentration was 7400 ng.m^{-3}, with concentrations never exceeding 50000 ng.m^{-3}. In November 2008, during the dry season, average diurnal profiles also show a large morning peak (between 7 a.m. and 2 p.m.) and a clear afternoon commuting

peak (between 5 and 7 p.m.), with maximum mean concentration of 30000 ng.m^{-3}. A well defined minimum occurs at 3 p.m. and at night time. Diurnal profiles in November are not very different from those in July, except that maximum morning BC concentrations were higher, approaching nearly 80000 ng.m^{-3} whilst the afternoon maximum was more than twice as high. Morning BC peaks arise from the combined effect of boundary layer development, which mixes aerosols from the nocturnal residual layer to the surface shortly after sunrise and from increasing local anthropogenic activities in the urban area. Low BC concentrations in the afternoon are attributed to aerosol dispersion, due to boundary layer thickening in addition to lower traffic density. As shown earlier, lower BC values in July can be partly explained by wet deposition, the beginning school vacation in Dakar and the absence of biomass burning influence.

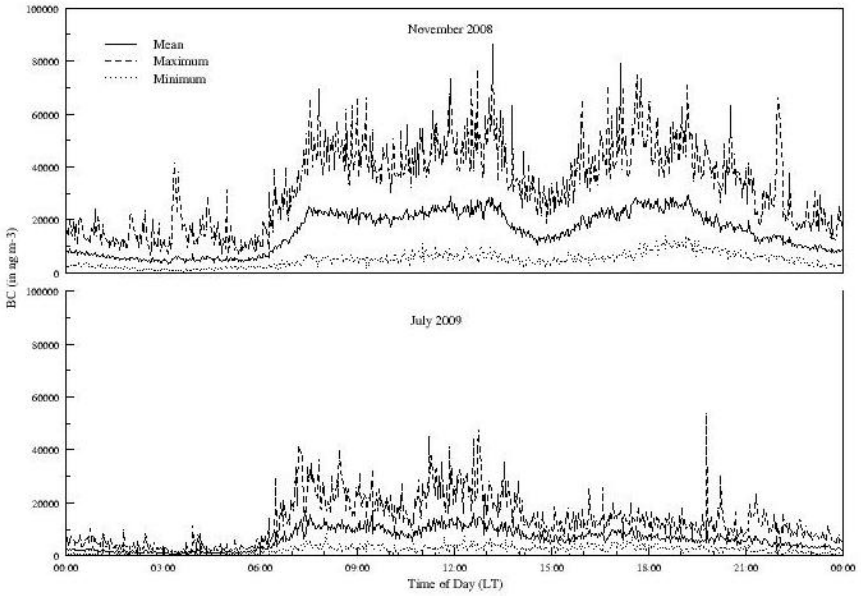

Fig. 4. Diurnal profiles of the maximum, average and minimum aethalometer measured BC concentrations in Dakar for two selected months (hours in local time LT).

Fig.5 displays the time series of integrated BC concentrations observed at Bamako in April 2008 (dry season), at Cotonou in May 2005 (beginning of the wet season) and at Yaounde in June 2004 (end of the wet season). Average, maximum and minimum BC values display consistent diurnal variations, with morning and evening peaks. At Bamako, average BC values are about 19000 ± 13000 ng.m^{-3}, with minimum values of about 1000 ng.m^{-3} occurring at night time (1-6 a.m.) and in the afternoon (from about 1 to 6 p.m.), then increasing to 50000-70000 ng.m^{-3} in the evening (***Fig.5a***). In the morning, there is a peak between 6 and 8 a.m., consistent with morning rush hour traffic combined with the low boundary layer height

which prevents aerosol particle vertical dispersion. The most striking feature of this figure is that higher BC concentrations are observed during evening hours (7-9 p.m.) than in the morning. This may be attributable to two features:

- Firstly, local source contribution is high: at this time, intense domestic fires occur (most people use wood and charcoal combustion for cooking); tire burning is often observed in the city; and traffic sources are important due to commuting people.

- Secondly, this is due to the fumigation effect since Bamako is located in a basin and in the evening pollutants become trapped near the surface in the residual boundary layer.

Such a peak is later than in Dakar (6 p.m.). Also, BC concentrations in Bamako are about 2 times higher than in Dakar.

Observed diurnal BC profiles at Cotonou present a large peak in the morning, pretty much at the same time as in Bamako, although the morning and late afternoon peaks are lower in Cotonou (***Fig.5b***). Average BC concentrations were about 5000 ± 4000 $ng.m^{-3}$. Patterns for both cities display strong morning rush hour peaks and decreased concentrations during the afternoon. However, evening BC concentration peak in Cotonou occurs later and is narrower than in Bamako (about 9 p.m. only). Concentrations are up to four times lower in Cotonou than in Bamako. This is largely due to the meteorological conditions at Bamako which do not favor pollutant dispersion. In addition, the DHS report shows more vehicles in Bamako than in Cotonou in 2005 and charcoal is more widely used for cooking. Finally, Cotonou sampling is situated at the beginning of wet season whereas Bamako sampling was done during the dry season. Let us note that results also show that mean BC concentrations in Cotonou are in the same range compared to Dakar for the same month (7000 ± 3000 $ng.m^{-3}$).

Diurnal BC variations in Yaounde (***Fig.5c***) show the same profiles as in Dakar (***Fig.4***), with less important morning and evening peaks. Consequently, Yaounde and Dakar are expected to have identical local sources of BC emissions which are diesel. Average BC concentration during June is 3000 ± 700 $ng.m^{-3}$ and 6000 ± 2000 $ng.m^{-3}$ at Yaounde and Dakar, respectively. This difference can be explained by a difference in season: in Yaounde, June corresponds to the end of the wet season whereas in Dakar it is the beginning. Moreover let us underline the altitude of the measurement site (1002 m for Elig-Essomo site) whereas Dakar is at sea level. In summary, even if only a limited number of BC measurements are presented in this work, BC levels measured at traffic site at Bamako appear significantly higher than in Dakar, Cotonou and Yaounde. This comparative study also highlights the strong variability in

pollutant sources in major cities in Africa (e.g. different diurnal variations have been shown).

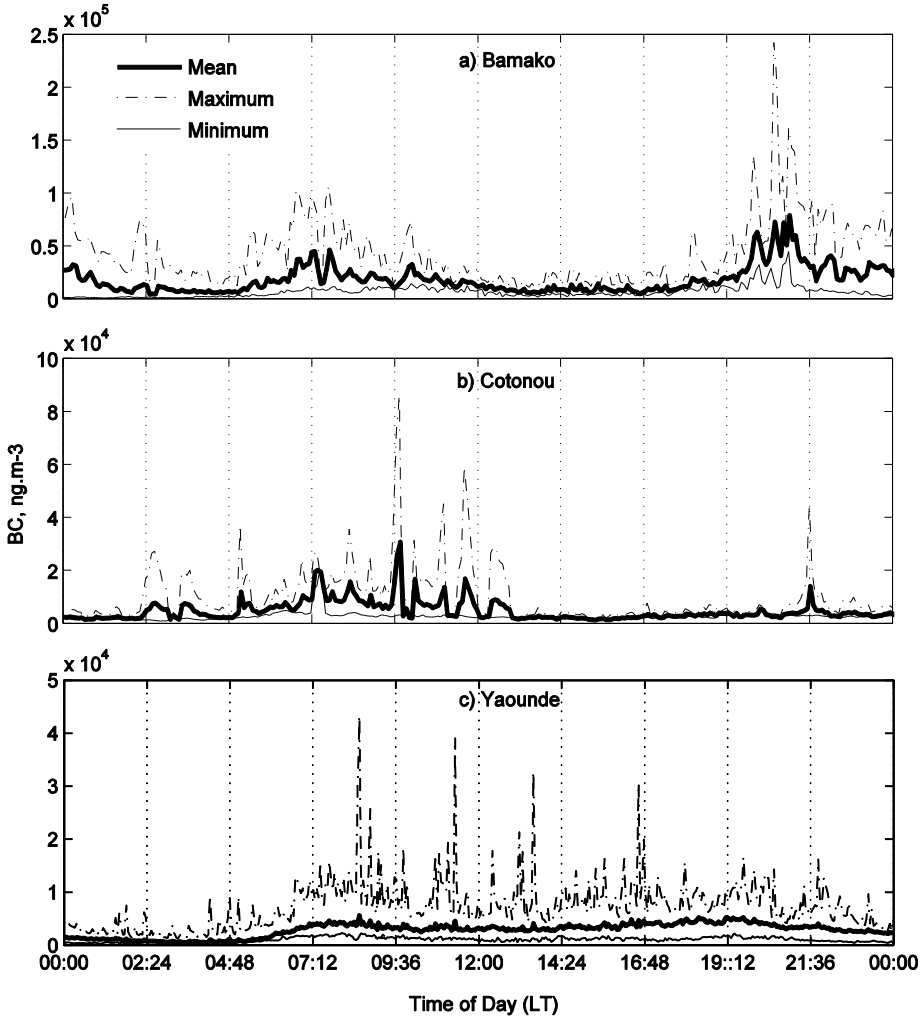

Fig. 5. Diurnal profiles of the maximum, average and minimum Aethalometer BC concentration in Bamako (April 2008), Cotonou (May 2005) and Yaounde (June 2004) (hours in local time LT).

3.3. Weekly BC concentration variations in different cities

We examined BC concentrations as a function of the day of the week in our sampling sites. Weekday measurements, from Mondays to Thursdays, provide robust baseline data for these four days and were averaged so as to generate a single, typical diurnal profile while profiles for Fridays, Saturdays, and Sundays were generated separately. The resulting profiles for Dakar, Bamako and Yaounde are shown in ***Fig.6***. At Dakar, from Mondays through Fridays, midnight concentrations are about 5000 $ng.m^{-3}$, decreasing to a minimum of 2500 $ng.m^{-3}$ at 5 a.m. (***Fig.6a***). The morning traffic peaks rise rapidly to about 19000 $ng.m^{-3}$ just before 8 a.m., before remaining approximately constant until 1 p.m. Thereafter, concentrations rapidly decrease to values of 8000 $ng.m^{-3}$, before rising again to 15000 $ng.m^{-3}$ at 6 p.m., followed by

another rapid decrease to 5000 ng.m^{-3} at midnight. The individual BC profiles of weekend days shows several different features from this general pattern. The first significant difference is found for Sundays, when BC peaks are much lower than the rest of the week. Mean BC concentrations are 50% lower on Sundays than during weekdays (from Mondays to Thursdays). This is also the case on Saturdays, with concentrations 18% lower than on weekdays. Note that on Sunday night BC values are higher than the other days, implying enhanced vehicle circulation, likely a result of the population returning after the weekend. Unfortunately, traffic count data are not available to confirm these hypotheses.

Fig.6b shows day of the week BC data gathered during the month of April 2008 at Bamako. Results display similar trends to those observed in Dakar. However, morning and evening peaks are much higher and evening peaks occurred later as previously shown (about 8 p.m.). The figure clearly shows that the Friday morning BC peak is much higher than the Monday to Thursday peaks due to more intense activities on Friday (last day of the week, preparation of the weekend, day of market). Also, this Friday morning peak is as high as the BC peaks found during Friday and Saturday evening: that is certainly due to the use of domestic fires for cooking, in addition to other population activities. Note that meteorological conditions contribute to high BC values when the wind was usually low. The generated diurnal profiles in Bamako were fairly consistent throughout the week but the largest differences between the different profiles were during the nighttime.

Finally, ***Fig.6c*** presents weekly BC concentrations in Yaounde in June 2004, with lower values on Sundays. This figure confirms that pollution sources in Yaounde and Dakar are quite comparable. Note that at a monthly or seasonal scale, lower BC values in Yaounde than in Dakar can be also partly explained by the two rainy seasons and more aerosol wet deposition.

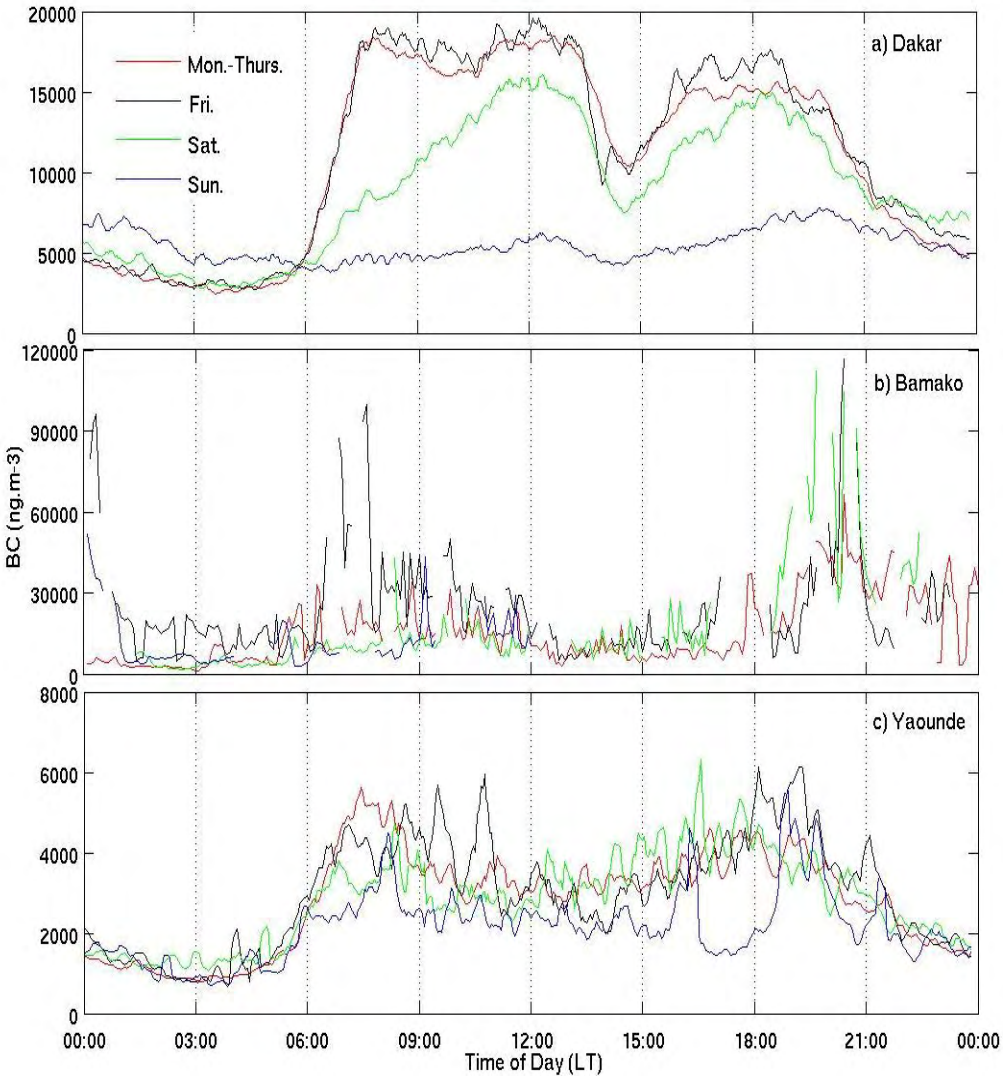

Fig. 6. Diurnal plots of the geometric mean of BC measurements for different days of the week averaged: a) Dakar, during the period from June 2008 to July 2009; b) Bamako during April 2008; and c) Yaounde during June 2004.

3.4. In-town BC variability: the Bamako case

A mobile experiment was carried out in the streets of Bamako by a vehicle equipped with a portable aethalometer. During the experiment, the vehicle was stopped at particular points and measurements taken for a few minutes, before continuing. ***Fig.7*** displays the time series of 1-min integrated BC concentrations observed along the vehicle's trajectory in Bamako on January 23, 2009. Clearly, BC data showed high isolated peaks, with concentrations significantly increasing for periods of only a few minutes to values exceeding 90000 ng.m^{-3}. These results are in agreement with previous studies conducted in Milan or Los Angeles (**Invernizzi et al., 2011 ; Zhu et al., 2002**). Indeed in such works, BC concentration changes have been observed in a distance of less than 1-km far from the emission source due to rapid

BC dilution and/or differences in traffic density in the same road. Our measurements also show similar average BC concentrations downtown and at our sampling site, whereas the market site shows much higher concentrations. These higher values are likely due to intense traffic within and just around the market. In addition, many activities such as small outdoor restaurants using charcoal, motorcycle repairs, etc, are found within the market and possibility contributes as manifesting particulate sources. Outside the market and in the city center, BC values are lower, for example at Point G near the hospital and near the Niger River BC concentrations was found to be about 1000 ng.m^{-3}. These latter points can be considered as representative of background pollution. From these results, it can be inferred that Bamako has various sources of particulate BC which strongly affect the city in highly localized areas. Let us recall that our site is representative of downtown conditions. Such a phenomenon of large variation in the concentrations within town center is also noticed in Yaounde when scrutinizing BC concentration levels at two different sites (***Table.1***).

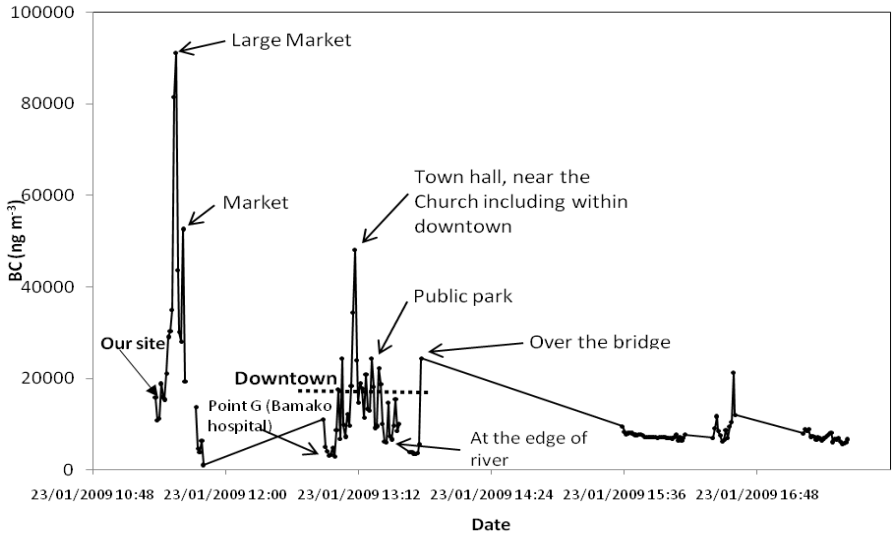

Fig. 7. Spatial variability of BC concentrations as measured in different places of Bamako (January, 2009).

3.5. BC concentration measurements compared with African rural sites and other worldwide metropolis

Table.1 summarizes BC data obtained in our study with literature data. In our sites, we have found that a yearly mean BC value is about 10.4 ± 3.5 µg.m^{-3} at Dakar. Average BC concentration obtained during April in Bamako is 19.2 ± 8.9 µg.m^{-3} whereas in Yaounde measured BC is from 2 to 8 µg.m^{-3} (from June to August). At Cotonou mean BC value is 4.9 ± 3.9 µg.m^{-3} in May. In the ***Table 1***, it may be seen that, these values are in the same range

than those obtained at some African rural sites during intense winter biomass burning periods. For example, BC at Cotonou, Yaounde and at Djougou is of the same order (0.4-8.2 µg.m^{-3}) (**Liousse et al., 2010**), thus confirming that urban pollution can be as important as the biomass burning source in West Africa.

Average BC levels obtained in our study are at the top of the range of values found in the literature, and of the order of those for some megacities and/or traffic sites. **Green (2007)** has reported BC values of 12.2 µg.m^{-3} at Marylebone, London (traffic site). **Ruellan and Cachier (2001)** measured average BC concentrations ranging between 10 and 20 µg.m^{-3} in Paris also at a roadside site (***Table 1***). **Guinot et al. (2007)** reported average BC concentration varying from 1.2 - 16.3 µg.m^{-3} in Beijing, China. BC measurement in Karachi, Pakistan, in April 2006 and April 2007 by **Vincent et al. (2009)** ranged between 2 to 15 µg.m^{-3}, whereas measurements by **Balasubranmanian et al. (2003)** varied from 3 to 14 µg.m^{-3} in Singapore. With such a comparison, we may underline exceptionally high pollution levels found in Africa comparable to other megacities and/or industrial areas. As mentioned here, sources are different (very aged vehicle fleet, poor quality fuel, charcoal burning) than in developed countries and often much more polluting. Indeed, recent measurements of emissions have demonstrated that BC and OC emission factors have to be multiplied by factors of about 10 for 2-stroke motorbikes compared to those of northern countries (**Guinot at al., 2011 ; Assamoi and Liousse, 2010**). Moreover such large values in our study are associated with other meteorological effects (e.g. the location of Bamako in a basin, as well as low wind speeds and stable atmospheric conditions which affect the West African region as a whole).

Table.1: Average BC concentrations in different sites including our measurements (all the data were obtained with optical methods).

Type	Location	Period	BC (µg.m^{-3})	References
Urban, traffic	Dakar. Senegal	June 08-July 09	**5.7-15.4**	This work
	Bamako. Mali	April 2008	**19.2 ± 8.9**	This work
	Cotonou. Benin	May 2005	**4.9 ± 3.9**	This work
	Yaounde. Cameroon Site 1	June-July 2004	**2.4 ± 0.8**	This work
	Site 2	August 2010	**5.7 ± 2.3**	This work
	Paris. France	Aug.-Oct. 97	**10-20**	Ruellan et Cachier, 2001
	Singapore. Asia	Jan.-Dec. 00	**3-14**	Balasubranmanian et al., 2003
	Kanpur. India	December 04	**12.3**	Tripathi et al., 2005
	Karachi. Pakistan	Apr. 06-Apr. 07	**2-15**	Vincent et al., 2009
	Beijing. China	Jan. 03- Aug. 04	**1.2-16.3**	Guinot et al., 2007
	Xi'an. China	Sept 03-April 04	**16.5 ± 9.8**	Li Y. et al., 2004
	Marylebone. London	Oct-Dec 06	**12.2**	Green, 2007
	California. USA	May 99-Dec 99	**1.4**	Watson, 2001
Suburban	Gif sur Yvette. France	Oct 89-March 90	**0.3-15**	Liousse et Cachier, 1992
Rural	Lamto. Ivory Coast	Jan 1991	**3.4 ± 1.1**	Cachier et al., 1995
	Djougou. Benin	Dec 05-feb 06	**0.4-8.2**	Liousse et al., 2010
	Banizoumbou.	Dec. 04-Nov.05	**0.4-1.6**	Liousse et al., 2010

4. Derivation of estimated $PM_{2.5}$ mass concentrations

Exceptionally high BC concentrations have been obtained in Dakar and it is of interest to see if such pollutant levels may have an impact on health. However, even if there is an evident link between BC and health issues, no legal limit of concentration exists for BC in Senegal or for the world. Let us note that there is recent proposition to consider BC as a new metric or indicator of air pollution in urban megacities (**Jansen et al., 2011**). The World Health Organization (WHO) suggests only guidelines for particles smaller than 2.5 µm ($PM_{2.5}$) that are considered to contribute to the health effects observed in urban environments. Consequently, in this section we tentatively derive $PM_{2.5}$ mass concentrations from our BC trends by establishing a ratio between BC and $PM_{2.5}$. The method used is based on chemistry measurements performed at Dakar on $PM_{2.5}$ aerosols. Starting from June 1, 2008 to July 9, 2009, BC measurements were performed using an aethalometer. From November 16, 2007 to June 16, 2008, $PM_{2.5}$ aerosol samples were collected on a weekly basis and analyzed for carbonaceous aerosol (BC and OC) determined using DRI method (**Chow et al., 1993**), water soluble ions (Na^+, NH_4^+, Ca^{2+} , NO_3^-, SO_4^{2-}, Cl^-, etc.) by Ion Chromatography (**Kouvarakis et al., 2002**) and other trace elements (Al, Ti, Cr, Fe, Ni, Zn, Pb, Cd, Cu, etc.) using ICP-MS (**Rocholl et al., 1997**). Note that for the first 16 days in June, 2008 (the only period common to these two series of experiments) BC concentrations as measured by aethalometer, are comparable with BC measured on filters using the DRI analyzer (thermo-optical method). The $PM_{2.5}$ mass reconstructed from our chemical analysis is then defined as:

$$MassPM_{2.5} = [BC] + [OM] + [SO_4^{2-}] + [NH_4^+] + [NO_3^-] + [Dust] \quad (6)$$

For deriving the amount of carbonaceous material in aerosols, we consider the sum of $[BC]+[OM]$, assuming that $[OM]=1.3\times[OC]$, the 1.3 conversion factor having been derived from other urban studies with an estimated uncertainty of ± 0.20 (**Stelson and Seinfeld, 1981**). Dust concentration was explicitly determined from aerosol composition (Al concentration obtained from ICP-MS) following **Guieu et al. (2002)** and a conversion factor of Al to dust of 1/0.071 was used. Nevertheless, Al concentration is only available for November 16, 2007-February 18, 2008 period. Therefore, the second period uses calcium data obtained from November 16, 2007 to June 16, 2008 with the IC to calculate dust mass concentrations. According to **Sciare et al. (2005)**, we determine dust mass concentrations in $PM_{2.5}$ using the following relationship**:** dust mass = 10.96 ± 1.00 nss-Ca^{2+}, where nss-Ca^{2+} = Na^+ - 0.038xCa^{2+} refers to non sea salt calcium concentrations. Thus, estimated dust from $PM_{2.5}$ in Dakar using Al and Ca^{2+} concentrations are 8.42 ± 6.67 µg.m^{-3} and 7.90 ± 5.86 µg.m^{-}

^{3}, respectively. Consequently, the reconstructed $PM_{2.5}$ masses generated by Eq. (6) are associated with uncertainties due to chemical analysis but also to missing species in Eq. (6) such as some ions and anthropogenic metals which were measured to be negligible in mass. Taking into account such uncertainties with the uncertainties due to OC-to-OM and Ca^{2+}-to-Dust conversion factors, estimated reconstructed mass uncertainty was assumed to be of the order of 30%.

$BC/PM_{2.5}$ ratios were calculated from the two dust estimates from November, 2007 to February, 2008 and November, 2007 to June, 2008 respectively, to be 0.18 ± 0.10 and 0.22 ± 0.12. Using these values, we considered an average ratio of 0.2 ± 0.10 to estimate $PM_{2.5}$ mass concentrations from BC in Dakar.

Resulting daily mean $PM_{2.5}$ varied from about 24 to 80 µg.m^{-3}, with an average 57 µg.m^{-3} for the dry season. This is sometimes more than the US-EPA daily $PM_{2.5}$ standard of 65 µg.m^{-3}. This value is comparable to previous studies in Dakar by **Guerreiro et al., (2005b**), who found that daily $PM_{2.5}$ concentrations ranged from 23 to 62 µg.m^{-3} with a mean value of 38 µg.m^{-3}. From June 2008 to May 2009, annual average $PM_{2.5}$ concentrations in Dakar were 44.4 ± 14.3 µg.m^{-3}, four times higher than the WHO (2005) annual threshold of 10 µg.m^{-3} (***Fig.8***). This result is of the order of concentrations (64.5, 39 or 39-53 µg.m^{-3}) reported for traffic sites in Beijing, Chine (**Guniot et al., 2007**), Paris (**Ruellan and Cachier, 2001**) or Accra, Ghana (**Dionosio et al., 2010**), respectively. Consequently, pollutants in urban African areas need to be urgently monitored.

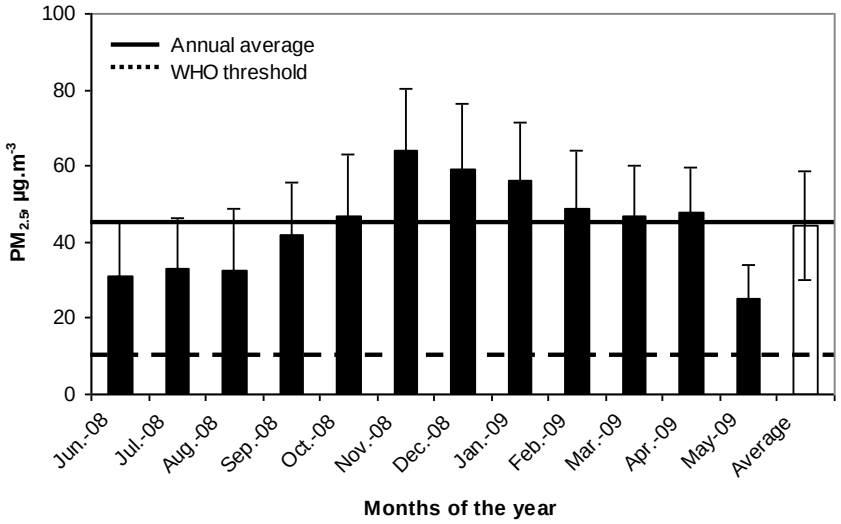

Fig. 8. Monthly mean $PM_{2.5}$ mass concentrations in Dakar.

5. Conclusion:

Aethalometer BC measurements were conducted at Dakar from June 2008 to July 2009, at Bamako during April 2008, at Cotonou during May 2005 and Yaounde from June to July 2004 and June 2010. BC values display strong temporal and spatial variations. Annual average BC concentrations at Dakar were 10500 ± 3500 $ng.m^{-3}$, comparable to levels found at African rural sites during biomass burning periods and as high as those found in European and Asian megacities. BC concentrations in Dakar were higher in the dry season (13000 ± 3500 $ng.m^{-3}$) than in wet season partly due to biomass burning transport with north-easterly winds. Also in wet season, lower BC concentrations (of about 8000 ± 3200 $ng.m^{-3}$) may be due to prevailing monsoon winds, indicative of south-western air masses bringing relatively clean marine aerosols to Dakar, in addition to wet deposition and school vacation at this period. Finally a source apportionment from aethalometer data has shown that BC concentrations in Dakar are largely influenced by traffic emissions (88%) compared to biomass burning emissions (12%).

At Dakar, Cotonou and Yaounde, diurnal BC concentrations show highest values between 5-9 a.m., coincident with the commuting period and lowest values from 10 a.m. to 5 p.m. In contrast, in Bamako, highest observed BC concentrations occurred between 7 and 9 p.m. with two peaks and lowest values appeared during the mid-afternoon. Diurnal patterns largely result from traffic and meteorological conditions (e.g. changes in the mixed layer height) with a strong contribution from domestic fires at Bamako and Cotonou. Note that increased mixed layer heights favour dilution of pollutants in the late morning and afternoon. Also, BC measurements were functions of days of the week, with highest values occurring on Fridays and lowest ones on Sundays. Note that these concentrations are expected to vary within cities following results obtained in Bamako during our mobile experiments. These results confirm that in West and Sub-Saharan African great cities there is now a “hot spot” of emissions, particularly due to the emissions from vehicle engines, domestic fires and in some cases biomass burning.

Estimated $PM_{2.5}$ concentrations in Dakar indicate that daily averages vary from about 24 to 80 $\mu g\ m^{-3}$. The annual average is 44.4 ± 14.3 $\mu g.m^{-3}$, well above the WHO threshold of 10 $\mu g.m^{-3}$. Clearly, aerosol particles in these regions can play a significant role in public health issues for the local population. This is what we are going to study now with results of intensive POLCA experiments in Dakar and Bamako.

References (A1)

Assamoi, E.-M., Liousse, C., 2010. A new inventory for two-wheel vehicle emissions in West Africa for 2002. Atmospheric Environment, 44, 3869-3996.

Balasubramanian, R., Qian, W.B., Dccesari, S., Facchini, M.C., Fuzzi, S., 2003. Comprehension characterization of $PM_{2.5}$ aerosols in Singapore. Journal of Geophysical Research 108 (D16), 4523.

Cachier, H.,C. Liousse, P. Buat-Menard, 1995. Particulate content of savanna fire emissions. J. atmos. Chem. 22 , 123–148.

Caquineau, S., Gaudichet, A., Gomes, L., Magonthier, M. C., and Chatenet, B., 1998. Saharan dust: clay ratio as a relevant tracer to assess the origin of soil-derived aerosols. Geophysical Research Letters, 25(7), 983-986.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies, Atmos. Environ., 27A (8), 1185–1201.

Collaud. C.M., Weingartner, E., Apituley, A., Ceburnis, D., Fierz-Schmidhauser, R., Flentje, H., Henzing, J.S., Jennings, S.G., Moerman, M., Petzold, A., Schmid, O., Baltensperger, U., 2010. Minimizing light absorption measurement artifacts of the Aethalometer: evaluation of five correction algorithms, Atmos. Meas. Tech., 3, 457-474.

Delmas, R.A. et al., 1999. Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO): An overview, J. Geophys. Res., 104, D23,30, 609-30, 624, doi:10.1029/1999JD900291.

Dionisio, K.L., Arku, R.E., Hughes, A.F., Vallarino, J., Carmichael, H., Spengler, J.D., Agyei-Mensah, S., Ezzati, M., 2010. Air Pollution in Accra Neighborhoods: Spatial, Socioeconomic, and Temporal Patterns. Environ. Sci. Technol., 44, 2270–2276.

DHS (Demography Health Survey), 2006. DHS Final Reports. Available from: http://. www.measuredhs.com/pubs/browse_region.cfm .

Fanou, L.A., Mobio, T.A., Creppy, E.E., Fayomi, B., Fustoni, S., Moller, P., Kyrtopoulos, S., Georgiades, P., Loft, S., Sanni, A., Skov, H., Ovrebo, S., Autrup, H., 2006. Survey of air pollution in Cotonou, Benin air monitoring and biomarkers. Science of the Total Environment, 358, 85-96.

Favez, O., Cachier, H., Sciare, J., Alfaro, S.C., El-Araby, T.M.,. Harhash, M.A, Abdelwahab, M.M, 2008. Seasonality of major aerosol species and their transformations in Cairo megacity. Atmospheric Environment, 42,7,1503-1516.

Favez, O., El Haddad, I., Piot, C., Bor´eave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., D'Anna, B., 2010. Intercomparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France), Atmos. Chem. Phys., 10, 5295–5314.

Fialho, P., Hansen, A.D.A., Honrath, R.E., 2005. Absorption coefficient by aerosols in remote area: a new approach to decouple dust and black carbon absorption coefficients using seven-wavelength Aethalometer data. Aerosol Science 36, 267-282.

Galy-Lacaux, C., Carmichaël, G.R., Song, C.H., Lacaux, J.P., Modi, I., 2001. Heterogeneous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations Region. Journal of Geophysical Research, 106, D12pp 12559-12578.

Green, D., Alexander J., Fuller, G., 2007. Marylebone Road Aethalometer Trial Raport. Environmental Research Group, King's College London, 41p.

Guerreiro, C., Laupsa, H. and Sivertsen, B., 2005b. Ambient Air Pollution Screening Study Dakar 2005. Kjeller (NILU OR 17/2006).

Guieu, C., Loye-Pilot, M.-D., Ridame, C., Thomas, C., 2002. Chemical Characterization of the Saharan dust end-member: Some biochemical implications for the Western Mediterranean sea, J. Geophysical Res., 107, doi: 10.1029/2001JD001536.

Guinot, B., Cachier, H., Sciare, J., Tong, Y., Xin, W., Jianhua, Y., 2007. Beijing aerosol: atmospheric interactions and news trends. Journal of Geophysical Research, 112, D14314, doi:10.1029/2006JD008195.

Guinot, B., Liousse, C., Cachier, H., Guillaume, B., et al., 2011. New emission factor estimates for bio-fuels and mobile sources. Submitted to Atmospheric Environment, 2010.

Hansen, A.D.A., Rosen, H., Novakov, T., 1984. The aethalometer: an instrument for the real time measurement of optical absorption by particles. Sci. Tot. Environ 36, 191-196.

Hansen, J.E., R. Ruedy, Mki. Sato, M. Imhoff, W. Lawrence, D. Easterling, T. Peterson, T. Karl, 2001. A closer look at United States and global surface temperature change. J. Geophys. Res., 106, 23947-23963.

Husain, L., Dutkiewicz, V.A., Khan, A.J., Ghauri, B.M., 2007. Characterization of carbonaceous aerosol in urban air. Atmospheric Environment 41, 6872-6883.

Invernizzi, G., Ruprecht, A., Mazza, R., De Marco, C., Mocnik, G., Sioutas, C., Westerdahl, D., 2001. Measurement of black carbon

concentration as an indicator of air quality benefits of traffic restriction policies within the ecopass zone in Milan, Italy. Atmospheric Environment, 45:3522-27.

Janssen N.A, Hoek G, Simic-Lawson M, Fischer P, Bree L.V, Brink H.T, Keuken M, Atkinson R, Anderson H.R, Brunekreef B, Cassee F.R. Black carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared to PM_{10} and $PM_{2.5}$. Environ Health Perspect. 2011 Aug 2, epub ahead of print.

Klose M., Shao, Y., Karremann M.K., Fink, A.H., 2010. Sahel dust zone and synoptic background. Geophysical Research Letters 37, L09802, doi: 10.1029/2010GL042816.

Kouvarakis, G., Doukelis, Y., Mihalopoulos, N., Rapsomanikis, S., Sciare, J., Blumthaler, M., 2002. Chemical, physical and optical characterization of aerosol during PAUR II experiment, J. Geo-phys. Res., 107, 814, doi:10.1029/2000JD000866.

Lacaux, J.P., Cachier, H., Delmas, R., 1993. Biomass burning in Africa: an overview of the impact on the atmospheric chemistry. in Fire in the Environment : Its Ecological, Climatic and Atmospheric Importance, N. W., 159-191.

Liousse, C., Cachier, H., 1992. Measurement of black carbon aerosols in the atmosphere of two different source regions: real time data for the Paris region and a savana site of the Ivory Coast. Environment Technology 13, 959-967.

Liousse, C., Cachier, H., Jennings, S.G., 1993. Optical and thermal measurements of black carbon aerosol content in different environments: variation of the specific attenuation cross-section. Atmos. Environ., 27A, 1203-1211.

Liousse, C., Guillaume, B., Grégoire, J.M., Mallet, M., Galy, C., Pont, V., Akpo, A., Bedou, M., Castéra, P., Dungall, L., et al., 2010. Western african aerosols modelling with updated biomass burning emission inventories in the frame of the AMMA-IDAF program. Atmos. Chem. Phys., 10, 7347–7382.

Liousse, C. et Galy-Lacaux, C., 2010. Pollution urbaine en Afrique de l'ouest, La Météorologie, 71.

Matcheubou, A., Nkeng, G.E., Tsalefac, M., Tatietse, T.T., 2009. Problématique de la gestion de la pollution de l'air en milieu urbain: le cas de Yaoundé. African Journal of Science and Technology, Vol. 10, No. 1, pp. 1-15.

Petzold, A., et al., 1997: Near field measurements on contrail properties from fuels with different sulfur content, J. Geophys. Res., 102, 29,867–29,880.

Pope, A., Burnett, R., Thun, M., Calle, E., Krewski, D., Ito, K., Thurston, G., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. The Journal of the America Medical Association 287, 1132-1141.

Ruellan, S., Cachier, H., 2001. Characterization of fresh particulate vehicular exhausts near a Paris high flow road. Atmospheric Environment 35, 453-468.

Rocholl, A.B., Simon, K., Jochum, P., Bruhn, F., Gehann, R., Kramar, U., Luecke, W., Molzahn, M., Pernicka, E., Seufert, M., Spettel, B., Stummeier, J., 1997. Chemical characterization of NIST silicate glass certi"ed reference material SRM 610 by ICPMS, TIMS, LIMS, SSMS, INAA, AAS and PIXE. Geostandard Newsletters 21, 101-114.

Sandradewi, J., Prèvôt, A.S.H., Szidat, S., Perron, N., Alfarra, M.R., Lanz, V.A., Weingartner, E., and Baltensperger, U., 2008a: Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter, Environ. Sci. Technol., 42, 3316–3323.

Schmid, O., Artaxo, P., Arnott, W.P., Chand, D., Gatti, L.V., Frank, G. P., Hoffer, A., Schnaiter, M., Andreae, M.O., 2006. Spectral light absorption by ambient aerosols influenced by biomass burning in the Amazon Basin. I: Comparison and field calibration of absorption measurement techniques. Atmos. Chem. Phys., 6, 3443-3462.

Sciare, J., Oikonomou, K., Cachier, H., Mihalopoulos, N., Andreae, M.O., Maenhaut, W., Sarda-Esteve, R., 2005. Aerosol mass closure and reconstruction of the light scattering coefficient over the Eastern Mediterranean Sea during the MINOS campaign. Atmos. Chem. Phys., 5, 2253-2265.

Sciare, J., d'Argouges, O., Sarda-Est`eve, R., Gaimoz, C., Dolgorouky, C., Bonnaire, N., Favez, O., Bonsang, B., Gros, V., 2011. Large contribution of water-insoluble secondary organic aerosols in the region of Paris (France) during wintertime, J. Geophys. Res. doi:10.1029/2011JD015756.

Stelson, A.W., Seinfeld, J.H., 1981. Chemical mass accounting of urban aerosol. Environmental Science and Technology 15, 671-679.

Tripathi, S.N., Dey, S., Tare, V., Satheesh, S.K., 2005. Aerosol black carbon radiative forcing at an industrial city in northern India. Geophysical Research Letters 32, L08802.

Viidanoja, J., Sillanpaa, M., Laakia, J., Kerminen, V.-M., Hillamo, R., Aarnio, P., Koskentalo, T., 2002. Organic and black carbon in $PM_{2.5}$ and PM_{10}: 1 year data from an urban site in Helsinki, Finland. Atmospheric Environment 36, 3183-3193.

Vincent, A., Dutkiewicz, Alvi, S., Ghauri, B.M., Choudhary, M.I., Husain, L., 2009. Black

carbon aerosols in urban air in South Asia. Atmospheric Environment 43, 1737-1744.

Watson, J.G., and Chow, J.C., 2001: Estimating Middle-Neighborhood and Urban-Scale Contributions to Elemental Carbon in Mexico City with a Rapid Response Aethalometer. J. Air & Waste Mgmt. Assn., 51, 1522-1528.

WHO (World Health Organization), 2005. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulphur dioxide. Global update 2005 – Summary of risk assessment.

Zhu,Y.F., Hinds, W.C., Kim, S., Shen, S., Sioutas, C., 2002. Study of ultrafine particles near a major highway with heavy-duty diesel traffic. Atmospheric Environment, 36, 4332-35.

CHAPITRE III : CARACTERISATION PHYSICO-CHIMIQUE DE L'AEROSOL A BAMAKO ET DAKAR

Introduction

Un aérosol est caractérisé par sa masse, par le nombre de particules par unité de volume, par la distribution en taille, par sa composition chimique, par ses propriétés optiques, … Ces paramètres dépendent de la nature des sources et varient fortement suivant la zone d'étude. De ce fait, afin de procéder à une caractérisation physicochimique complète de l'aérosol sur deux sites urbains de trafic en Afrique de l'Ouest, des mesures de ces différents paramètres ont été menées. Notre démarche a consisté à collecter les particules d'aérosol suivant différentes tailles et de déterminer leur composition chimique mais également à mesurer en temps réel certaines de leurs propriétés physiques (absorption, diffusion). La stratégie expérimentale élaborée est basée sur des campagnes de mesures intensives (deux semaines) réalisées sur chacun des sites dans le cadre du programme POLCA. Ce chapitre également présente une étude préliminaire d'identification des différentes sources.

Dans ce travail, un intérêt particulier est accordé aux méthodes analytiques et à la qualité des mesures. En effet, durant ma thèse, l'équipe dans laquelle j'ai travaillé a fait l'acquisition d'un nouvel analyseur de carbone (modèle G4 ICARUS CS TF, Bruker Axs, Allemagne). J'ai été en charge de faire les premières calibrations de l'appareil après sa mise en service par Benjamin Guinot (chercheur au LA), y compris les premières mesures du contenu en carbone de filtres exposés spécialement pour les tests. D'autre part, le laboratoire de Géoscience Environnement de Toulouse (GET) où devaient se faire les analyses des métaux disposait d'un four à micro-ondes Mars 5 System de la société CEM avec lequel aucune analyse d'aérosol atmosphérique n'a été effectuée. Ainsi, il fallait tester d'autres protocoles de détermination des éléments traces. C'est un travail que j'ai effectué en collaboration avec M. Ouafo (étudiante en thèse au LA). C'est seulement après validation des protocoles que j'ai analysé les échantillons de Dakar et Bamako. Ce travail a fait l'objet d'une publication intitulée « Urban West Africa aerosols concentration levels and differentiated PM characteristics at Bamako (Mali) and Dakar (Senegal)» **(Article A2)** en cours de soumission.

III.1. Description des campagnes intensives 2009

Les mesures de terrains ont eu lieu en saison sèche en plein carrefour des centres villes (***Figure III.1***) du 20 Janvier au 2 Février 2009 à Bamako puis du 1 au 13 Décembre 2009 à

Dakar. Sur chaque site été installé, un set d'instruments permettant de collecter l'aérosol par impaction et par filtration pour différentes classes de taille, de mesurer en temps réel certaines propriétés physiques des particules (absorption, diffusion) utile à leurs caractérisations (sources, propriétés, …) mais également les paramètres météorologiques (température, humidité relative, intensité et direction du vent).

Une fois collectés, les filtres ont été analysés à l'Observatoire Midi Pyrénées (au laboratoire d'Aérologie et au laboratoire de Géoscience de l'Environnement de Toulouse) pour la détermination des espèces carbonées (BC, OC), ioniques (Na^+, Mg^{2+}, Ca^{2+}, NO_3^-, SO_4^{2-}, K^+, Cl^- et NH_4^+), métaux (plus de 50 éléments). Le carbone organique hydrosoluble (WSOC) a été analysé à Gif sur Yvette par H. Cachier, les Hydrocarbures Aromatiques Polycycliques (HAPs) au Laboratoire de Chimie de l'Environnement (LCE) par N. Marchand et son équipe. Le ***Tableau III.1*** résume les différents instruments et techniques analytiques utilisés.

Figure III.1. Sites de prélèvements et instrumentation.

Tableau III.1: Liste des différentes espèces mesurées en fonction du type d'instrument.

Type d'instrument	Eléments mesurés
Collecteur PM	Masse, $PM_{2.5}$, PM_{10} et TSP, BC, OC, Ions, Métaux
DEKATI/ELPI 13-étages	Masse, BC, OC, Ions, WSOC, Métaux, Nombre, Surface, Toxicologie
SIOUTAS 5-étages	Masse, BC, OC, Ions, Métaux
Haut volume Staplex	HAPs, WSOC
Néphélométre	Diffusion
Aethalométre	Absorption, BC

III.2. Présentation des principaux résultats

Les résultats développés ici s'appuient sur les prélèvements journaliers des fractions $PM_{2.5}$, PM_{10} et TSP à Bamako et à Dakar, ainsi que sur trois prélèvements par impacteur caractérisant chacun une source spécifique: BMDust, échantillon collecté lors d'un événement de poussière à Bamako survenu le 22 Janvier 2009 ; BM, prélèvement après l'épisode de poussière et représentatif de l'aérosol moyen à Bamako hors épisode de poussière ; et DK, échantillon caractéristique de la campagne à Dakar.

Les suivis journaliers montrent un pic de concentration à Bamako à la date du 22 Janvier 2009 (***Figure III.2a***). L'analyse des rétrotrajectoires à cette date indique une intrusion de masses d'air provenant du Nord-Est et des hautes altitudes. Ce pic correspond donc à un épisode de poussière et contribue aux niveaux très élevés de concentrations particulaires mesurées. Les concentrations moyennes journalières de $PM_{2.5}$ et de PM_{10} s'élèvent respectivement à 276,8 ± 94,7 et 503,6 ± 112,4 $\mu g/m^3$ à Bamako pour toute la campagne. L'évolution temporelle des concentrations journalières de PM à Dakar présente plusieurs pics (***Figure III.2b***). L'analyse des rétrotrajectoires associées ne montre pas de lien direct entre

pics observés et origine des masses d'air laissant supposer que les concentrations à Dakar sont modulées par l'activité du marché Sandaga où se situe notre site. Des concentrations moyennes journalières de 155,9 ± 15,7 et 138,2 ± 12,7 µg/m^3 sont obtenues pour les PM_{10} et $PM_{2.5}$ respectivement. Les valeurs mesurées sur les sites de Bamako et Dakar sont largement supérieures aux normes journalières recommandées par la Commission Européenne et l'Organisation Mondiale de la Santé (50 µg/m^3 pour les PM_{10} et la valeur cible de 25 µg/m^3 pour les $PM_{2.5}$).

Les distributions en tailles de l'aérosol présentent des courbes monomodales centrées autour de 2.5 µm pour les éléments Al, Be, Ca, Fe, Na, Mg et Ti, indiquant l'origine naturelle de ces éléments. Les espèces telles que Cd, Sb, Tl, BC, OC montrent des distributions bimodales avec une abondance plus grande dans le mode fin (<1µm). Ce qui suggère qu'ils sont majoritairement d'origines anthropiques. Les autres composés, montrant des distributions beaucoup plus hétérogènes, supposent qu'ils peuvent être soit d'origine naturelle ou anthropique. Ces derniers indiquent des compositions chimiques spécifiques à chaque site. Les résultats présentés montrent également que les fractions de $PM_{2.5}$, PM_{10} et TSP à Bamako sont majoritairement composés de poussières crustales (45-51%) et de matière organique particulaire (22-30%). C'est également le cas à Dakar avec 39 à 44% de poussières minérales et 25 à 39% de particules organiques. Notons cependant que les proportions de BC sont plus importantes à Dakar qu'à Bamako. Cette étude préliminaire d'identification des sources est primordiale dans la mesure où elle servira à l'interprétation des différents facteurs (ici les sources) fournis par les modèles multivariés (ACP et PMF) pour la quantification de ces sources (chapitre IV, **Article A3**).

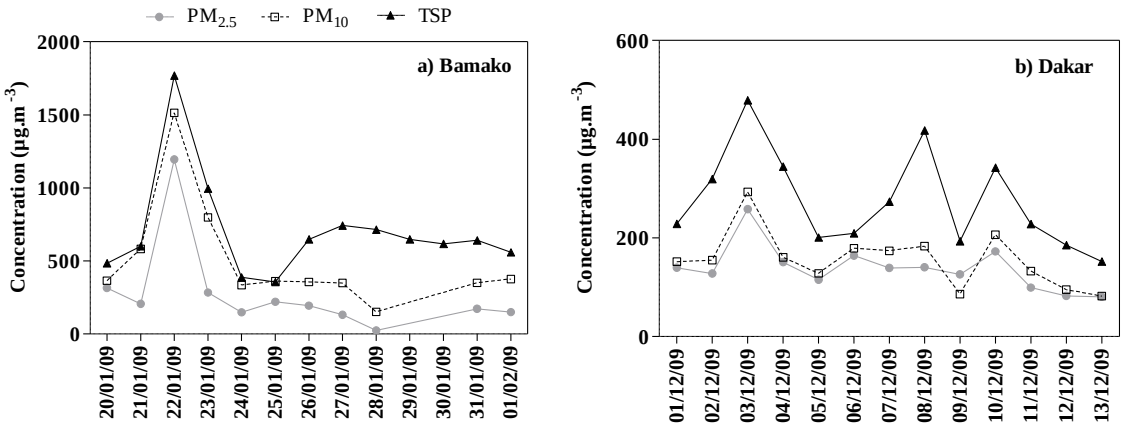

Figure III.2: Evolution journalière des concentrations de $PM_{2.5}$, PM_{10} et de TSP mesurées à Bamako et Dakar.

III.3. Article A2

"Urban West Africa aerosols concentration levels and differentiated PM characteristics at Bamako (Mali) and Dakar (Senegal)"

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En cours de soumission

Abstract

PM samples were collected during the dry season on traffic sites in Bamako, Mali (January 2009) and in Dakar, Senegal (December 2009) to investigate aerosol mass concentrations, particle size distributions, and potential sources of aerosol chemical composition, differentiated between organic carbon (OC), black carbon (BC), metals and water soluble components. This study is part of a larger program (POLCA) aimed at correlating urban pollution in West Africa capitals to human health impacts.

Interestingly, a typical dust episode has been sampled for reference in Bamako during the observing period. This Saharan dust event has resulted in largely increasing daily levels in mineral elements at Bamako with a subsequent significant relative decrease of the levels of carbonaceous aerosols. However, in any case BC and OC were the most abundant aerosol components at both sites. Water soluble species were the second most abundant elements in Dakar, probably due to nearby emissions from industries, local smelters and Atlantic Ocean.

This study strongly confirms the existence of various degrees of mixing between aerosol sources, mainly the following three sources in Bamako and Dakar: (i) mineral dust sources due to Saharan desert (indicated by Al, Fe, Ti and Be) and re-suspended dust from human activities (Ca, Mg and Na), (ii) typical anthropogenic sources such as traffic and fuel combustion with the following elements and species: BC, OC, Cd, Sb, Pb, Zn and (iii) both anthropogenic and/or natural origins for Ni, Mn, Co, Cr, V, K, Rb, Se, Cu, Tl, As, Cl^-, NO_3^- and SO_4^{2-}. Secondary formation of NO_3^- and SO_4^{2-} aerosols are present, together with the marine origin of Mg, Na, Cl^- at Dakar.

Key words: $PM_{2.5}$, PM_{10}, TSP, size distribution, traffic, dust, metals, West Africa, BC, OC

1. Introduction

Many epidemiological studies have concluded that particulate pollution is directly related to serious human health risks such as respiratory tract infections and cardiovascular diseases **(Dockery and Pope, 1994 ; Pope et al., 2006)**. Also, strong health effects and risks are observed in populations directly exposed to traffic emissions (vehicle exhaust) in the United States **(Pope et al., 2002)**, in Europe **(Gehring et al., 2010)**, in Asia **(Ye et al., 2000)** and more recently in West African urban sites **(Dieme et al., 2012 ; Val et al., 2013)**. Particulate Matter (PM) is a kerb road traffic pollutant of specific interest for its respiratory and cardiopulmonary effect **(Brugge et al., 2007 ; Mazzoli-Rocha et al., 2010 ; Ling and Van Eeden, 2009)**, with toxicological properties depending on their size differentiated chemical composition **(Cho et al., 2009 ; Val et al., 2013)**. The mechanisms underlying PM related health effects still remain uncertain, possibly due to the presence of specific organic and transition metal components apt to induce biological effects. Studies by **Dieme et al. (2012)** and **Val et al. (2013)** demonstrate that aerosol particles in West African cities may have strong implications for population health, both due to high aerosol concentration levels **(Doumbia et al., 2012a ; Liousse and Galy-Lacaux, 2010)** and specific toxicities originated from their pollutant emissions sources. **Val et al. (2013)** highlighted high toxicity of fine and ultrafine particles in Bamako and Dakar, with still stronger implications than European cities such as Paris. These findings confirm specific public health problems to which West African populations are confronted, the more so that there are practically no emission regulations there.

Studies of **Liousse et al. (1996) ; Derimian et al. (2008) ; Deboudt et al. (2010) ; Marticorena et al. (2010) and Flament et al. (2011)** have evidenced the presence of mixture of mineral dust and carbonaceous aerosols in the tropospheric atmosphere of West Africa. Furthermore, **Skonieczny et al. (2011)** have shown various mixture of dust sources in this region during wintertime. The presence of carbonaceous aerosols in West Africa region are known to result from traffic, fuel burning and biomass burning emissions **(Liousse et al., 1996 ; Liousse et al., 2010 ; Flament et al., 2011 ; Doumbia et al., 2012a)**. In these studies, aerosol components emitted into the atmosphere from both natural and anthropogenic sources are distributed over a large range of particle sizes. Particles diameter (Dp) larger than 1µm originate mainly from natural sources, for example, windborne sea spray, mineral dust. Coarse particles (2.5µm < Dp < 10µm) are also linked to engine, catalyst and exhaust system deterioration, to road, brake and tire wear **(Hays et al., 2011)**. On the other hand, particles below 1µm arise mostly from anthropogenic sources, e.g., fuel combustion, biomass burning,

industrial processes, and non-industrial sources such as local smelters **(Seinfeld and Pandis, 2006)**. Particles smaller than 2.5µm are transported over long distances. In contrast, coarse particles, mostly containing soil particles, are either from local sources such as resuspended dust **(Makkonen et al., 2010)** or resulted from Saharan dust transport, which is the case in West Africa regions **(McTainsh et al., 1997)**. Minor contribution of secondary organic aerosol from biogenic VOC may be also noted in the different size distribution classes.

Briefly, there exists some information about West African aerosol including particle size distribution but mainly in rural sites of West Africa. No exhaustive study exists in urban areas. For this reason, the POLCA (POLlution des Capitales Africaines) program was constructed aiming to characterize the health impact of atmospheric pollution on West African populations. POLCA started in 2007 with an assessment of complete physico-chemical characterization of particulate matter (PM). The two selected cities (Bamako in Mali and Dakar in Senegal), typical of West Africa developing countries with strong population growth, are impacted by a variety of emission sources dominated by traffic and subject to contrasted meteorological conditions. Intensive measurements were conducted in the dry season from 20 January to 1 February 2009 in Bamako (Mali) and from 01 to 13 December 2009 in Dakar (Senegal). This dry period coincides with the Harmattan dust season in West Africa, with high influence of dust storm episodes **(McTainsh et al., 1997 ; Ozer et al., 2006 ; Deboudt et al., 2010)**. In this regard, the Bamako field campaign was subject to a Sahara dust event at the beginning of our measurements (***Figure 1***). Note that biomass burning occurring around Dakar may impact our site **(Doumbia et al., 2012a)**. Further, in addition to Saharan dust and biomass burning events, anthropogenic particulate pollution sources are still the main PM anthropogenic sources which are quite different over these two sites. In Bamako, PM anthropogenic emissions are mostly due to traffic from two wheels gasoline or gasoline/oil motored vehicles (46% of individuals possess two-stroke vehicles, **DHS (2006)**) and to solid fuel combustion (35-50% of the population use wood and charcoal as their main source of domestic energy) **(Assamoi and Liousse, 2010)**. In Dakar however, road traffic is the main PM anthropogenic source, with more than 60% of public transport diesel vehicles which are older than 10 years. Emissions from industries are also expected to be an important pollutant anthropogenic source in Dakar.

This paper focusing on aerosol measurements during POLCA, discusses concentrations of 24-h integrated $PM_{2.5}$ (aerodynamic diameter of particle Dp < 2.5µm), PM_{10} (Dp < 10µm) and TSP (total suspended particles) and 48-h integrated cascade impactor samples collected at Bamako and Dakar. Samples were analyzed by Thermal-optical (24-h PM samples) and

Thermal methods (48-h PM samples) for black carbon (BC) and organic carbon (OC) determination, ion chromatography (IC) for ionic species and acid digestion combined with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyzer for metal measurements. The discussion is focused on PM chemical concentration levels and size distributions as well as on the potential sources of urban aerosol in Bamako (including the specific dust episode) and Dakar. This article is a first contribution to aerosol source identification at the two sites, prior to an exhaustive reconstruction of aerosol mass concentration.

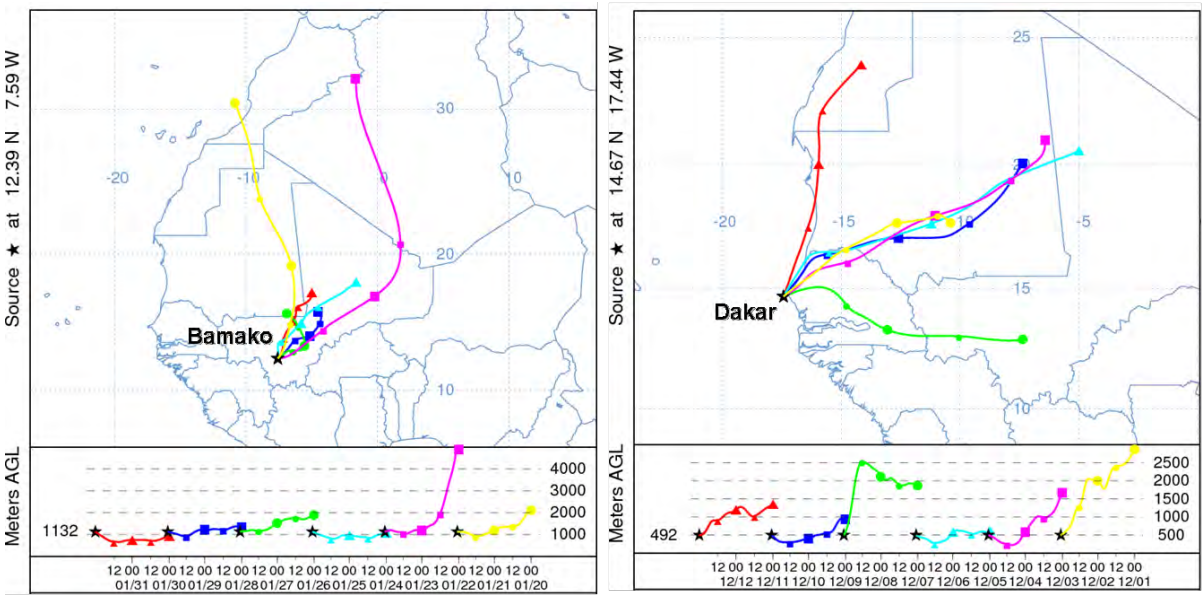

Figure 1: HYSPLIT 48-h air mass back trajectories ending at Bamako (left) for the period from 20 January to 01 February 2009 and Dakar (right) for the period from 01 to 13 December 2009.

2. Experiments

2.1. Monitoring sites and sample collection

The POLCA program and measurement sites are extensively described in **(Doumbia et al., 2012a)**. Briefly, particulate matter (PM) including size distributions of aerosols was monitored at Bamako and Dakar, two West African traffic sites, during the dry season. In Bamako, measurements were made at a downtown crossroad between 20 January and 01 February 2009. In Dakar, measurements were performed between 01 and 13 December 2009, also near a crossroad with heavy traffic. Thus, the two sampling sites are greatly influenced by transportation activities, though with different sources emissions (two-wheel two-strokes in Bamako and diesel vehicles in Dakar).

24-h integrated PM samples were collected at the two sites with PM collector (IDAF model) which was mounted with cut off sizes of 2.5 and 10µm respectively for $PM_{2.5}$ and PM_{10} measurements, and for total suspended particles (TSP) (**IDAF, 2011 ; Goix et al., 2011 ; Ouafo et al., 2012**). In this collector, each particle mode was sampled separately with an individual pump. Particles were collected on 47mm quartz filters (QMA, Whatman) and 47mm Teflon filters (Zefluor, Pall Corporation), operated at an average flow rate of 18 ± 7 $l.min^{-1}$ in both two sites. Thirteen (seven at Bamako, six at Dakar) 48-h samples were also collected using both a 13-stage electrical low pressure impactor (Dekati/ELPI) and a 5-stage Sioutas impactor (**Pakbin et al., 2010**). Dekati and Sioutas impactors were mounted with 25 mm Nuclepore or Quartz filters working at flow rates of 30 and 9 $l.min^{-1}$, respectively. Aerodynamic particle diameters from Dekati ranged between 0.03 and 10µm, while the Sioutas cascade impactor collects particles in the following size ranges: >2.5µm, 1.0 to 2.5µm, 0.50 to 1.0µm, 0.25 to 0.50µm and <0.25µm (**Misra et al., 2002 ; Singh et al. , 2003**). Three of the thirteen 48-h size distribution samples, two in Bamako (BMDust sample collected during dust event and BM sample after this dust event) and one in Dakar (DK sample representative of measured mean aerosol), were selected for their representativeness for further exhaustive chemical examination. These samples illustrate different emission source characteristics and were also exploited for health impact studies. Results of the other ten samples are not presented here: they are used to support our discussion.

Total aerosol light scattering (σ_{scat}) and absorption (σ_{abs}) coefficients were monitored using a one wavelength (520nm) nephelometer (model M903, Ecotech) and a Magee Scientific aethalometer model AE-42 with seven wavelengths (370 to 950nm) in Dakar and AE-16 with one wavelength (880nm) in Bamako (no cut off at ambient relative humidity). Meteorological data including wind speed and direction, temperature (T), and relative humidity (RH) at the two sampling sites were also recorded by automated meteorological station collocated at each sampling site. ***Figures 2-3*** show clear diurnal patterns in σ_{scat} and σ_{abs} for the whole period both the measurement sites, with two daily peaks: morning peak between 7 and 9 a.m. and evening peak between 5 and 7 p.m., with second evening peak at 9 p.m. in Bamako **(Doumbia et al., 2012a)**. This diurnal variability is mostly associated to the traffic and to the evolution of the boundary layer during the day, **(Lyamani et al., 2008 ; Doumbia et al., 2012a)**, typical of urban areas. Such results could be further used for radiative studies. Diurnal variations in wind speed and direction, temperature and relative humidity in Bamako and Dakar are also shown in ***Figures 2-3***, respectively. The verticals

strips correspond to exhaustive chemistry and health study sampling. In Bamako (***Figure 2***) as mentioned earlier, σ_{scat} and σ_{abs} generally show evening peaks (9 p.m.) more pronounced than in Dakar **(Doumbia et al., 2012a)**, coinciding with a low boundary layer height and night time use of wood and two-strokes in Bamako. For the 22/01-24/01 period, the diurnal variation of BMDust sampling was associated with high light scattering, low aerosol absorption, and higher easterly wind speed (6-8 $m.s^{-1}$). The observed large difference between σ_{scat} and σ_{abs} is probably due to the dust event occurrence from 22/01 to 24/01. In addition, the 48-h back trajectories from HYSPLIT model (***Figure 1, left side***) show that air traveled across over Bamako from 22 to 24 January came from the southwest part of Algeria and had passed over the Great Western Erg. Note that Bamako was influenced by long range transport air masses at the beginning of measurements (from 20 to 22 January), while during the rest of days, the air masses were essentially of regional origin.

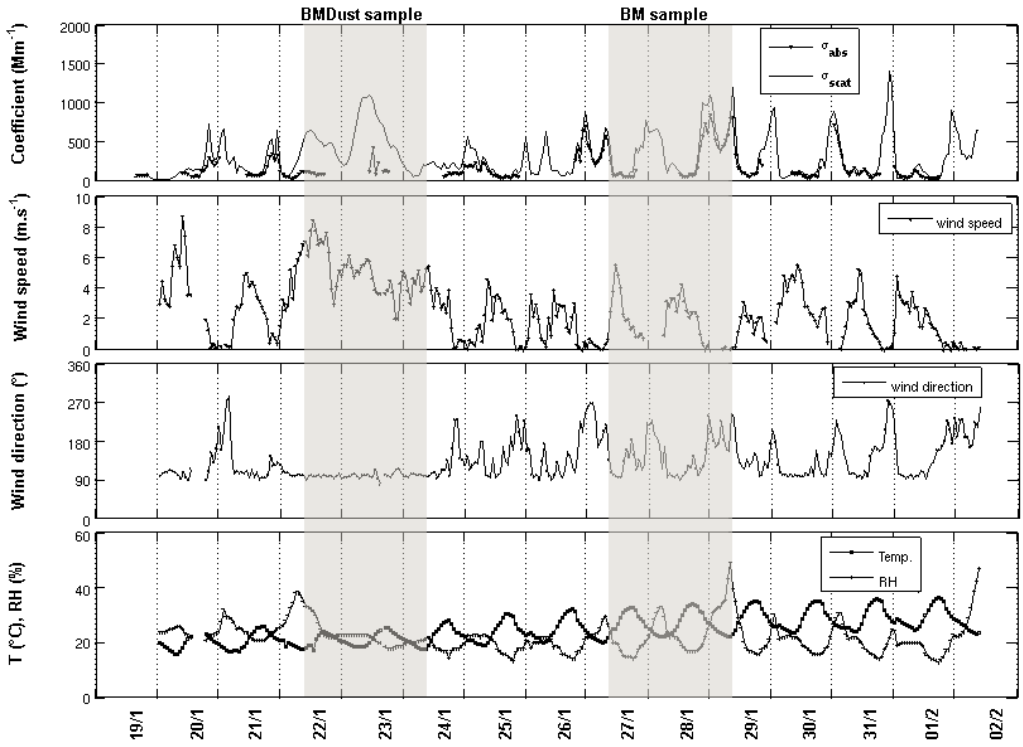

Figure 2: Light scattering (520 nm) and absorption coefficients (880 nm) and meteorological data relevant for the dry season 2009 (from 19 January to 02 February) at Bamako. The grey columns correspond to 48-h sampling periods for our size distribution study during the dust event (BMDust) and after the dust episode (BM).

In Dakar (***Figure 3***), σ_{scat} and σ_{abs} display clear diurnal variation with morning and evening peaks **(Doumbia et al., 2012a)**. The lower values were observed late at night when traffic volume and air temperatures were low. Dakar samples were characterized by low σ_{scat} (daily mean of 103.6 ± 28.8 Mm^{-1}) and high σ_{abs} (303.1 ± 90.9 Mm^{-1}) compared to Bamako (309.8 ± 142.9 Mm^{-1} and 180.9 ± 112.3 Mm^{-1}, respectively). This is likely due to the relative importance of the influence of different traffic types, biofuel or dust depending on the site. Single-scattering albedo ω_0 is an important parameter in assessing the climate and visibility impacts of an aerosol, and is calculated by taking the ratio of scattering (σ_{scat}) to extinction (σ_{scat} + σ_{abs}) coefficient. It depends on the relative source strengths of the various aerosol substances: purely scattering particles (e.g. sulphates) exhibit values close to 1, while very strong absorbers (e.g. black carbon) can have values of around 0.2 (**Schnaiter et al., 2003**). The ω_0 were plotted for Bamako and Dakar (***Figure S1***, Supplementary data). The mean value obtained at Dakar is 0.30 ± 0.04, 2 times lower than those at Bamako (0.61 ± 0.09), indicative of a higher contribution of absorbing aerosol (especially black carbon) to the aerosol load in Dakar.

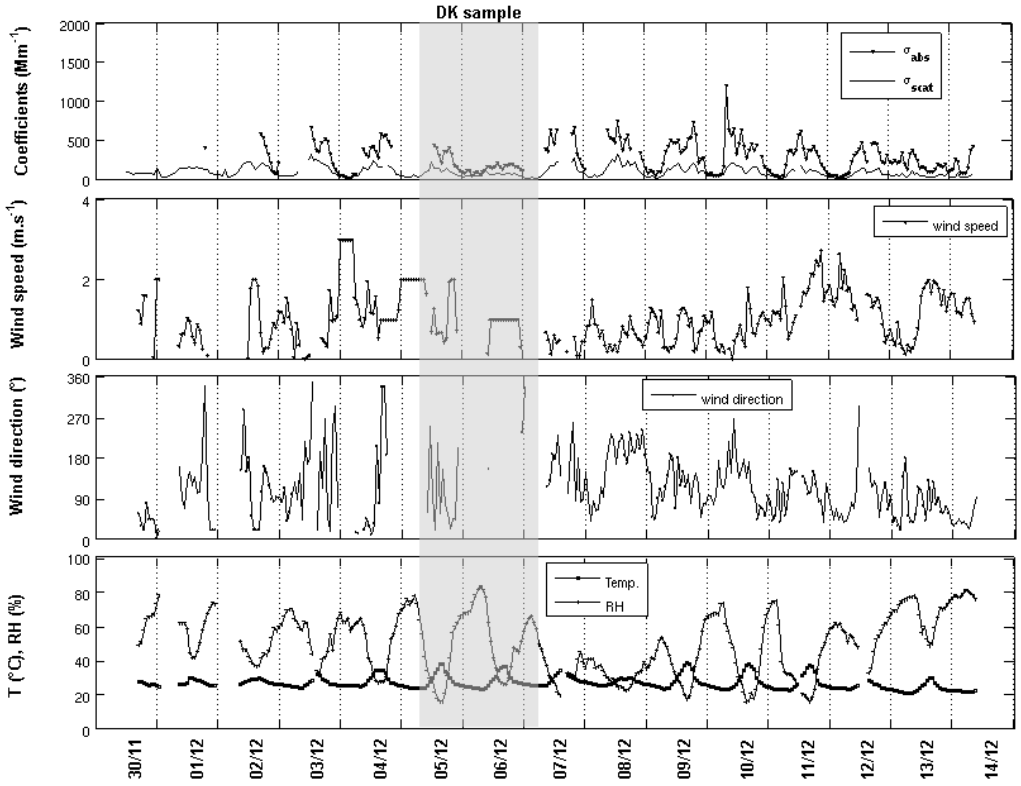

Figure 3: Light scattering and absorption coefficients and meteorological data relevant to the dry season 2009 (from 30 November to 14 December) in Dakar. The vertical grey area corresponds to 48-h sampling period for size distribution study (DK) during weekend days.

2.2. Analytical techniques

Collections of aerosols were performed with different types of filters depending on the analyses: Teflon for ICP-MS, mass and ionic chromatography; Nuclepore for mass and toxicology studies; and Quartz for carbon. Nuclepore and Teflon filters were weighed before and after sampling using a Mettler MC21S microbalance. Before weighing, the samples were kept for about 24-h in the weighing room at ambient relative humidity of 30 ± 15%. To lower carbon blanks, Quartz filters were preheated for 24-h at 600°C, before being exposed.

2.2.1. Ions analyses

Half of each Teflon filter was used in the analysis of inorganic ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^-, Cl^-), using ion chromatograph (IC) analyzer. These measurements were conducted following the analytical protocol described in **Adon et al., (2010)**. Briefly, cations are analyzed using Dionex DX-100 and anions with a Dionex DX-500. Water extraction of the filter samples was performed by a 10 min-long sonication in plastic vials with 30ml deionised ultra-pure water. All analyses were conducted immediately after extraction.

2.2.2. Carbonaceous analyses

Carbonaceous fractions were analyzed on quartz filter for two groups of samples. A first group of samples (24-h $PM_{2.5}$, PM_{10} and TSP) was analyzed both by the two-step combustion (Thermal) using a carbon analyzer (model G4 ICARUS CS TF, Bruker Axs, Germany) **(Cachier et al., 1989)** and Thermal-optical reflectance methods (TOR, Desert Research Institute analyzer), following the IMPROVE temperature protocol **(Chow et al., 1993)**. Briefly, carbonaceous materials are volatilized, pyrolized, and combusted to gas-phase compounds that leave the sample and are converted to carbon dioxide (CO_2). Temperature atmosphere fractions in pure He are 120 °C, 250 °C, 450 °C, and 550 °C and the corresponding carbon fractions are called OC1, OC2, OC3 and OC4. In an oxidizing atmosphere, temperature plateaus are 550 °C (BC1), 700 °C (BC2), and 800°C (BC3). The carbon measured after the introduction of thee He/O_2 atmosphere at 550 °C is defined as organic pyrolysis char (OP). Results produced by 24-h samples were also used to compare these two analytical methods. The second group of samples (48-h Dekati) were analyzed using only Thermal method where prior to analysis, carbonates were removed (decarbonatation) under HCl fumes due to carbonates interference with carbon measurements. Two similar aliquots containing half of the same filter were then separately analyzed. One aliquot was directly analyzed for its total carbon content (TC). The other aliquot was first

submitted to a pre-combustion step (2 hours at 340°C under pure oxygen) in order to eliminate organic carbon, and then analyzed for its black carbon content (10 min at 1100°C under O_2 atmosphere). Organic carbon concentrations were finally calculated as the difference between TC and BC. The TOR temperature protocol is given in ***Table S1*** (Supplementary data). The TOR method utilizes the detection of light reflectance through the filter sample for correction of OC charring that could occur during the analysis **(Chow et al., 1993)**. Note that, the two-step Thermal method has no correction for charring. Section 2.2.4 discusses intercomparisons of the two methods performed for data quality control purpose, since different analytical methods can result in large differences in OC and BC concentrations **(Schmid et al., 2001 ; Hitzenberger et al., 2006)**. Sensitivity studies on the influence of decarbonatation have been conducted on Bamako and Dakar samples. The decarbonatation procedure is responsible of a decrease of OC (range 40-46%) and an increase of BC (range 10-23%), depending on the site and size particle fraction (***Table S2 and S3***, Supplementary data). This can be explained by the portion of carbonate present in the OC fraction that turns to BC at high temperatures.

2.2.3. Metals analyses

Measurements of metals were performed using microwave assisted acid digestion prior to instrumental analysis, using inductively coupled plasma-mass spectrometry (ICP-MS) **(Celo et al., 2010)**. First, the samples, placed in 100ml Teflon bombs, were subject to a microwave-assisted digestion within a mixture of ultra-high pure acids (10ml 16N HNO_3, 0.5ml 28N HF). A closed vessel microwave assisted reaction system (MARS 5, CEM Corporation, Matthews, NC) was used, with a two-step digestion program. During the first step, the temperature was ramped within 15 min to 160 °C. After a 10 min dwell time, the temperature was ramped to 180 °C and samples were digested at this temperature for 30 min. The precision and accuracy of the analysis were checked by analyzing standard reference materials (NIST SRM 1648) prepared in the same way as the digested samples, spikes and duplicates. Blank filters were used for background substraction.

The digests were then transferred to clean polypropylene tubes and diluted to 10ml with HNO_3 0.37N. Samples were analyzed using ultra sensitive ICP-MS (7500ce Element Technologies). Concentrations of more than 50 metals (Be, B, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, Tl, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U, Na, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, K, Ge, As, Se) were determined but only some of them were considered in this work (Be, Rb, Cd, Sb, Tl, Pb, U,

Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, K, As and Se). The other metals are given for information.

3. Results and discussion

3.1. Quality control

In this work the overall uncertainty of the measurements arises mainly from (1) uncertainties in sampling, including possible gas-particle interactions and the particle bounce-off, (2) the relation between blank values, detection limits and concentrations measured, and (3) random contamination problems. The detection limit (DL) is here defined as three times the standard deviation (SD) of the procedure blank.

3.1.1. Blank values and detection limits of samples

3.1.1.1. Carbonaceous aerosol

Determination of a low amount of species in aerosol samples requires low and stable blank values for the analysis. Two parameters are important to determine: (1) mean value of blanks and (2) standard deviation (SD) of the blank value (to determine the DL). Since the magnitude of SD normally increases with the magnitude of the blank value, it is required that the blank value is low. ***Table 1*** provides a summary of the quality control measurements on BC/OC determinations that were performed during 2009 period at Bamako and Dakar traffic sites. The average DRI instrument DL corresponded to 0.45, 0.13 and 0.33 $\mu g.cm^{-2}$ for TC, BC and OC, respectively (***Table 1***). These values are close to those reported by the manufacturer. However, field blanks detection limit are around 20 times higher for OC and 10 times for BC, indicating high field contamination. The estimated uncertainty is calculated using the following equation given by **Chow et al. (2005)**:

$$Unc = \sqrt{\left\{\left(CV \times \overline{TC}\right)^2 + DL^2\right\}} \quad (1)$$

where CV is the coefficient of variance for the replicate analysis, DL is the measured detection limit and $\overline{TC}$ is the average filter blanks. The uncertainty on measured TC with the Thermal-optical method was less than 10%.

As part of the quality control of the Thermal method, filter blanks and instrument calibration were analyzed for two groups of samples: One for low carbon mass (< 25µgC) and one for high carbon level (> 25µgC). The instrument calibration consisted of manually injecting sucrose into the analyzer before an analysis cycle. ***Table 1*** shows, for both carbon calibrations (low and high carbon mass), a good agreement between measured and target sucrose masses,

with a ratio close to unity indicating excellent instrument calibration. Lower detection limits are given for the Carbon analyzer (Thermal method) compared to DRI analyzer (Thermal-optical method). Using the equation (1), an uncertainty of 5% was obtained with the Thermal method. Note that, uncertainties on BC and OC for both Thermal and Thermal-optical methods depend on the site due to different sources **(Hitzenberger et al., 2006).**

Table 1: Quality control performance measures for carbonaceous analyses in Bamako and Dakar.

DRI instrument (Thermal-optical)			
Instrument blank	**TC**	**BC**	**OC**
Average (µg.cm^{-2})	0.13	0.01	0.12
Standard deviation (µg.cm^{-2})	0.15	0.04	0.11
Detection limit (µg.cm^{-2})	0.45	0.13	0.33
Number of samples	16	16	16
Field blank	**TC**	**BC**	**OC**
Average (µg.cm^{-2})	4.29	0.63	3.66
Standard deviation (µg.cm^{-2})	2.85	0.53	2.36
Detection limit (µg.cm^{-2})	8.55	1.59	7.08
Number of samples	36	36	36

Carbon analyzer (Thermal)			
Calibration (sucrose)	low carbon (< 25µgC)	High carbon (> 25µgC)	
Ratio of sucrose to mass target	1.02	1.04	
Standard deviation	0.05	0.04	
Number of samples	23	22	
Field blank	**TC**	**BC**	**OC**
Average (µg.cm^{-2})	1.62	0.69	0.93
Standard deviation (µg.cm^{-2})	0.74	0.63	0.68
Detection limit (µg.cm^{-2})	2.22	1.89	2.04
Number of samples	22	15	15

3.1.1.2. Water-soluble species

Table 2 shows the detection limits (DL) and the blank values obtained for water-soluble ions species analyzed in Teflon filters. The calculated detection limits in ppb were 3 for SO_4^{2-}, Cl^-, Na^+ and K^+, 6 for NO_3^- and NH_4^+, 4 for Ca^{2+} and 7 for Mg^{2+}. The blank value of Mg^{2+} is below the DL (only 4 within the 24 filter blanks analyzed contain Mg^{2+}).

The estimated uncertainties using the equation (2) were 4% for SO_4^{2-}, 18% for NH_4^+, 44% for NO_3^-, 14% for Cl^-, 25% for Ca^{2+}, and 1% for Mg^{2+} and K^+. High uncertainty noticed on nitrate concentration may be due to evaporation problems such as in **Pakkanen et al. (2001)**. The analytical uncertainty is estimated to be about 15%. Only a few NH_4^+ data were obtained in Bamako, probably due to analytical problem. For this reason, NH_4^+ concentrations will not be presented here.

Table 2: Detection limits and blank values for water soluble species. Analyzed was performed on 24 filter blanks and all values are in ppb.

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Filter blank	13	24	4	8	9	2	0.3	25
DL	3	6	3	3	4	1	1	4

3.1.1.3. Metals

The concentrations of metals in two types of blanks, vessel blanks (VB) and Teflon filter blanks (FB), were measured. The concentrations of trace metals in the vessel blank were used to monitor the cleanliness of the microwave digestion and sample treatment process. The VB was composed of acid solutions as those used in sample digestions. The concentrations of metals in the FB were measured to establish a baseline from which the concentrations of elements in field samples were subtracted. It was composed of VB and the same amount of filter paper as used in the field for aerosol collection. The average concentrations in VB and FB are listed in ***Table 3***, along with the detection limits (DL). All elements are found to have higher background concentrations in the filter blank than those in the vessel blank. The DL for most minor elements is below 1 $\mu g.l^{-1}$, while for the major elements (Ca, Na, K, Fe, Al and Mg) the DL is ranged between 30 and 221 $\mu g.l^{-1}$. This high variability is due to the large range of concentration of species in the field blank filters. The high DL values do not present a problem for atmospheric samples, as the concentrations of these elements are usually well above these levels. The field blank values (***Figure S2***, Supplementary data) are slightly higher than filter blanks for the elements such as Na, K, Mg, Fe, Al, Ti, Zn, Mn, Pb, Be and Ni, indicating a small field contamination of field blanks for these elements.

Table 3: Detection limits, vessel blank (VB) and filter blank (FB) in a matrix of 10ml HNO_3 and 0.5ml HF.

Metals	Vessel blank (VB) ($\mu g.l^{-1}$)	Field blank (FB) ($\mu g.l^{-1}$)	DL_{VB} ($\mu g.l^{-1}$)	DL_{FB} ($\mu g.l^{-1}$)
Ag	0.07	0.02	0.20	0.10
Al	0.84	34	1.07	60
As	0.09	0.41	0.65	0.61
Ba	0.05	0.70	0.17	1.89
Ca	3	49	5	221
Cd	0.0005	0.006	0.0006	0.015
Ce	0.001	0.03	0.004	0.13
Co	0.001	0.02	0.001	0.07
Cr	0.03	0.9	0.20	3.2
Cs	0.0002	0.001	0.0002	0.002
Cu	0.038	0.2	0.036	0.7
Eu	0.001	0.002	0.003	0.008
Fe	0.7	15	4.2	86
Hf	0.0009	0.007	0.003	0.017
K	3	57	6	102
La	0.0009	0.01	0.0022	0.06
Mg	0.3	7	0.8	34
Mn	0.03	0.2	0.06	0.7
Mo	0.004	0.07	0.011	0.24
Na	3	34	6	132
Ni	0.04	0.12	0.05	0.19
Pb	0.006	0.11	0.018	0.38
Rb	0.01	0.10	0.01	0.16
Sb	0.002	0.39	0.004	3.03
Se	0.07	0.05	0.48	0.03
Sm	0.0002	0.003	0.0003	0.012
Sn	0.03	11	0.08	20
Sr	0.02	0.2	0.07	1.2
Th	0.0002	0.002	0.0006	0.006
Ti	0.07	4	0.29	10
U	0.001	0.006	0.005	0.025
V	0.01	0.05	0.03	0.17
W	0.002	0.03	0.005	0.09
Zn	0.5	15	4	120
Zr	0.01	0.2	0.05	0.5
Be	0.001	0.002	0.001	0.002
Tl	0.0001	0.002	0.0001	0.008

Nine replicate standard reference materials from NIST (SMRs-1648 Urban Particulate Matter) were measured for analytical quality assurance. These were directly used without any treatment, except for acids added to match their matrix against samples analyzed in the same sequence. ***Table S4*** (Supplementary data) shows the reported recovery values for certified and non-certified elements. The digestion method offers good recoveries (84-105%, with standard deviation SD range 2.7-6.5%) for SMRs referenced elements, except for Cr and Rb with a recovery of 60% and 69%, respectively. Similar low recovery for Cr was observed by several authors **(Swami et al., 2001 ; Sandroni and Smith, 2002)**. This could be due to the quantity of hydrofluoric (HF) acid used during mineralization, more HF being able to increase this recovery.

The uncertainty associated to each element was determined using methodology **(Alleman et al., 2010)**. The following equation was considered:

$$Unc = C\sqrt{u_r^2(m) + u_r^2(V) + \frac{u_c^2}{C^2}} \quad (2)$$

where C is the atmospheric concentration of the element in the sample, $u_r(m)$ is the relative uncertainty of the mass m, $u_r(V)$ is the relative uncertainty of the air volume V, u_c is the absolute uncertainty due to the contamination.

In Dakar, the estimated uncertainties for all metals were generally lower than 10%, except for Ni and Pb for which uncertainty of 13 and 14% were obtained. While in Bamako, these uncertainties were almost lower than 20% for all species. The levels of these errors are acceptable for using the data with source–receptor models such as positive matrix factorization (PMF).

3.1.2. Intercomparison of the analysis results

3.1.2.1. Thermal-optical versus Thermal methods

To assess the uncertainty of carbonaceous measurements, an intercomparison between the TOR and the Thermal methods with no decarbonatation procedure was performed, using PM samples from the two traffic sites impacted by a variety of sources including diesel exhaust, gasoline, biomass burning and a dust episode. The 47mm diameter quartz filters were separated in two 0.5cm^2 punches. One was analysed with the TOR protocol, the second punch being devoted to thermal analysis.

TC values obtained by the TOR method were close to those measured by the thermal method in both Bamako and Dakar samples (difference below 10%), with a coefficient

correlation of 0.96 and 0.92 respectively and a slope close to unity (***Figure 3***). These results are in accordance with the reported ones in the literature. Differences are observed between the two methods regarding BC and OC separately. For Dakar samples, OC TOR was around 0.94 times the value of OC thermal, against 0.85 (***Figure 3***) for Bamako samples. This implies that despite the differences in charring correction in the TOR method and different temperature protocol (***Table S1***, Supplementary data), the two methods are comparable regarding OC analysis (r^2 = 0.89-0.93). As shown in ***Figure 3***, BC values are dependant from the particular analytical method, possibly due to variable source contributions. BC concentrations measured by the TOR method are higher than those obtained by the thermal approach. The ratio of BC TOR to BC thermal was 1.03 for Dakar samples (r^2 = 0.78) and 1.29 for Bamako samples (r^2 = 0.49). **Hitzenberger et al., (2006)** found comparable BC concentrations from diesel traffic sources using different methods. This result is consistent with Dakar samples being heavily impacted by diesel emissions (TOR to BC thermal ratio of 1.03 was found). Such results indicate that discrepancies between these two analytical methods are more significant at Bamako than at Dakar site. This discrepancy can be attributed to three factors:

- the first one can be linked to the presence of components such as brown carbon in carbonaceous aerosol **(Andreae and Gelencsér, 2006 ; Lukács et al., 2007)**, since brown carbon could influence splitting between OC and BC due to light absorbing and medium thermal reactivity. Indeed, a fraction of brown carbon can be classified as OC, the rest as BC **(Cheng et al., 2011)**. It was shown that brown carbon was mainly emitted by incomplete combustion such as domestic fires or two-stroke emissions, the Bamako site being strongly impacted by this source **(Val et al., 2013)** ;
- the second factor is probably related to the artefact due to the presence of dust. As shown in ***Figure 3***, BC TOR to BC Thermal ratios decrease from Bamako strongly influenced by dust to Dakar heavily impacted by traffic diesel. It was assumed that in Bamako samples, the presence of dust particles affects thermal optical measurements, contributing to the observed large BC concentration variations ;
- third and last hypothesis, a sensivity of the BC (Thermal) to combustion aerosols of biofuel origin **(Sciare et al., 2008)**, since this source is more abundant in Bamako than in Dakar.

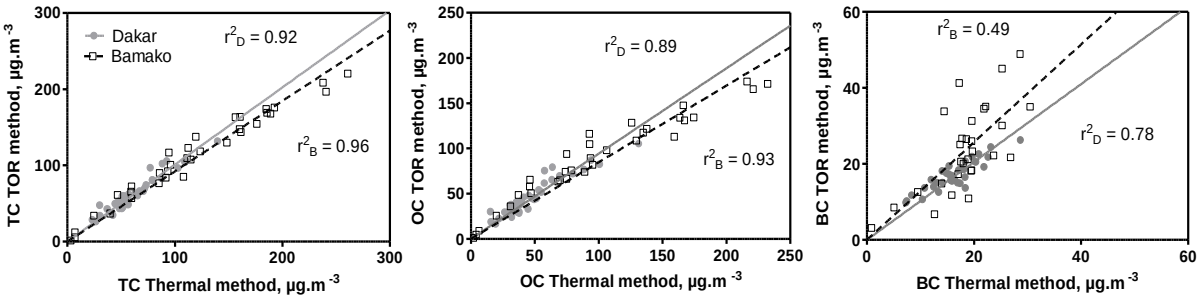

Figure 3: Comparison between the TOR and the Thermal methods at the two sites for TC, OC and BC. The linear regression results are displayed (r^2_D: correlation coefficient for Dakar and r^2_B: correlation coefficient for Bamako).

3.1.2.2. BC filter versus BC aethalometer

Here, an intercomparison between measured black carbon concentrations from filter sampling with Thermal analysis and aethalometer was performed (***Figure 4***). Comparison was made for both sampling sites separately. Relatively good agreement (r^2 = 0.63) between aethalometer measurements and filter analysis BC data (Thermal method) has been shown in Dakar for the whole campaign results, with an average a difference of 23%. When TOR method versus aethalometer was compared, the difference is reduced to 18%.

The correlation between aethalometer BC and Thermal BC is low (r^2 = 0.31) for Bamako samples, with a mean difference of 52%, while 60% is obtained comparing aethalometer with TOR method. This large discrepancy can be due to various factors: first, the presence of dust loadings in Bamako samples. Indeed, dust particles affect both the TOR and Thermal methods (see paragraph 2.2.2) and also the aethalometer method which is not corrected for mineral dust absorption **(Fialho et al., 2005)**.

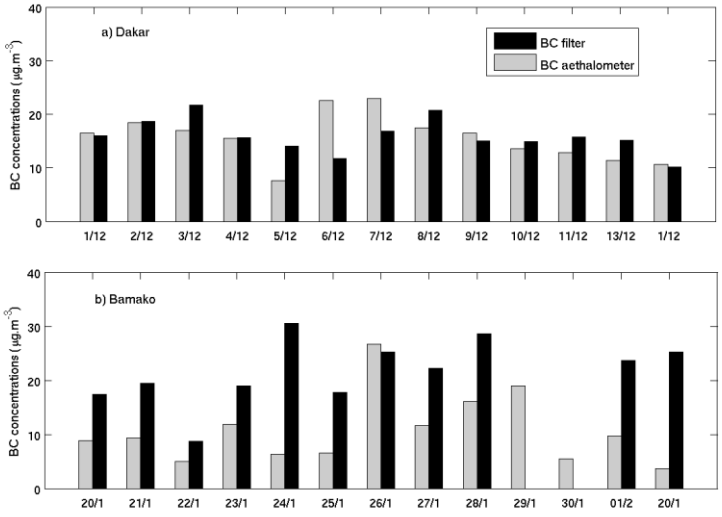

Figure 4: Comparison of BC results from aethalometer and filter (Thermal method) collected during the whole measurement period at a) Dakar and b) Bamako.

3.1.2.3. ICP-MS versus IC

The concentrations of calcium, potassium, sodium and magnesium measured in $PM_{2.5}$, PM_{10} and TSP both by ICP-MS and ion chromatography (IC) were compared to evaluate the ratio between soluble and non-soluble components. Indeed, ICP-MS measures total elemental concentrations (Ca, K, Na and Mg) and IC the water-soluble fraction (Ca^{2+}, K^+, Na^+ and Mg^{2+}). Linear regressions show slopes close to unity for the elements such as calcium and sodium (not shown here), denoting that these components are almost totally soluble for the sources present on the sites. This is illustrated by the relatively good correlation coefficient (r^2 = 0.79, with a slope of 0.84 ± 0.07) obtained for sodium in Dakar. In Bamako, the best observed correlation coefficient is for calcium (r^2 = 0.79, with a slope of 0.61 ± 0.06). The observed differences between the two analytical methods, particularly for magnesium and potassium, indicate the multiple sources of these two elements. Indeed, the concentration of total potassium (K) is approximately 3 times the concentration of soluble potassium (K^+) in both sites (not shown here), and this value reached 10 during the dust episode in Bamako. This is an important distinction, since soluble potassium (K^+) is one of the key markers for wood burning **(Andreae et al., 1988)**. Increasing K/K^+ ratio during the dust event indicates also a crustal dust origin of potassium **(Watson and Chow, 2001)**. The same results are obtained for magnesium (not shown here). Mg^{2+} is a tracer of marine aerosol. The increasing Mg/Mg^{2+} ratio during the dust event (from 4 to 16), suggests that this element is also from crustal material **(Watson and Chow, 2001)**.

3.2. Aerosol mass concentrations

Figure 5 shows the temporal variation of daily mean concentration of $PM_{2.5}$, PM_{10} and TSP collected during the POLCA campaign, with PM collector at Bamako between 20 January and 01 February 2009 and at Dakar between 01 and 13 December 2009. As shown in ***Figure 5a***, the Saharan dust episode (22 January 2009) is strongly reflected in high PM levels at Bamako. As a consequence, daily PM concentrations reached TSP values from 357 to 1769 $\mu g.m^{-3}$, from 151 to 1513 $\mu g.m^{-3}$ for PM_{10} and 24 to 1194 $\mu g.m^{-3}$ for $PM_{2.5}$. Note that all PM modes are affected by the dust episode. At Dakar, measured PM concentrations ranged from 152 to 479 $\mu g.m^{-3}$ for TSP, from 82 to 293 $\mu g.m^{-3}$ for PM_{10} and from 81 to 258 $\mu g.m^{-3}$ for $PM_{2.5}$ (***Figure 5b***). $PM_{2.5}$ values (138.2 ± 12.7 $\mu g.m^{-3}$) are in the same order to those obtained in previous study in Dakar (average value of 105.4 $\mu g.m^{-3}$) by **Dieme et al. (2012)**. Also, measured PM_{10} and $PM_{2.5}$ concentrations at Dakar are in the range of those measured at urban site in Conakry (Guinea) during the 2004 Harmattan period, mainly 145.2 ± 109.2 $\mu g.m^{-3}$ for PM_{10} and 70.3 ± 35.8 $\mu g.m^{-3}$ for $PM_{2.5}$ **(Weinstein et al., 2010)**. Finally, it is important to underline that $PM_{2.5}$ and PM_{10} at Bamako and Dakar sites exceeded daily recommended values of 25 $\mu g.m^{-3}$ for $PM_{2.5}$ and 50 $\mu g.m^{-3}$ for PM_{10} by the European Commission and the World Health Organisation. The high average PM values denoted a severe urban air pollutant problem in these towns.

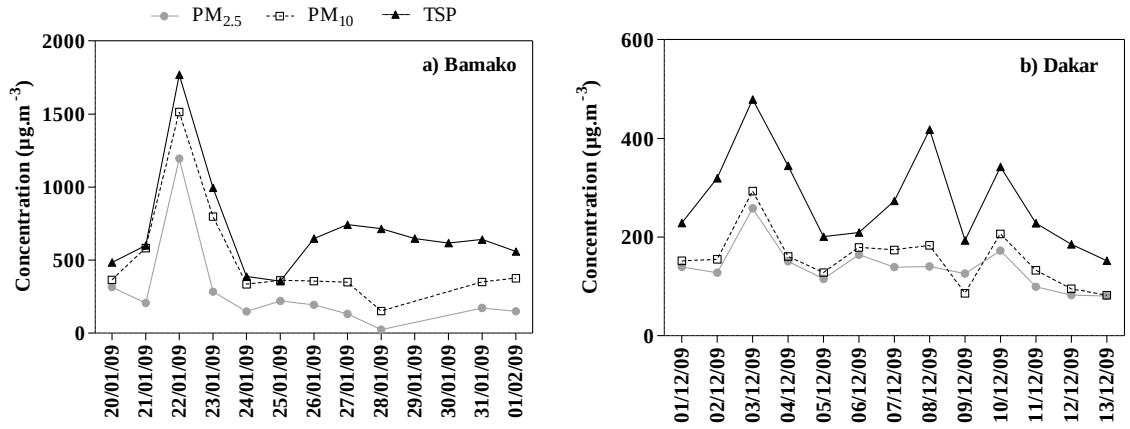

Figure 5: PM mass concentrations for the whole measurement periods at Bamako (January 2009) and Dakar (December 2009).

Table 4: Average 24-h concentrations for TSP, PM_{10}, $PM_{2.5}$ and associated elemental compositions in Bamako and Dakar. BC, OC and TC are determined by TOR method.

	Bamako			Dakar		
Species (µg.m^{-3})	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$
Mass PM	705.3 ± 99.3	503.6 ± 112.4	276.8 ± 94.7	274.9 ± 27.43	155.9 ± 15.7	138.2 ± 12.7
Cl^-	3.43 (<1)	3.36 (<1)	2.12 (<1)	8.45 (3)	8.13 (5)	1.77 (1)
NO_3^-	1.87 (<1)	1.87 (<1)	1.18 (<1)	2.06 (<1)	2.31 (1)	0.97 (<1)
SO_4^{2-}	4.44 (<1)	4.29 (<1)	2.98 (1)	6.18 (2)	7.49 (5)	4.75 (3)
Na^+	2.21 (<1)	1.70 (<1)	1.02 (<1)	5.1 (2)	5.04 (3)	1.21 (<1)
K^+	3.5 (<1)	3.17 (<1)	2.02 (<1)	0.99 (<1)	0.99 (<1)	0.59 (<1)
Mg^{2+}	0.87 (<1)	0.75 (<1)	0.49 (<1)	0.72 (<1)	0.71 (<1)	0.28 (<1)
Ca^{2+}	7.14 (1)	7.09 (1)	5.29 (2)	12.17 (4)	13.65 (9)	11.43 (8)
Inorganic ions	24.06 (3)	22.99 (5)	15.69 (6)	36.09 (13)	38.95 (25)	21.50 (16)
BC	23.34 (3)	18.85 (4)	27.11 (10)	20.14 (7)	16.41 (11)	15.88 (11)
OC	102.4 (15)	82.38 (16)	102.4 (37)	69.19 (25)	34.92 (22)	35.83 (26)
TC	125.74 (18)	101.23 (20)	129.51 (47)	89.33 (32)	51.33 (33)	51.71 (37)
Al	21.23 (3)	22.24 (4)	17.98 (6)	9.66 (3)	7.07 (4)	4.11 (3)
Fe	21.91 (3)	20.41 (4)	14.28 (5)	9.00 (3)	5.54 (3)	3.49 (2)
Ti	2.35	2.14	1.47	0.89	0.54	0.34
Mn	0.35	0.32	0.22	0.15	0.11	0.06
Zn	0.18	0.15	0.12	0.21	0.16	0.11
Cr	0.10	0.09	0.06	0.04	0.02	0.02
V	0.06	0.05	0.04	0.07	0.07	0.05
Cu	0.03	0.04	0.02	0.08	0.19	0.13
Ni	0.02	0.02	0.03	0.03	0.03	0.03
Pb	0.02	0.02	0.04	0.03	0.03	0.02
Rb	0.02	0.02	0.015	0.009	0.007	0.004
Co	0.009	0.008	0.005	0.004	0.002	0.0016
Sb	0.004	0.005	0.004	0.005	0.0044	0.0028
As	0.005	0.0045	0.003	0.003	0.0020	0.0014
Be	0.0008	0.0008	0.0005	0.0003	0.0002	0.0001
Cd	0.0007	0.0007	0.0008	0.0007	0.0006	0.0004
Se	0.0003	0.0003	0.0002	0.0007	0.0008	0.0005
Tl	0.0003	0.0003	0.0002	0.00005	0.00005	0.00003
Metals	46.29 (7)	45.53 (9)	34.29 (12)	20.18 (7)	13.78 (9)	8.38 (6)

Note: Values in parentheses are relative percentages in total masses.

3.3. Chemical mass concentrations

Figures 6-7 show the $PM_{2.5}$, PM_{10} and TSP components for OC, BC, major inorganic ions and twenty two metal in the atmospheric particulate matter measured at Bamako and Dakar, respectively. The average concentrations of species measured at Bamako and Dakar sites are summarized in ***Table 4***. Most generally, OC, BC, metals components and inorganic ions, respectively account for 15-37%, 3-10%, 7-12% and 3-6% in $PM_{2.5}$, PM_{10} and TSP in

Bamako, whereas these percentages account to 22-26%, 7-11%, 6-9% and 13-25% in Dakar (***Table 4***). The most abundant component in the PM_{10} and $PM_{2.5}$ was total carbon (OC + BC), which accounts for 20-47% in Bamako and 33-37% in Dakar. These results are consistent with the recent values **(Putaud et al., 2004 ; Querol et al., 2004 ; Yu et al., 2004)** for urban aerosols, with reported contributions between 20–40% and 25–50% to the ambient PM_{10} and $PM_{2.5}$ mass, respectively. Daily trends of BC and OC show that these elements display lower concentrations during the dust episode at Bamako (***Figure 6***). Average BC and OC concentrations for the whole measurement period at Bamako were 23.34 $\mu g.m^{-3}$ and 102.40 $\mu g.m^{-3}$ for TSP, 18.85 $\mu g.m^{-3}$ and 82.38 $\mu g.m^{-3}$ for PM_{10} and were 27.11 and 102.40 $\mu g.m^{-3}$ for $PM_{2.5}$. The values of $PM_{2.5}$ higher than those of PM_{10} are not normal and a few other cases are given in the ***Table 4***. This is probably due to many factors: an analytical problem of black carbon, sample collection problems with important artifacts. In Dakar, BC and OC concentrations were 20.14 $\mu g.m^{-3}$ and 69.19 $\mu g.m^{-3}$ for TSP, 16.41 $\mu g.m^{-3}$ and 34.92 $\mu g.m^{-3}$ for PM_{10} and were 15.88 $\mu g.m^{-3}$ and 35.83 $\mu g.m^{-3}$ for $PM_{2.5}$. Note that, the BC to OC ratio is higher in Dakar (0.29-0.47 range) than in Bamako (0.23-0.26 range). ***Figure 6*** shows that carbonaceous particles significantly decrease while elements associated to mineral dust significantly increase (especially in TSP and the PM_{10} fractions) during the dust event, during which low σ_{abs} was measured and then low BC concentrations.

The second most abundant components in Bamako were metals, due to strong mineral dust influence from Saharan desert but also re-suspended road dust. Aluminium (Al) was the most abundant metal found in all particle modes at Bamako (***Table 4***), with an average daily concentrations of 17.98 $\mu g.m^{-3}$ ($PM_{2.5}$), 22.24 $\mu g.m^{-3}$ (PM_{10}) and 21.23 $\mu g.m^{-3}$ (TSP), followed by Iron (Fe) with daily average concentrations of 14.28 $\mu g.m^{-3}$ ($PM_{2.5}$), 20.41 (PM_{10}) and 21.91 $\mu g.m^{-3}$ (TSP). During the dust episode, daily Al and Fe concentrations show large increases, by a factor of nearly 13 and 12, from 6.30 to 82.17 $\mu g.m^{-3}$ and from 5.34 to 66.72 $\mu g.m^{-3}$, respectively. Al abundance of the order of 4.6% is lower than obtained in upper crustal (8.04%) while for Fe our value (3.7%) is close to 3.5% reported by **McLennan (2001)** in upper crustal. That confirms the upper crustal origin of dust during the dust event. When discarding the dust event, in the mean value, measured concentrations ranged in the values found in typical atmospheric dusty environment measured by **Bowen (1966)**, which implies that Al and Fe were mainly associated with crustal dust sources. Ca and K were the next most abundant components at Bamako, with average daily concentrations of 5.29 and 2.02 $\mu g.m^{-3}$ ($PM_{2.5}$), 7.09 and 3.17 $\mu g.m^{-3}$ (PM_{10}), 7.14 and 3.5 $\mu g.m^{-3}$ (TSP), respectively. However as shown in the time patterns, daily K concentrations increase more largely than Ca (***Figure 6***),

rising from 3.14 to 34.55 µg.m^{-3} (11 fold increase) against 3.57 to 22.87 µg.m^{-3} for Ca (6 fold increase). Obtained K abundance (1.9%) in TSP during the dust episode is higher than 1.1% in typical bulk crust (**Taylor and McLennan, 1985**) but lower than 2.8% in upper crust **(McLennan, 2001).** That suggests that there is an additional source. Mg, Na and Ti were highly present as elemental components at Bamako, with day-to-day variations reflecting the dust signal occurring between on 22 January 2009. Comparison between total measured Mg and Na by ICP-MS and the fraction of those elements measured as Na^+ and Mg^{2+} by IC shows a correlation coefficient of 0.67 (slope 0.76) for sodium and 0.08 (slope 0.13) for magnesium (not shown here), revealing that practically all Na was water-soluble (around 76%), while Mg was only 13% water-soluble in Bamako. Consequently at Bamako, 87% of Mg was considered as being mainly issued from crustal dust as reflected in maximum concentrations of 20.9 µg.m^{-3} close to typical values (20.9-34.55 µg.m^{-3}) in typical crustal rocks **(Vinogradov, 1959 ; Adepetu et al., 1988)**. This may be explained by the presence of rock quarries salt in Mali. Maximum concentrations of 7.17 µg.m^{-3} for Na was by far less than the typical 28.3 µg.m^{-3} crustal rocks, though in the range 5.9 to 7.2 µg.m^{-3} mass concentrations for Harmattan or atmospheric dust environments **(Adepetu et al., 1988)**. This suggests the existence of distinct dust sources in Bamako (Harmattan dust transport and local dust sources (re-suspended aerosols)). Elements such as Arsenic (As), Beryllium (Be), Cobalt (Co), Chromium (Cr), Copper (Cu), Manganese (Mn), Nickel (Ni), Rubidium (Rb), Selenium (Se), Thallium (Tl) and Vanadium (V) show distinct peaks during the dust event period, with corresponding concentrations in As, Co, Be, Cr and Se following the concentration patterns of typical soils and crustal rocks **(Iskander, 1985 ; Adepetu et al., 1988 ; McLennan, 2001)**. Conversely, the observed concentration ranges for Mn, Rb and V follow concentrations typical of atmospheric dust environment, suggest they can from desert dust or re-suspended particles. Note that in some case these elements can also emitted by anthropogenic sources **(Karanasiou et al., 2007)**. The trends for Cadmium (Cd), Antimony (Sb), Lead (Pb) and Zinc (Zn) measured in all aerosol modes in Bamako did not show peaks during the dust episode, suggesting that these elements are primarily emitted by anthropogenic activities such as traffic (mainly brakes and tyre wear), fuel combustions or biomass burning **(Sternbeck et al., 2002 ; Thorpe and Harrison, 2008)**.

Among water-soluble species, only SO_4^{2-} trends exhibit a peak during the dust event, suggesting the possible interaction between SO_4^{2-} and dust with heterogeneous processes **(Manktelow et al., 2010)**. As BC and OC, Cl^- and NO_3^- were generally associated with

anthropogenic activities or secondary aerosol production **(Watson and Chow, 2001 ; Liousse et al., 2010)**.

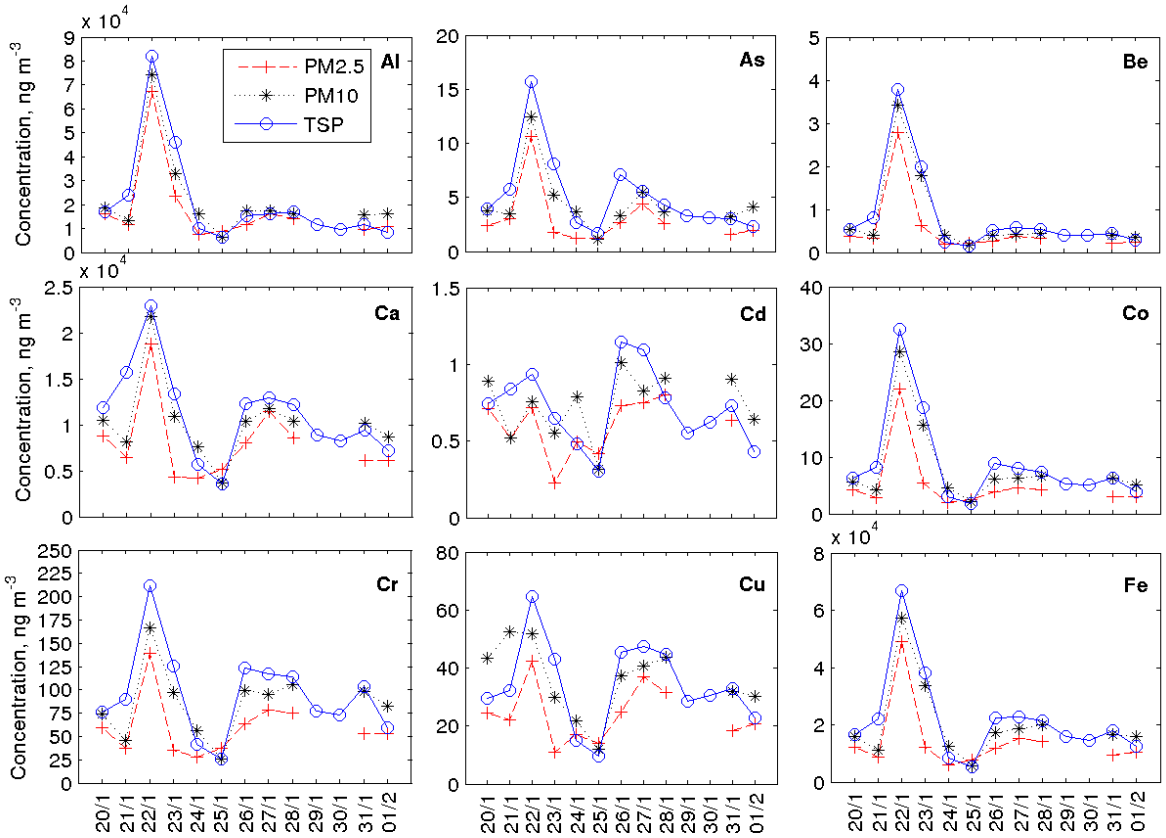

Figure 6: Time variations of component in $PM_{2.5}$, PM_{10} and TSP concentrations measured at Bamako between 20 January and 01 February 2009.

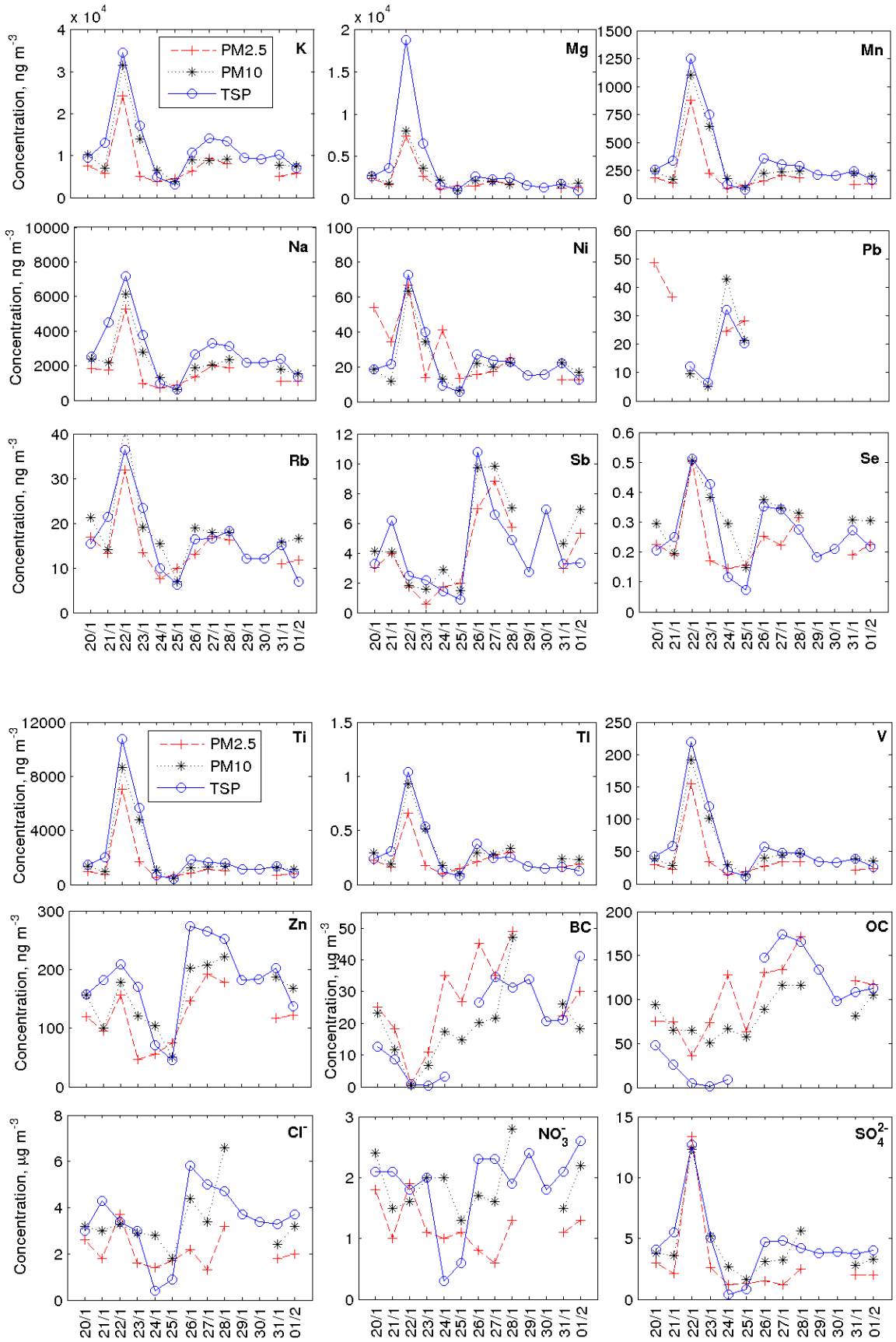

Figure 6: (continued).

Figure 7 shows the $PM_{2.5}$, PM_{10} and TSP particulate concentrations measured at Dakar between 01 and 13 December 2009 using the same format than in ***Figure 6***. For Dakar however, water-soluble species are the dominant components after carbonaceous aerosol (***Table 4***), probably due to industries and the proximity of the Atlantic Ocean. In Dakar, Ca was the second most abundant component, with daily average concentrations of 11.43 $\mu g.m^{-3}$ ($PM_{2.5}$), 13.65 $\mu g.m^{-3}$ (PM_{10}) and 12.17 $\mu g.m^{-3}$ (TSP). The relatively high calcium concentrations possibly results from a combination of resuspension of coarse particles derived from urban sources, such as traffic, combustion, construction activities and industries **(Chow et al., 1994 ; Gianini et al., 2012)**. This element is also known to derive from cement factories **(Favez et al., 2010)**. So, a probable additional source in Dakar could be the emissions of cement dust industry and the open limestone quarry covering around 1 km^2 area and located 20 km east of Dakar site. Moreover, during the measurement period, air masses mainly came from this direction (East South-East direction) (***Figure 2 and Figure S3***, Supplementary data). Dakar site is close to the sea, which means that Na (average daily concentrations of 1.21 $\mu g.m^{-3}$ for $PM_{2.5}$, 5.04 $\mu g.m^{-3}$ for PM_{10} and 5.10 $\mu g.m^{-3}$ for TSP) and Mg (average daily concentrations of 0.28 $\mu g.m^{-3}$ for $PM_{2.5}$, 0.71 $\mu g.m^{-3}$ for PM_{10} and 0.72 $\mu g.m^{-3}$ for TSP) are probably mainly originated from sea salt sources produced by bubble bursting at the sea surface **(Beavington et al., 2004 ; Rodríguez et al., 2004)**. This is consistent with the Na/Mg ratios obtained in TSP and PM_{10} (7.08 and 7.09, respectively) in the same order of reported value of 8.4 in sea water **(Millero et al., 2008)**. Sum of Cl^-, SO_4^{2-} and NO_3^- account for 5 to 11% of total water-soluble aerosol fraction (***Table 4***), with relative higher proportions as compared to Bamako (1.4 to 2.4%). However, SO_4^{2-} only approximately account for 17% of total water-soluble components in TSP, 19% in PM_{10} and 22% in $PM_{2.5}$ which is similar as the SO_4^{2-} abundance obtained in Bamako. This points out the relative importance of SO_4^{2-} in both sites, probably linked to sea salt in Dakar and interaction between sulphate and dust in Bamako **(Manktelow et al., 2010)**. It is the same case for NO_3^-, with a proportion ranging from 4 to 6% in Dakar and from 7-8% in Bamako. Note that ambient concentrations of Ca^{2+}, Na^+, Cl^- and SO_4^{2-} at Dakar were 2-6 times higher than those obtained at Bamako.

As in Bamako, concentration levels of both Al (average daily concentrations of 4.11 $\mu g.m^{-3}$ for $PM_{2.5}$, 7.07 $\mu g.m^{-3}$ for PM_{10} and 9.66 $\mu g.m^{-3}$ for TSP) and Fe (average daily concentrations of 3.49 $\mu g.m^{-3}$ for $PM_{2.5}$, 5.54 $\mu g.m^{-3}$ for PM_{10} and 9.00 $\mu g.m^{-3}$ for TSP) are high in Dakar, but values are higher in Bamako than in Dakar (the dust event excluded), probably due to more unpaved roads favourable for re-suspending surface dust. All

concentrations of the metal elements as well as Al and Fe, rapidly decrease during weekend days (05/12-06/12 and 12/12-13/12), indicating that both re-suspended mineral dust and anthropogenic emissions by traffic were driven by population activity levels near the site. All elements have concentrations a lot less than typical values within Harmattan dust, except for Zn, As and Se which are more than an order of magnitude over what is considered as natural occurrence in typical soils and rocks **(Iskander, 1985 ; Vinogradov, 1959 ; Adepetu et al., 1988)**. This suggests the anthropogenic origin of such elements at Dakar site (traffic, industry or both). Cu is also abundant, indicating its anthropogenic origin (traffic emissions and probably informal sector of copper smelting at Dakar).

Note that concentration levels for all components were more important in Bamako than in Dakar, except for water-soluble ones. This is likely related to differences in location and meteorology, since Bamako is located in a basin under strong influence of continental air masses, while Dakar is a typical coastal site with high impact of sea breeze which facilitating pollutant dispersion. The size distributions and correlations coefficient in the following sections can help strengthen these preliminary observations.

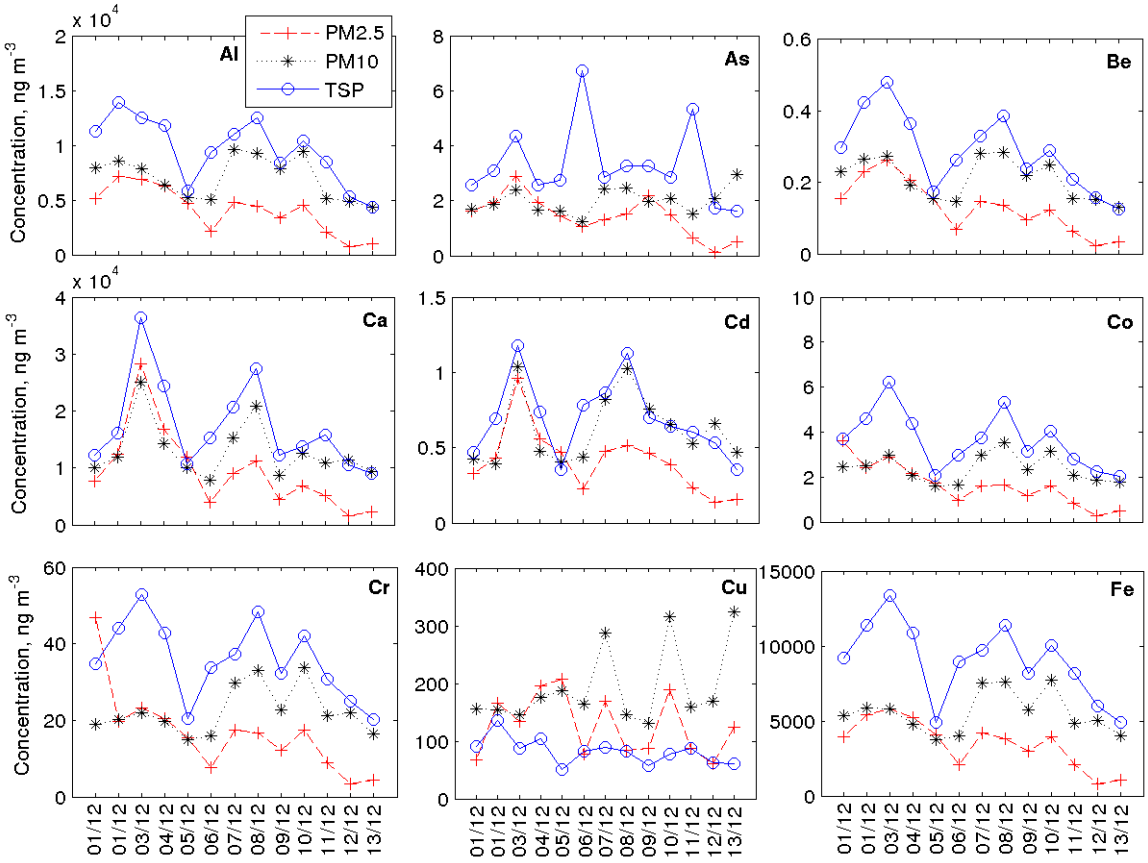

Figure 7: Time variations of components in $PM_{2.5}$, PM_{10} and TSP concentrations measured at Dakar between 01 and 13 December 2009.

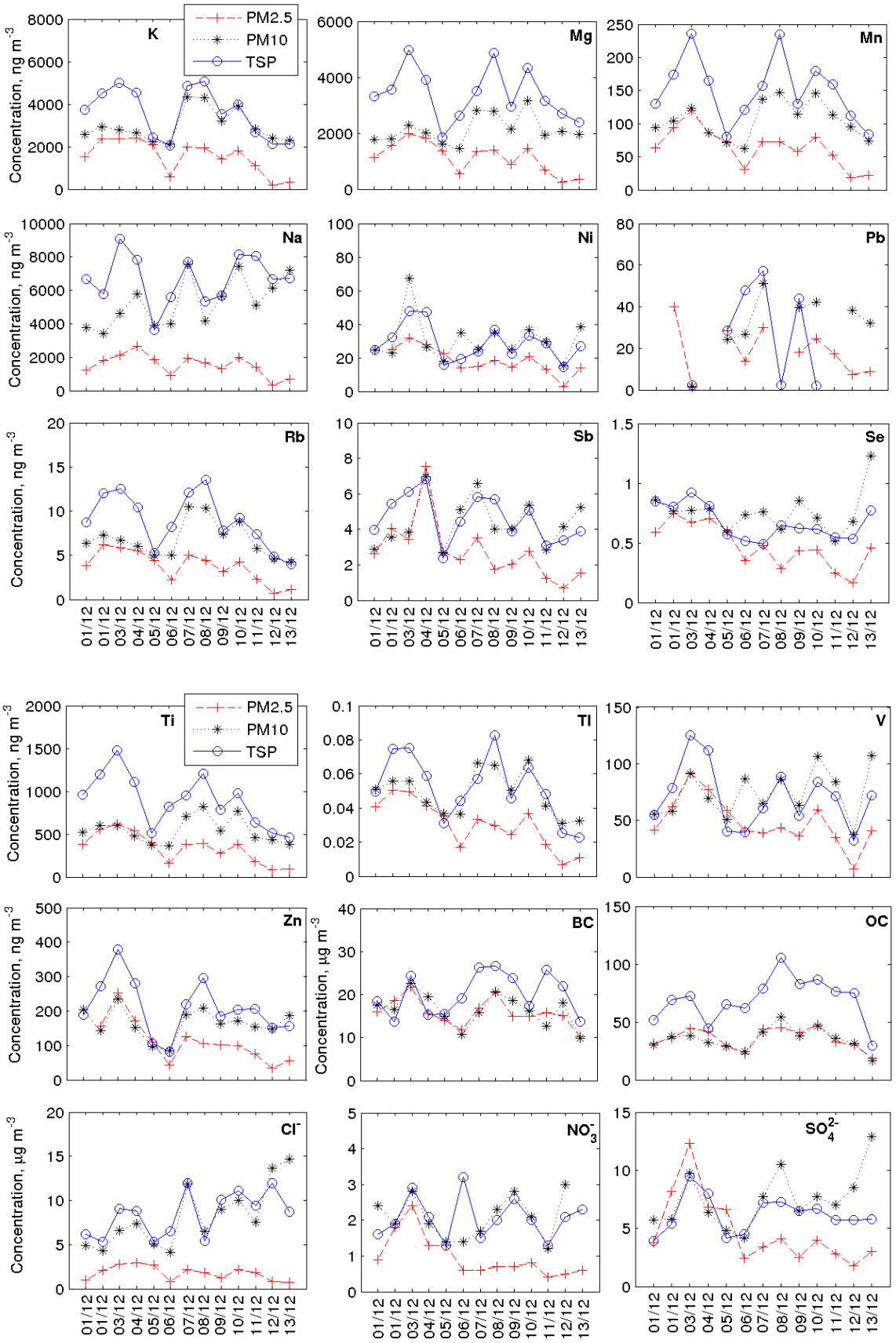

Figure 7: (continued).

3.4. Particulate size distributions

Size distribution study is focussed on selected three samples characteristics of aerosol: two in Bamako (dust event and an average situation after the dust episode) and one in Dakar representing an average situation during the campaign. ***Figure 8*** shows the relative elemental size distributions (mass of components in each class of size particles/total mass of components over all particles size) for particulate OC, BC, ions, and metals measured at Bamako (BMDust and BM) and Dakar (DK). This figure highlights the individual size distributions, while minimizing the potential impacts on absolute concentrations due to different meteorology. In contrast, particle size distributions in ***Figure S4*** (Supplementary data) show variations in elemental concentrations between sites and sampling periods.

BMDust and BM samples display bimodal OC and BC size distributions centred in the accumulation mode in the range 0.26-0.4µm particle diameters and in the coarse mode (2.5 to 4.4µm), while DK sample exhibits wide OC and BC peaks, with maximum concentration in the fine particulates. The unimodal size distribution of carbonaceous aerosols in the fine mode observed in Dakar may have resulted from freshly formed primary aerosols **(Andriejauskienė, 2008)**. This is in line with the founding of **Herner et al., (2006)** who have reported that carbonaceous particles directly emitted from combustion sources typically display mass distribution diameter peaking between 0.1 and 0.32µm. However, the coarse mode of carbonaceous particles in Bamako, which have concentration values some times larger than fine particles (case of dust episode sample), reflects the interaction between BC/OC and dust. Approximately 60% of OC and 41% of BC were in fine particles (Dp < 1µm) within BMDust sample, 71% and 66% in BM sample and about 53% and 59% within DK sample. This is indicative of carbonaceous aerosols being the main components of fine particulates, except during BMDust sample in which BC was more abundant in the coarse mode (59%).

The relative size distributions of Al, Be, Ca, Fe, Mg, Na and Ti were generally similar, despite larger variations in absolute concentrations between BMDust, BM and DK samples (***Figure S4***). Our results show that 28-32% of Al, Be, Ca, Fe, Mg, Na and Ti masses occur in the 1-2.5µm particle diameter range for BMDust, while for BM and DK, respectively, 35-41% and 30-39% occur in the 1.6-4.4µm particle size. The lower particle diameter for BMdust is in agreement with **Kuloglu and Tuncel (2005)**, with mass median diameters of crustal elements smaller in samples impacted by Saharan dust. These elemental size distributions exhibit a single coarse mode between 1.6 and 2.5µm particle diameters, with approximately 65% (Al) to 75% (Ca) of the masses occurring in the coarse mode (Dp >

1.6µm) for BMDust sample, 61% (Na) to 73% (Fe) for BM and 58% (Al) to 75% (Ca) for DK. In contrast, less than 15% of masses were found in particles smaller than 1µm. The relative size distributions of Pb, Cd, Tl, Sb, Se, Rb, K, Zn, Cu, Co and Cr were generally similar for BMDust, BM and DK samples. These elements exhibit distinct a bimodal distribution with a smaller mode between 0.11 and 0.4µm and a larger one between 1.0 and 2.5µm diameter. Co and Cr are mostly located in coarse particles (51-67%) at all sampling sites, which suggests the predominance of soil dust origin. The group of elements including Cd, Tl, Sb, Pb and Se is mostly concentrated (for 54 to 88%) in small particles, whatever the sampling site: these results demonstrate that various anthropogenic sources emit these elements **(Karanasiou et al., 2007)**. Rb, K and As are abundant in coarse particles (for 54 to 79%) only in the BMDust sample; in contrast, they are more concentrated in fine particle modes in BM and DK samples, suggesting multiple source contributions that may include fuel combustion, re-suspended soil dust from vehicular traffic or typical crustal material. This last point is confirmed by the peak occurring during the dust episode in Bamako (***Figure 8***). Also, Ni, Zn, Mn and V display heterogeneous size distributions among sampling sites (***Figure 8***), revealing that these elements may be released in to the environment from both natural and anthropogenic sources.

Chloride and nitrate size distributions peak in small (0.17µm) and large (2.5µm) sizes in Bamako (dust episode included), with small particles (Dp < 1µm) accounting for 67% and 53% respectively within BMDust sample and for 78% and 68% in BM sample. However, in Dakar, size distributions of Cl^- and NO_3^- only peak in large size particles, for 92% and 78%, respectively. ***Figure S4*** (Supplementary data) also shows that concentrations are relatively more abundant in Dakar than in Bamako samples as previously seen. Trends of Cl^- and NO_3^- support the conclusion that the presence of these elements in fine particles at Bamako could be associated with anthropogenic emissions, particularly from fuel combustion, while Cl^- and NO_3^- in DK sample may be attributed primarily to a marine origin and nitrate formation by reaction processes, respectively. Several studies have shown that the most likely main source of Cl^- is oceanic emission **(Graedel and Keene, 1995 ; Rasmussen et al., 1980)**, with fuel combustion as the second largest source **(Blake et al., 1996)**. The location of the Dakar site close to the sea (less than 1 km) is favourable to reactions producing chloride. In addition, Cl^- and NO_3^- display similar relative size distributions as Mg and Na, with approximately 85% and 86% of their masses occurring in coarse modes respectively. Moreover, these elements are also known to be produced by bubble bursting at the sea surface **(Beavington et al., 2004 ; Rodríguez et al., 2004)**. Like Cl^- and NO_3^-, sulphate is mainly associated with coarse

particles, with a 59% contribution to measured coarse particle mass in Dakar. Concentrations of particle (Dp < 1µm) sulphates in Dakar (1363 ng.m^{-3}) Bamako, are assumed to be related to reaction processes between ambient pollution and sea salt.

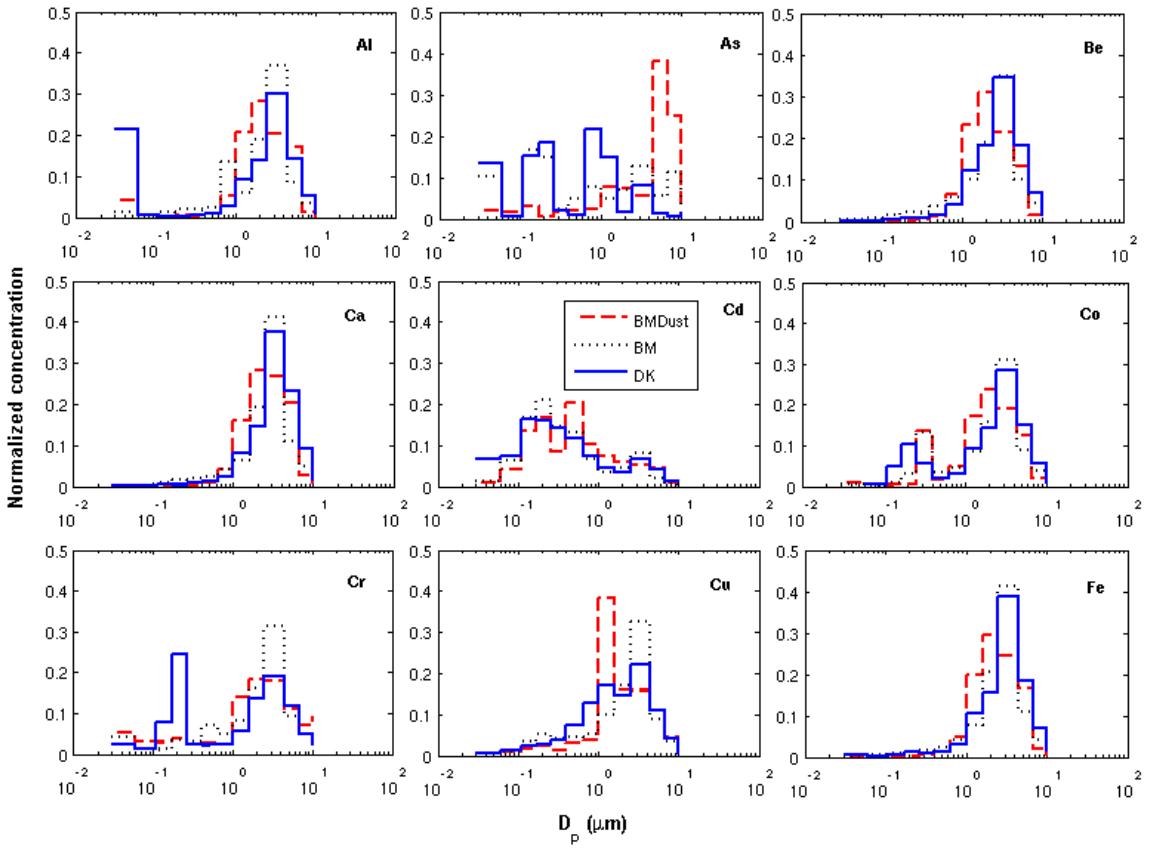

Figure 8: Relative particulate size distributions for twenty two metals, BC, OC, Chloride, Sulphate and Nitrate in Bamako (during the dust event (BMDust) and in the absence of dust event (BM)) and in Dakar (DK).

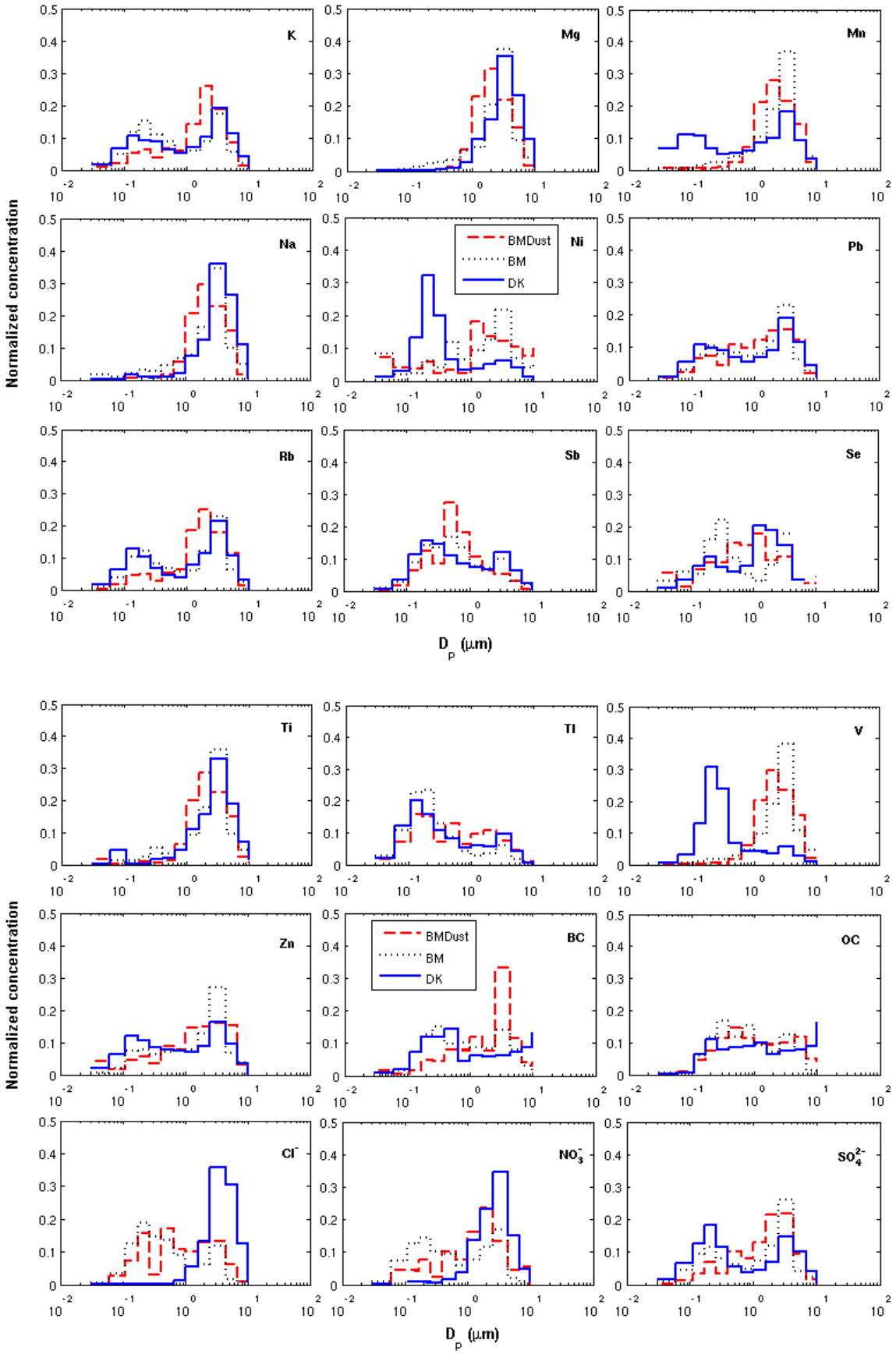

Figure 8: (continued).

3.5. Correlation coefficient analyses

Figures 9-11 show the matrix of correlation coefficients for every combination of PM size distribution described previously, for BMDust, BM and DK respectively, in order to explain observed size distributions of various elements, with varying results depending on the site locations as well as emission sources. Each square reflects the value of correlation coefficients between the shapes of two size distributions for 13 particle sizes. Correlation coefficients of 0.47, 0.95 and 0.75 between OC and BC were found for BMDust (***Figure 9***), BM (***Figure 10***) and DK (***Figure 11***) samples, respectively. Weak correlation coefficients obtained during the dust episode at Bamako suggest that anthropogenic emissions were less significant during the dust event. Several studies have used OC/BC ratios to identify the sources, formation and aging of carbonaceous species **(Guinot et al., 2007 ; Sandradewi et al., 2008 ; Pio et al., 2011)**. In our study, OC/BC ratio of 2.1 ± 1.0 is obtained for DK sample. For BM sample the ratio is 3.5 ± 1.3, relatively more important than in DK sample, suggesting that incomplete combustion such as domestic fuel and two-stroke emissions are predominant in Bamako than in Dakar (with important diesel emissions). However, for BMDust sample this ratio is 9.1 ± 4.9. This high value suggests: 1) relatively more OC associated to the interaction between OC and dust and; 2) an underestimation of BC due to the presence of dust. This is consistent with our previous results for the size distributions. BC and OC are also significantly correlated with Pb, Zn, Se and Sb in Bamako (including the 2 sample types), which demonstrates a mixing sources (wood combustion and non-exhaust and exhaust traffic) of all these elements. However in Dakar, the correlations between carbonaceous matter (BC and OC) and Pb, Zn, Se and Sb are weak ($R^2 < 0.41$), though these latter elements correlate with each other, suggesting a distinct sources with BC and OC in Dakar. In order to determine the contribution levels of biofuel/wood burning at our two sites, the mass ratios of fine particles potassium to BC were calculated **(Andreae, 1983)**. These K^+/BC ratios ranged from 0.17 to 0.45 in Bamako, close to the values generally measured in aerosols from wood combustion (0.21 to 0.46; **(Andreae, 1983)**). In contrast, theses ratios in Dakar are about 0.06, so 3 to 7 times lower than in Bamako, similar to values usually found in urban atmospheres dominated by fossil fuel burning (K^+/BC between 0.02 and 0.09, **Yang et al. (2005)**). Furthermore, the relationships between K^+ and other elements were examined. Indeed, during the dust event (BMDust sample), K^+ displays strong correlations with Al, Ti, Na, Fe, V, Mn, Mg, Be and Ca (R^2 = 0.90-0.94), implying a possible crustal origin. However, in both BMDust and BM samples, K^+ is highly correlated with Rb (R^2 = 0.91-0.98), SO_4^{2-} (R^2 = 0.87-0.96) and NO_3^- (R^2 = 0.93-0.94), whereas the most pertinent correlations in Dakar are

with Pb (R^2 = 0.99), Rb (R^2 = 0.98) and Zn (R^2 = 0.95). This result supports the assumption that K^+ is also due to anthropogenic emissions such as fossil fuel combustion **(Sciare et al., 2003 ; Yang et al., 2005)**.

Being major components in coarse particles and giving a clear peak signal during the dust episode, Al, Ti, Na, Fe, V, Mn, Mg, Be and Ca, are generally highly correlated with each other in BMDust, BM and DK samples (R^2 > 0.95), thus confirming that these elements coexist in the same particles such as mineral dust. However, within the same sample, the relationships between these crustal elements may be affected by other elements from other natural origin (marine or biogenic source), also abundant in coarse particles. For example, in DK sample, the associations of Mn, Na, Mg and Ca with other crustal elements are much weaker (R^2 < 0.70, ***Figure 11***), demonstrating the influence of marine source for these elements, Na and Mg being tracers of sea salt aerosol **(Watson and Chow, 2001)**. Cr, Ni, Cu and Co are slightly correlated with dust crustal elements, but not so much between each other. In addition, these elements display bimodal distribution except for Cu, suggesting that mineral dust was a major but not exclusive source for these elements in Bamako. In Dakar, only Co and Cu are somewhat correlated with crustal elements. Se, Sb, As, Cd and Tl show very heterogeneous relationships as evidenced by the lack of correlations with other elements and between each other, as previously seen. This result tends to confirm the impact of specific sources such as coal and oil combustion, non-exhaust traffic emissions like tire/brake/road wear, and waste incineration, according to individual particular samples **(Watson and Chow, 2001 ; Thorpe and Harisson, 2008 ; Amato et al. 2011)**.

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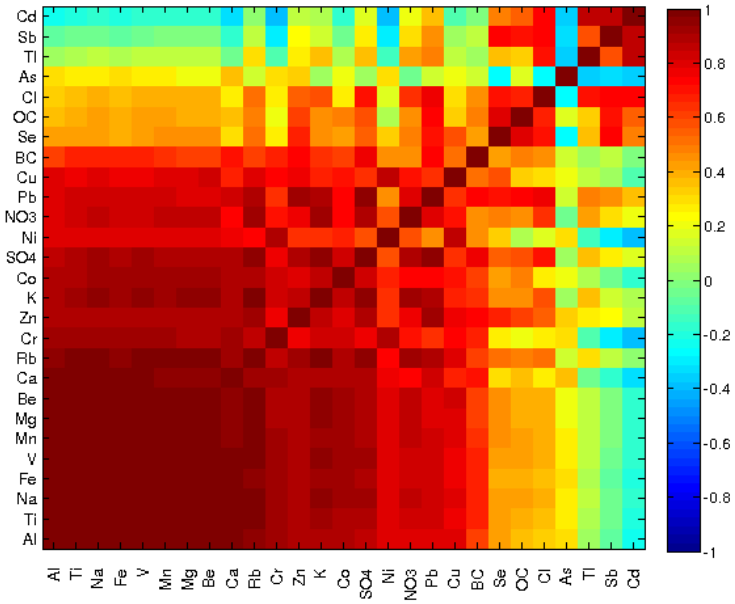


Figure 9: Correlation coefficients (R^2) for particulate matter component size distributions measured at Bamako during the dust episode (BMDust).

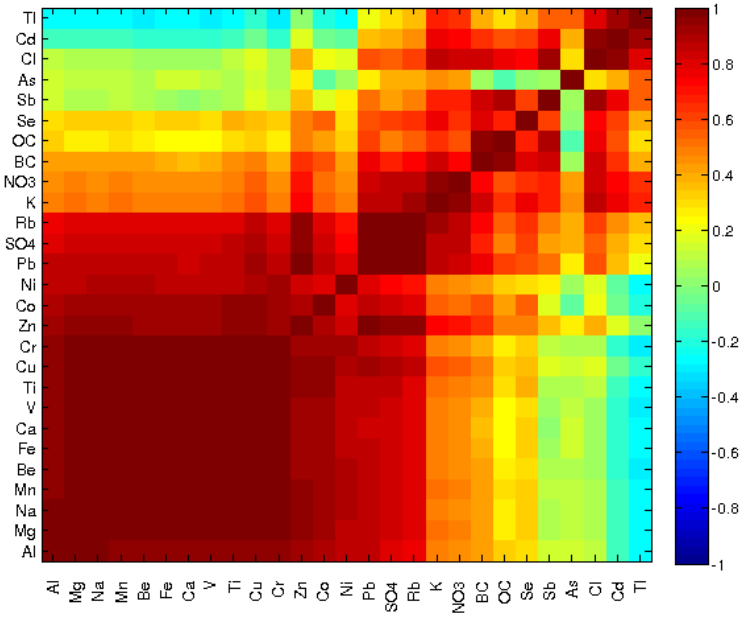


Figure 10: Correlation coefficients (R^2) for particulate matter component size distributions measured at Bamako during no dust period (BM).

Relatively high correlations were observed in BMDust sample (***Figure 9***) between ions such as SO_4^{2-}, NO_3^- and Cl^- with Rb, K and Pb ($R^2 > 0.91$) suggesting similar sources (likely fuel burning). These size distribution correlations were relatively similar with those obtained in BM sample (***Figure 10***). In contrast to BM, DK and BMDust size distributions exhibit slightly better correlations between NO_3^-, Al, Be and Ti ($R^2 > 0.97$), indicating the contribution of mineral dust in NO_3^- production. Such processes are less important in Bamako

than in Dakar certainly due to different NO_3^-/dust sources in Dakar. SO_4^{2-} size distribution correlated reasonably well with Pb, Zn, Sb and Ni ($0.80 < R^2 < 0.83$), suggesting that anthropogenic emissions (construction, cement production and traffic) are the major but not exclusive source of sulfate in Dakar. Cl^- size distribution strongly correlates with Mg, Ca and Na ($R^2 > 0.98$). All these four species have been associated primarily with marine aerosols. The second most important source is probably industrial area emissions of Dakar, including cement kilns which are close to our site. In this study, high correlations are observed between elements of various origins. This suggests strong mixing interactions between crustal dust, anthropogenic and marine aerosols in the studied West African traffic sites.

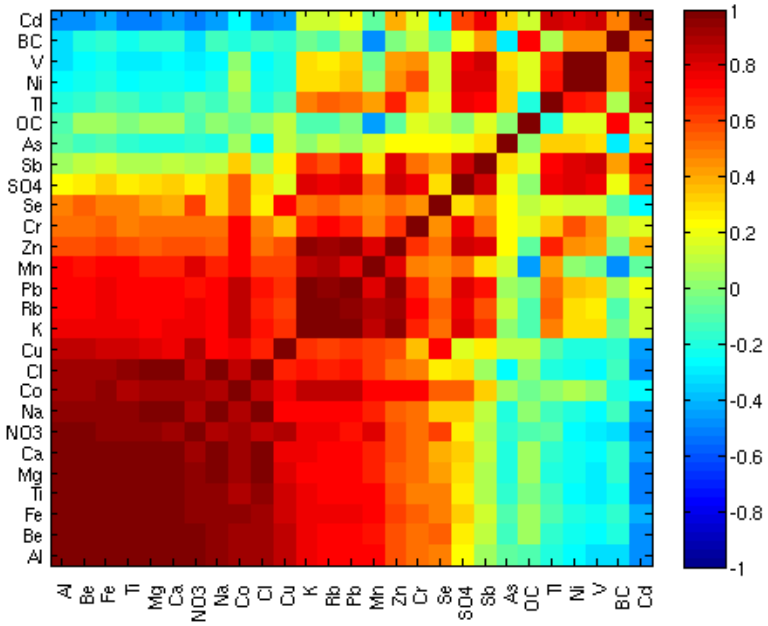


Figure 11: Correlation coefficients (R^2) for particulate matter component size distributions measured at Dakar during weekend days (DK).

3.6. Aerosol mass reconstructed

An aerosol mass reconstruction was conducted to explore the relative contributions of the measured chemical species and their relationship to the TSP, PM_{10} and $PM_{2.5}$ gravimetric mass. The mass reconstruction has been performed for Bamako and Dakar Dekati samples in **(Val et al., 2013)**. Mass retrieval was performed considering the sum of four major components as follows: dust, particulate organic matter (POM), black carbon (BC) and ions. Dust is calculated based on our knowledge of the different elements contributing to mineral dust and methodologies found in the literature **(Guinot et al., 2007 ; Terzi et al., 2010)**. Dust is assumed to be the sum of Al, Si, Ca, Fe and Ti multiplied by factors to convert them to their

common oxides (2.20, 2.49, 1.63, 1.42 and 1.94, respectively). Si is not directly measured in Bamako and Dakar but is estimated based on the relationship given by **Alastuey et al. (2005)** (SiO_2 = 3*Al_2O_3 mass ratios)). POM can be estimated using the OC-to-POM conversion factor ranging from 1.2 to 2.5 **(Turpin and Lim, 2001)**. In this study, OC-to-POM conversion factor is modulated in order to obtain a reconstructed mass as close as possible below the weighted mass of the filters **(Hueglin et al., 2005 ; Guinot et al., 2007):** values of 1.4 and 1.7 are obtained for Dakar and Bamako, respectively. Ion fraction is calculated as the sum of, SO_4^{2-}, NO_3^-, Cl^- and Na^+. Due to the closeness of Dakar site to the sea, ions are categorized in water soluble inorganic (WSI) and sea salt (SS). WSI (= NO_3^- + NH_4^+ + $nssSO_4^{2-}$, where $nssSO_4^{2-}$ is the non sea salt sulphate) and SS (= Na^+ + 1.8Na^+ + 0.12Na^+ + 0.036Na^+ + 0.038Na^+ + 0.252Na^+) are determined following **Terzi et al., (2010)** methodology. PM reconstruction is assumed when the gravimetric measurement of filter samples matches the sum of the masses of individually identified chemical species. The difference between the aerosol weighted mass and the reconstructed mass is referred here as not determined (n.d.) mass. After treatment of analytical data, the mass closure is obtained for TSP, PM_{10} and $PM_{2.5}$ in each sampling site with an n.d. component ranging from 12% to 24% in Bamako (***Figure 12a***) and from 2 to 12% in Dakar (***Figure 12b***). The relatively high n.d. percentage in Bamako is linked to the dust episode due to measurements influenced by dust.

In Bamako, mineral dust contributes to about 50% of mass in each aerosol mode, attributed to the dust episode during the campaign. The relative abundance of POM ranges from 22 to 30%. The two other components account for 3-6% (BC), and 4-5% (Ions).

In Dakar, the relative abundance of mineral dust is less important than in Bamako. POM concentrations remain dominant in Dakar, with 38, 25 and 39% in TSP, PM_{10} and $PM_{2.5}$, respectively. Also, relative abundance of BC is higher in Dakar than in Bamako. Ions (Water Soluble Ion and Sea Salt) are more present in Dakar with SS percents more important than WSI ones due to the high influence of marine aerosol origin. Finally, relatively good correlations, with slopes ranging from 0.69 to 0.86 are seen between the gravimetric and chemically determined mass, for both sites and all size modes (***Figure S5***, Supplementary data).

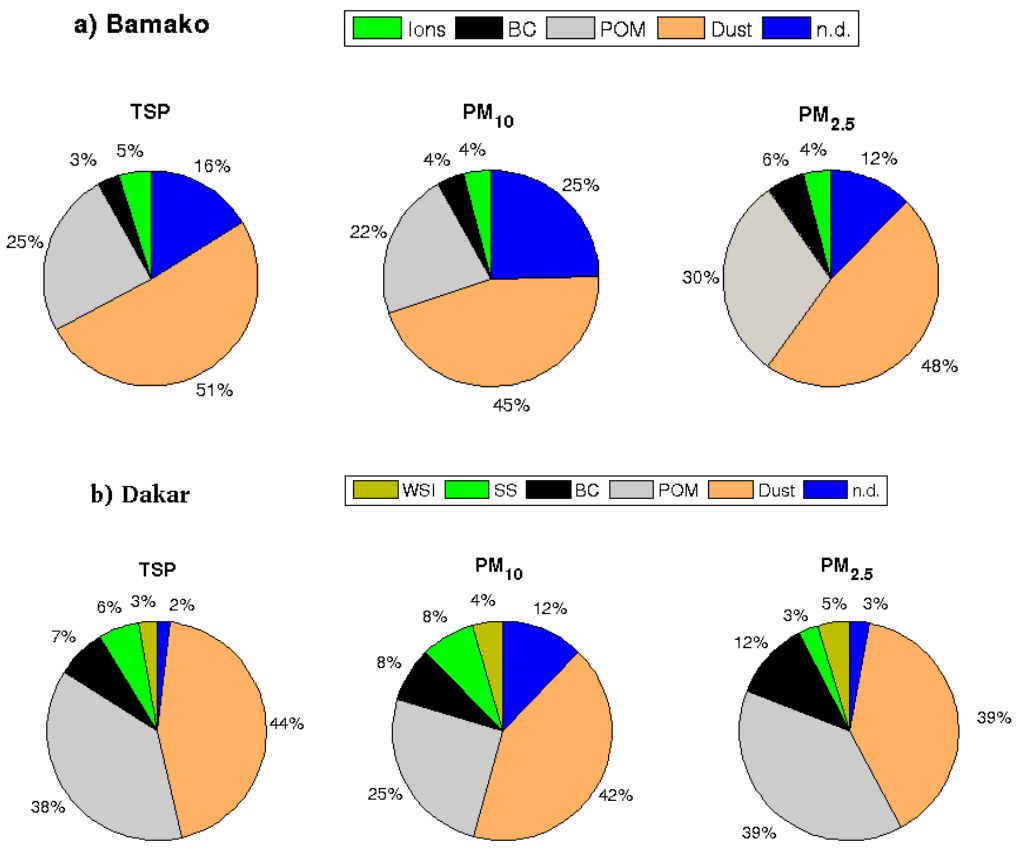


Figure 12: Aerosol mass reconstruction results for TSP, PM_{10} and $PM_{2.5}$ samples collected at a) Bamako site and b) Dakar site.

4. Conclusions

This paper presents the chemical composition, size distribution of particulate matter and associated relationships during the dry season both in Bamako and in Dakar. This study has to be considered as a preliminary analysis of pollution sources and characteristics in two typical West African traffic sites.

Carbonaceous aerosol (OC and BC) was the dominant component at our two measurement sites, with the largest contribution observed for fine particles in the 0.26-0.40µm size range, a contribution accounting for 60% of OC (41% of BC) and 71% of OC (66% of BC) during the Bamako dust event (BMDust) and out of the dust period (BM), respectively. In contrast, in Dakar (DK), carbonaceous matter peaks in fine particles in the 0.17-0.26µm size range, accounting for 53% of OC and 59% of BC. These results are consistent with previous ones found in urban areas dominated by traffic sources, with some notable differences in the fuels used in traffic and presence of domestic fires, as evidenced from the differences in OC/BC

and K^+/BC ratios between Bamako and Dakar. For example, lower OC/BC ratio (2.1 ± 1.0) in Dakar than Bamako reveals incomplete source emission in Bamako, and then K^+/BC ratio in Bamako are linked to high wood combustion.

The second most abundant component in Bamako is metals, with aluminum being the most important element, both in the presence and absence of dust events, whereas inorganic ions are the second dominant components in Dakar, with Calcium being the most abundant species, due to site location and meteorology. The metals such as Al, Ti, Na, Fe, Mn, Mg, Be and Ca measured in this study display peaks in the large particle sizes range with significant inter-correlations, thus suggesting their primary crustal rock origin in Bamako and atmospheric dusty environment origin in Dakar with most probably, the high impact of re-suspended road particles in all samples (BMDust, BM and DK samples). In contrast, Na, Mg and Ca are also associated to a marine origin in Dakar, since all these components are strongly correlated with Cl^-. The other elements exhibit high variability in size distributions and relationships between samples, with the difficulty to delineating precisely characterization of their sources. In order to get more information about these elements and to quantify each source contribution more precisely, more investigations using for example cluster analysis associated with enrichment factor calculations are necessary and presently on-going.

This study was a preliminary assessment using size distribution and linear regression analysis to characterize urban sources of aerosols in West Africa region and should be a precursor for further studies.

Supplementary data

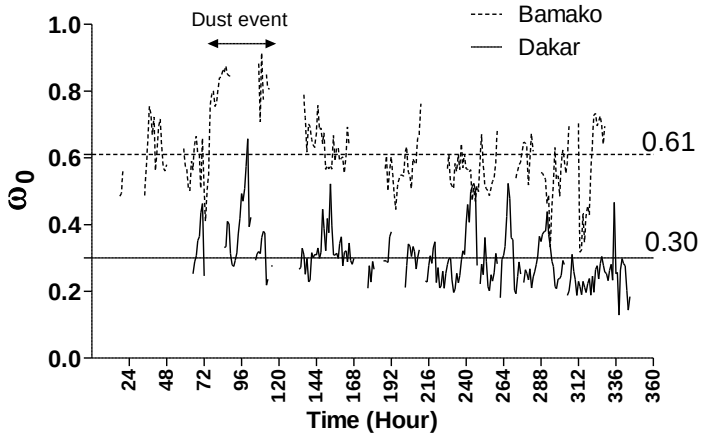


Figure S1: Temporal evolution of single scattering albedo ($\omega_0 = \sigma_{scat} / \sigma_{abs} + \sigma_{scat}$) in Bamako and Dakar.

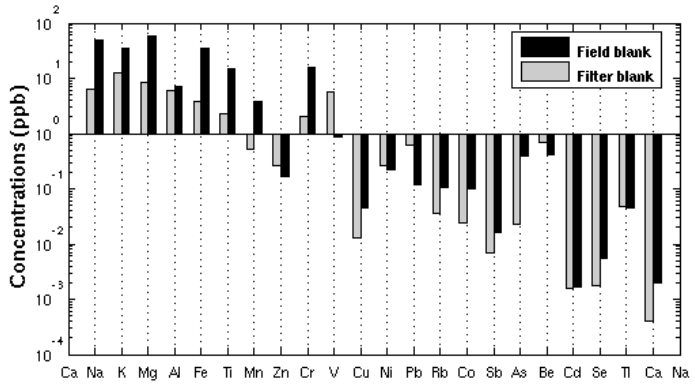


Figure S2: Comparison between average concentration of field blanks and filter blanks.

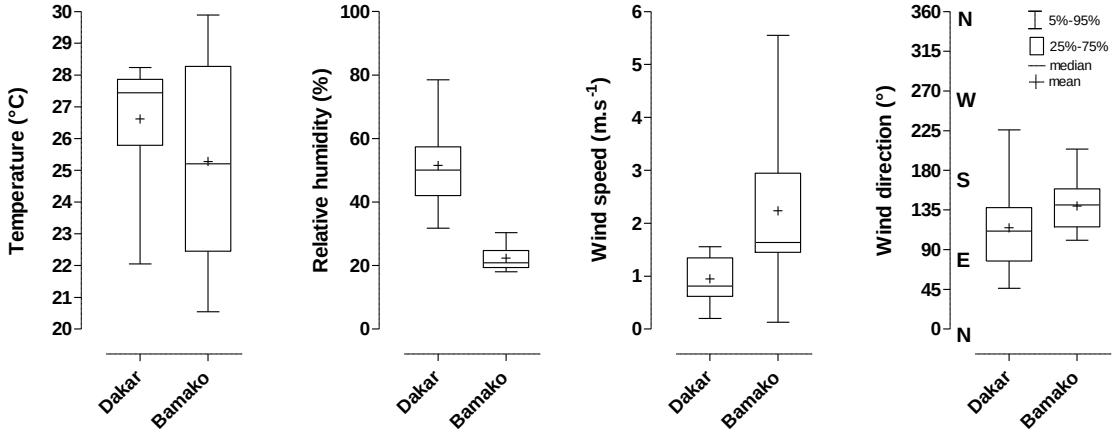
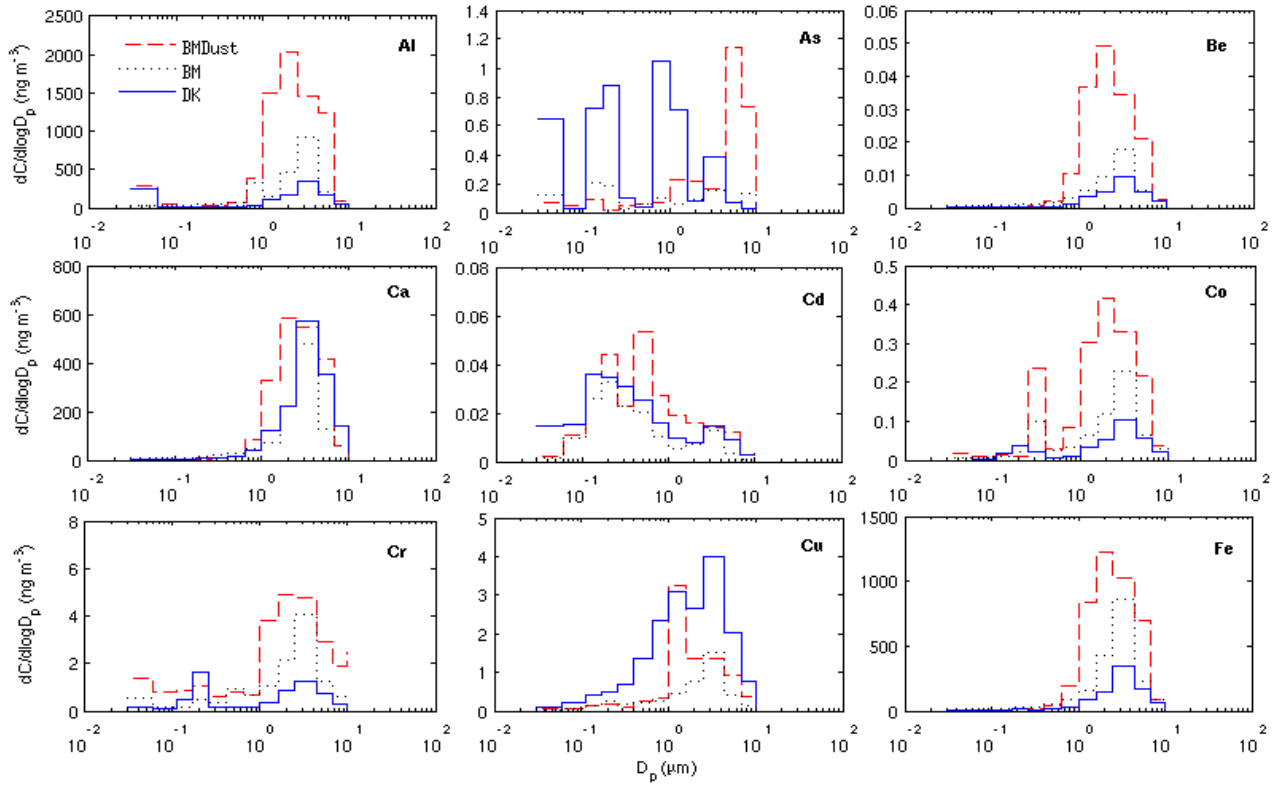
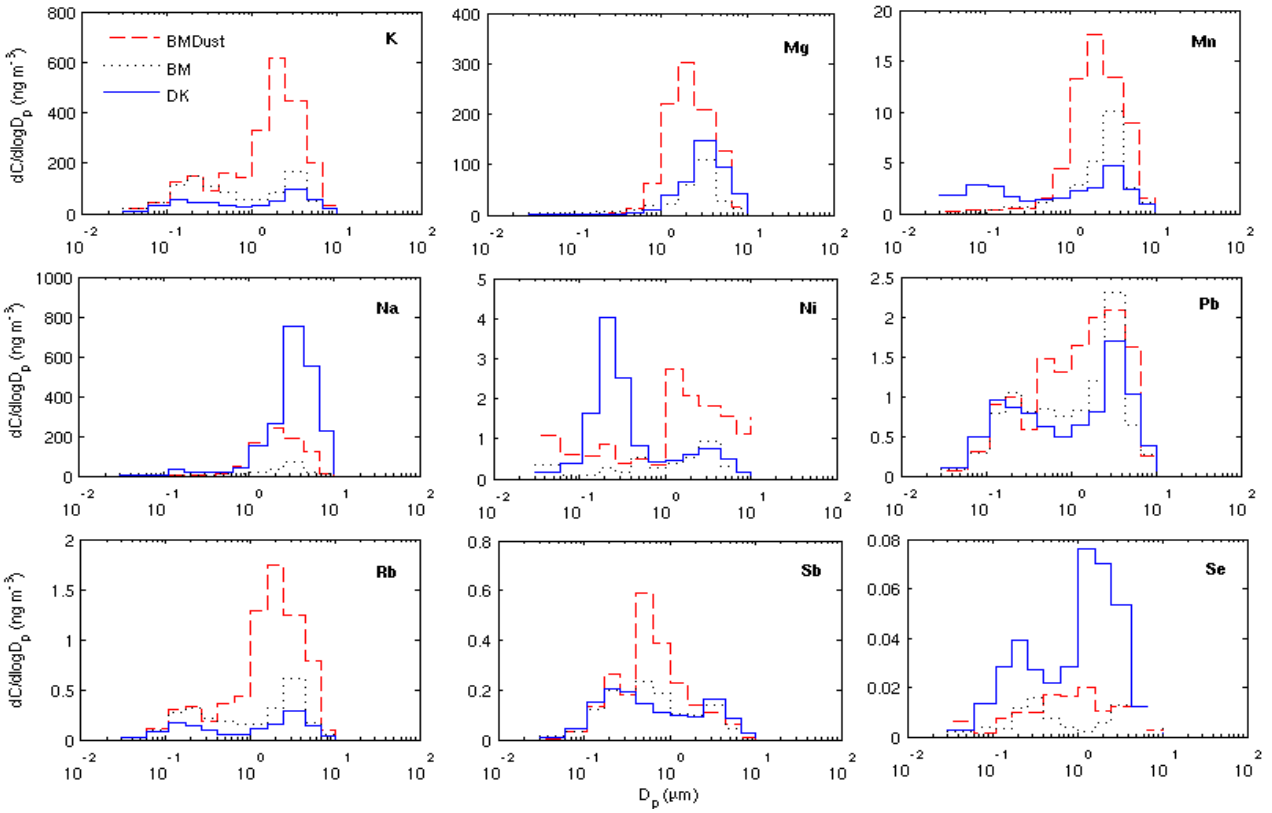


Figure S3: Meteorological parameters during the whole measurement period at Bamako and Dakar.


BMDust
BM
DK
Al
As
Be
Ca
Cd
Co
Cr
Cu
Fe
dC/dlogD$_p$ (ng m^{-3})
D$_p$ (µm)


BMDust
BM
DK
K
Mg
Mn
Na
Ni
Pb
Rb
Sb
Se
dC/dlogD$_p$ (ng m^{-3})
D$_p$ (µm)

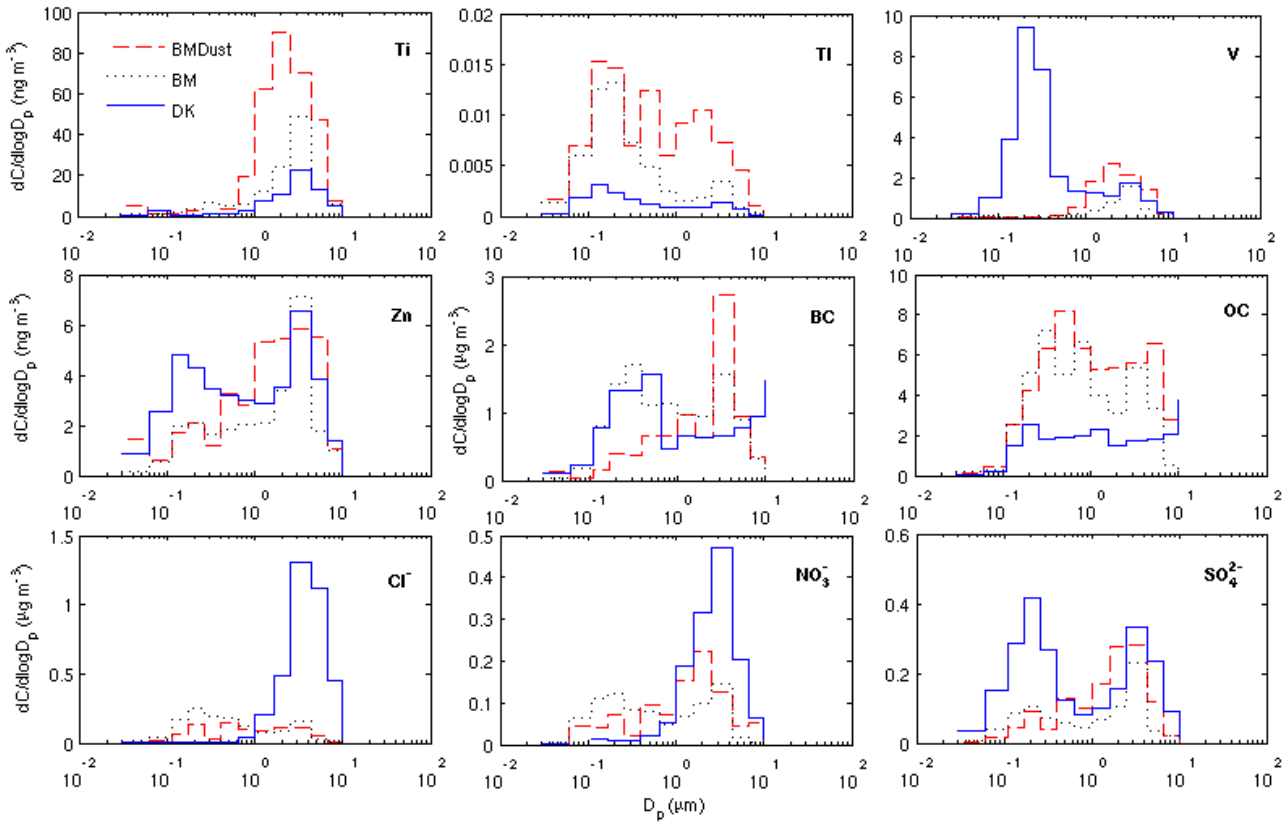


Figure S4: Size distribution of particulate OC, BC, NO_3^-, SO_4^{2-}, Cl^-, and for twenty two trace elements measured in Bamako (BMDust and BM) and in Dakar (DK).

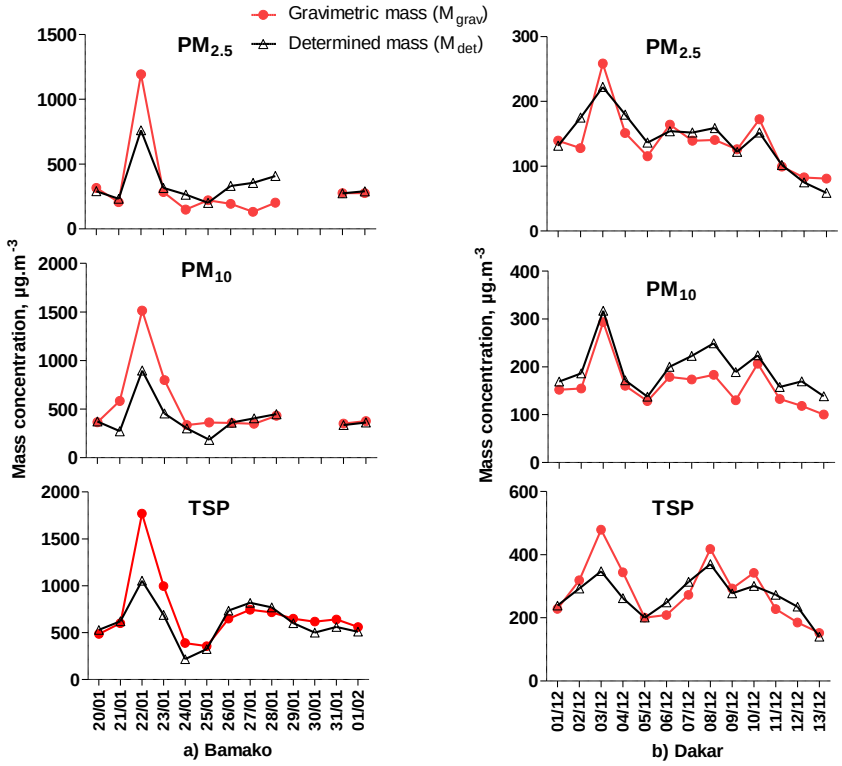


Figure S5: Temporal variation of aerosol mass concentration obtained from gravimetric measurements and chemical analyses for TSP, PM_{10} and $PM_{2.5}$ size modes of a) Bamako and b) Dakar.

Table S1: Summary of the thermal optical reflectance (TOR) and thermal protocols (Schmid et al., 2001).

Protocol	TOR	Thermal
Combustion environment for OC	He	O_2
Combustion environment for BC	98%He, 2%O_2	O_2
Temperature plateau for OC (°C)	550	340
Residence time for OC (s)	580	7200
Temperature plateau for BC (°C)	800	1100
Residence time for BC (s)	580	600
Optical/charring correction	Reflectance	10% of OC; BC decomposition of 0.22% per min during OC analysis
Convert and detector	Methanator FID/CH_4	Coulometric titration/CO_2

Table S2: Comparison between no decarbonatation (noDC) and decarbonatation (DC) procedures on measurements of OC, BC and TC (OC + BC) at Bamako.

Comparison		Filter	Mean ratio	Correlation	Mean values (µg.cm^{-2})			
noDC	DC	n	DC/noDC	r^2	noDC	DC	noDC - DC	Difference (%)
$PM_{2.5}$								
OC1	OC1	11	0.03 ± 0.05	-0.86	8.46	0.23	8.23	-97
OC2	OC2	11	0.11 ± 0.20	0.02	50.11	4.63	45.48	-91
OC3	OC3	11	0.40 ± 0.15	0.66	49.40	19.40	29.99	-61
OC4	OC4	11	0.72 ± 0.12	0.47	12.19	8.77	3.42	-28
BC1	BC1	11	1.33 ± 0.11	1.00	96.61	124.84	-28.24	29
BC2	BC2	11	0.15 ± 0.03	0.92	16.44	2.55	13.89	-84
BC3	BC3	11	1.02 ± 0.44	0.05	0.72	0.71	0.02	-2
OP	OP	11	0.90 ± 0.24	0.94	65.36	63.11	2.25	-3
TC	TC	11	0.70 ± 0.08	0.98	233.93	160.97	72.96	-31
OC	OC	11	0.51 ± 0.11	0.94	185.44	95.97	89.47	-48
BC	BC	11	1.42 ± 0.29	0.91	48.49	64.99	-16.51	34
PM_{10}								
OC1	OC1	11	0.01 ± 0.05	0.89	8.18	0.09	8.09	-99
OC2	OC2	11	0.08 ± 0.05	0.92	47.66	2.72	44.94	-94
OC3	OC3	11	0.48 ± 0.11	0.95	44.49	20.00	24.49	-55
OC4	OC4	11	0.83 ± 0.15	0.22	11.60	9.58	2.02	-17
BC1	BC1	11	1.29 ± 0.10	1.00	88.18	110.23	-22.05	25
BC2	BC2	11	0.18 ± 0.05	0.72	15.64	2.84	12.80	-82
BC3	BC3	11	1.27 ± 0.45	-0.24	0.73	0.88	-0.15	20
OP	OP	11	1.02 ± 0.35	0.84	63.65	68.03	-4.38	7
TC	TC	11	0.69 ± 0.05	1.00	216.48	146.27	70.21	-32
OC	OC	11	0.57 ± 0.10	0.94	175.58	100.36	75.23	-43
BC	BC	11	1.28 ± 0.37	0.77	40.90	45.91	-5.01	12
All								
OC1	OC1	22	0.02 ± 0.03	-0.29	8.32	0.15	8.17	-98
OC2	OC2	22	0.09 ± 0.15	0.11	48.89	3.68	45.21	-92
OC3	OC3	22	0.44 ± 0.13	0.74	46.94	19.70	27.24	-58
OC4	OC4	22	0.78 ± 0.15	0.27	11.90	9.17	2.72	-23
BC1	BC1	22	1.31 ± 0.10	1.00	92.39	117.54	-25.14	27
BC2	BC2	22	0.17 ± 0.04	0.79	16.04	2.70	13.35	-83
BC3	BC3	22	1.15 ± 0.45	-0.09	0.73	0.79	-0.07	9
OP	OP	22	0.96 ± 0.30	0.88	64.51	65.57	-1.06	2
TC	TC	22	0.70 ± 0.06	0.99	225.21	153.62	71.59	-32
OC	OC	22	0.54 ± 0.11	0.93	180.51	98.16	82.35	-46
BC	BC	22	1.35 ± 0.33	0.82	44.69	55.45	-10.76	24

Table S3: Comparison between no decarbonatation (noDC) and decarbonatation (DC) procedures on measurements of OC, BC and TC (OC + BC) at Dakar.

Comparison		Filter	Mean ratio	Correlation	Mean values			
noDC	DC	n	DC/noDC	r^2	noDC	DC	noDC - DC	Difference (%)
$PM_{2.5}$								
OC1	OC1	13	1.08 ± 1.08	0.25	4.47	2.98	1.49	-33
OC2	OC2	13	0.99 ± 0.29	0.30	27.63	26.56	1.07	-4
OC3	OC3	13	0.97 ± 0.26	0.13	27.85	25.96	1.89	-7
OC4	OC4	13	0.46 ± 0.09	0.06	11.38	5.13	6.25	-55
BC1	BC1	13	1.21 ± 0.34	0.19	45.78	53.11	-7.33	16
BC2	BC2	13	0.17 ± 0.08	0.31	10.18	1.39	8.79	-86
BC3	BC3	13	1.23 ± 0.46	-0.21	0.54	0.63	-0.09	16
OP	OP	13	0.68 ± 0.39	0.23	17.66	9.93	7.72	-44
TC	TC	13	0.93 ± 0.23	0.37	127.82	115.75	12.07	-9
OC	OC	13	0.82 ± 0.24	0.22	88.98	69.67	19.31	-22
BC	BC	13	1.20 ± 0.21	0.51	38.84	46.08	-7.25	19
PM_{10}								
OC1	OC1	13	0.05 ± 0.05	0.35	3.95	0.06	3.89	-98
OC2	OC2	13	0.05 ± 0.01	0.29	28.80	1.27	27.53	-96
OC3	OC3	13	0.61 ± 0.19	0.11	25.79	14.86	10.93	-42
OC4	OC4	13	0.70 ± 0.22	-0.34	13.49	9.01	4.48	-33
BC1	BC1	13	1.05 ± 0.11	0.94	45.54	48.44	-2.91	6
BC2	BC2	13	0.27 ± 0.10	0.93	6.98	1.59	5.38	-77
BC3	BC3	13	1.61 ± 0.37	0.61	0.54	0.84	-0.30	56
OP	OP	13	0.82 ± 0.52	0.42	13.30	9.60	3.70	-28
TC	TC	13	0.62 ± 0.05	0.96	125.08	76.16	48.93	-39
OC	OC	13	0.41 ± 0.06	0.87	85.94	34.45	51.49	-60
BC	BC	13	1.08 ± 0.15	0.77	39.15	41.71	-2.56	7
All								
OC1	OC1	26	0.72 ± 1.00	0.15	4.21	1.52	2.69	-64
OC2	OC2	26	0.52 ± 0.52	-0.01	28.22	13.91	14.30	-51
OC3	OC3	26	0.79 ± 0.29	0.20	26.82	20.41	6.41	-24
OC4	OC4	26	0.58 ± 0.21	0.22	12.43	7.07	5.36	-43
BC1	BC1	26	1.13 ± 0.26	0.58	45.66	50.78	-5.12	11
BC2	BC2	26	0.22 ± 0.10	0.45	8.58	1.49	7.09	-83
BC3	BC3	26	1.42 ± 0.45	0.26	0.54	0.74	-0.20	36
OP	OP	26	0.75 ± 0.46	0.32	15.48	9.77	5.71	-37
TC	TC	26	0.78 ± 0.23	0.43	126.45	95.96	30.50	-24
OC	OC	26	0.62 ± 0.27	0.26	87.46	52.06	35.40	-40
BC	BC	26	1.14 ± 0.19	0.63	38.99	43.90	-4.90	13

BC components were assumed to consist of the sum of the three BC fractions obtained by TOR minus the pyrolysis correction (OP) so that BC = BC1 + BC2 + BC3 – OP. OC components were assumed to consist of the four fractions plus the pyrolysis correction obtained by TOR so that OC = OC1 + OC2 + OC3 + OC4 + OP.

Table S4: Certified /non certified and resulting concentration for elements in SRM 1648.

Element	Concentration ($\mu g.g^{-1}$)	SD (%)	Certified SRM 1648 ($\mu g.g^{-1}$)	Recovery (%)
Na	4416 ± 1277	3.5	4250 ± 20	104
Mg	6732 ± 1723	3.9	(8000)	84
Al	30025 ± 7885	3.8	34200 ± 1100	88
K	10051 ± 2594	3.9	10500 ± 100	96
Cr	243 ± 73	3.3	403 ± 12	60
Mn	729 ± 188	3.9	786 ± 17	93
Fe	33207 ± 8425	3.9	39100 ± 1000	85
Co	16 ± 4	3.9	(18)	88
Ni	81 ± 24	3.4	82 ± 3	99
Cu	543 ± 135	4.0	609 ± 27	89
Zn	4489 ± 1222	3.7	4760 ± 140	94
As	115 ± 31	3.7	115 ± 10	100
Se	27 ± 10	2.7	27 ± 1	99
Be	3.2 ± 0.7	3.4	-	-
Cd	68 ± 19	3.6	75 ± 7	91
Sb	37 ± 9	4.1	(45)	83
Cs	3.2 ± 0.9	3.6	(3)	105
Ba	668 ± 167	4.0	(737)	91
Ce	46 ± 12	3.9	(55)	83
Ca	37781 ± 7883	3.9	58400 ± 1900	-
Rb	50 ± 13	3.2	(52)	69
Pb	6413 ± 1014	6.3	6550 ± 80	98
Th	7.3 ± 1.1	6.4	(7.4)	98
U	5.4 ± 0.8	6.5	5.5 ± 0.1	97
V	119 ± 30	3.9	127 ± 7	94
Ti	3332 ± 784	4.2	(4000)	83

SD, the relative standard deviation between replicates ($n = 9$). Values in parenthesis are non-certified and are given for information.

Référence A2

Adepetu, J.A., Asubiojo, O.I., Iskander, F.Y., Bauer, T.L., 1988. Elemental composition of Nigerian harmattan dust. Journal of radioanalytical and nuclear chemistry 121, 141–147.

Adon, M., Galy-Lacaux, C., Yoboué, V., Delon, C., Lacaux, J.P., Castera, P., Gardrat, E., Pienaar, J., Al Ourabi, H., Laouali, D., others, 2010. Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers. Atmos. Chem. Phys 10, 7467–7487.

Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., Romero, P.-M., Exposito, F., García, O., Pedro Diaz, J., Dingenen, R.V., Putaud, J.P., 2005. Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan Dust Episode (July 2002). Atmospheric Environment 39, 4715–4728.

Alleman, L.Y., Lamaison, L., Perdrix, E., Robache, A., Galloo, J.-C., 2010. PM10 metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. Atmospheric Research 96, 612–625.

Amato, F., Pandolfi, M., Moreno, T., Furger, M., Pey, J., Alastuey, A., Bukowiecki, N., Prevot, A.S.H., Baltensperger, U., Querol, X., 2011. Sources and variability of inhalable road dust particles in three European cities. Atmospheric Environment 45, 6777–6787.

Andreae, M.O., 1983. Soot Carbon and Excess Fine Potassium: Long-Range Transport of Combustion-Derived Aerosols. Science 220, 1148–1151.

Andreae, M.O., Browell, E.V., Garstang, M., Gregory, G.L., Harriss, R.C., Hill, G.F., Jacob, D.J., Pereira, M.C., Sachse, G.W., Setzer, A.W., Dias, P.L.S., Talbot, R.W., Torres, A.L., Wofsy, S.C., 1988. Biomass-burning emissions and associated haze layers over Amazonia. J. Geophys. Res. 93, 1509–1527.

Andreae, M.O., Gelencsér, A., 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics Discussions 6, 3419–3463.

Andriejauskienė, J., 2008. Black carbon aerosol at the background site in the coastal zone of the Baltic Sea. Lithuanian Journal of Physics 48, 183–194.

Assamoi, E.-M., Liousse, C., 2010. A new inventory for two-wheel vehicle emissions in West Africa for 2002. Atmospheric Environment 44, 3985–3996.

Beavington, F., Cawse, P.A., Wakenshaw, A., 2004. Comparative studies of atmospheric trace elements: improvements in air quality near a copper smelter. Sci. Total Environ. 332, 39–49.

Blake, N.J., Blake, D.R., Sive, B.C., Chen, T.-Y., Rowland, F.S., Jr, J.E.C., Sachse, G.W., Anderson, B.E., 1996. Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region. J. Geophys. Res. 101, 24151–24,164.

Bowen, H.J.M., 1966. Trace elements in biochemistry. Academic Press.

Brugge, D., Durant, J.L., Rioux, C., 2007. Near-highway pollutants in motor vehicle exhaust: A review of epidemiologic evidence of cardiac and pulmonary health risks. Environmental Health 6, 23.

Cachier, H., Brémond, M.P., Buat-Ménard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. Tellus Series B-Chemical and Physical Meteorology 41(B), 379–390.

Callot, Y., Marticorena, B., Bergametti, G., 2000. Geomorphologic approach for modelling the surface features of arid environments in a model of dust emissions: application to the Sahara desert. Geodinamica Acta 13, 245–270.

Celo, V., Dabek-Zlotorzynska, E., Mathieu, D., Okonskaia, I., 2010. Validation of simple microwave-assisted acid digestion method using microvessels for analysis of trace elements in atmospheric PM 2.5 in monitoring and fingerprinting studies. The Open Chemical & Biomedical Methods Journal 3, 141–150.

Cheng, Y., Zheng, M., He, K., Chen, Y., Yan, B., Russell, A.G., Shi, W., Jiao, Z., Sheng, G., Fu, J., Edgerton, E.S., 2011. Comparison of two thermal-optical methods for the determination of organic carbon and elemental carbon: Results from the southeastern United States. Atmospheric Environment 45, 1913–1918.

Cho, S.-H., Tong, H., McGee, J., Baldauf, R., Krantz, Q., Gilmour, M., 2009. Comparative Toxicity of Size-Fractionated Airborne Particulate Matter Collected at Different Distances from an Urban Highway. Environmental Health Perspectives.

Chow, J.C., Watson, J.G., Chen, L.-W.A., Chang, M.-C.O., Miranda, G.P., 2005. Comparison of the DRI/OGC and Model 2001 Thermal/Optical Carbon Analyzers.

Chow, J.C., Watson, J.G., Fujita, E.M., Lu, Z., Lawson, D.R., Ashbaugh, L.L., 1994. Temporal and spatial variations of PM2.5 and PM10 aerosol in the southern California air quality study. Atmos. Environ. 28, 2061–2080.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The dri thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies. Atmospheric Environment. Part A. General Topics 27, 1185–1201.

Deboudt, K., Flament, P., Choël, M., Gloter, A., Sobanska, S., Colliex, C., 2010. Mixing state of aerosols and direct observation of carbonaceous and marine coatings on African dust by individual particle analysis. J. Geophys. Res. 115, D24207.

Derimian, Y., Léon, J.-F., Dubovik, O., Chiapello, I., Tanré, D., Sinyuk, A., Auriol, F., Podvin, T., Brogniez, G., Holben, B.N., 2008. Radiative properties of aerosol mixture observed during the dry season 2006 over M'Bour, Senegal (African Monsoon Multidisciplinary Analysis campaign). J. Geophys. Res. 113, D00C09.

DHS, 2006. DHS (Demography Health Survey) Final Reports [WWW Document]. URL http://. www.measuredhs.com/pubs/browse_region.cfm.

Dieme, D., Cabral-Ndior, M., Garçon, G., Verdin, A., Billet, S., Cazier, F., Courcot, D., Diouf, A., Shirali, P., 2012. Relationship between physicochemical characterization and toxicity of fine particulate matter (PM2.5) collected in Dakar city (Senegal). Environ. Res. 113, 1–13.

Dockery, D.W., Pope, C.A., 1994. Acute Respiratory Effects of Particulate Air Pollution. Annual Review of Public Health 15, 107–132.

Doumbia, E.H.T., Liousse, C., Galy-Lacaux, C., Ndiaye, S.A., Diop, B., Ouafo, M., Assamoi, E.M., Gardrat, E., Castera, P., Rosset, R., Akpo, A., Sigha, L., 2012a. Real time black carbon measurements in West and Central Africa urban sites. Atmospheric Environment 54, 529–537.

Esteve, A.R., Estellés, V., Utrillas, M.P., Martínez-Lozano, J.A., 2012. In-situ integrating nephelometer measurements of the scattering properties of atmospheric aerosols at an urban coastal site in western Mediterranean. Atmospheric Environment 47, 43–50.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., D'Anna, B., 2010. Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France). Atmospheric Chemistry & Physics 10, 5295–5314.

Fialho, P., Hansen, A.D.A., Honrath, R.E., 2005. Absorption coefficients by aerosols in remote areas: a new approach to decouple dust and black carbon absorption coefficients using seven-wavelength aethalometer data. Journal of aerosol science 36, 267–282.

Flament, P., Deboudt, K., Cachier, H., Châtenet, B., Mériaux, X., 2011. Mineral dust and carbonaceous aerosols in West Africa: Source assessment and characterization. Atmospheric Environment 45, 3742–3749.

Gehring, U., Wijga, A.H., Brauer, M., Fischer, P., Jongste, J.C. de, Kerkhof, M., Oldenwening, M., Smit, H.A., Brunekreef, B., 2010. Traffic-related Air Pollution and the Development of Asthma and Allergies during the First 8 Years of Life. Am. J. Respir. Crit. Care Med. 181, 596–603.

Gianini, M.F.D., Gehrig, R., Fischer, A., Ulrich, A., Wichser, A., Hueglin, C., 2012. Chemical composition of PM10 in Switzerland: An analysis for 2008/2009 and changes since 1998/1999. Atmospheric Environment 54, 97–106.

Goix, S., Point, D., Oliva, P., Polve, M., Duprey, J.L., Mazurek, H., Guislain, L., Huayta, C., Barbieri, F.L., Gardon, J., 2011. Influence of source distribution and geochemical composition of aerosols on children exposure in the large polymetallic mining region of the Bolivian Altiplano. Science of the Total Environment.

Graedel, T.E., Keene, W.C., 1995. Tropospheric budget of reactive chlorine. Global Biogeochemical Cycles 9, 47–77.

Guinot, B., Cachier, H., Oikonomou, K., 2007. Geochemical perspectives from a new aerosol chemical mass closure. Atmospheric Chemistry and Physics 7, 1670.

Guinot, B., Cachier, H., Sciare, J., Tong, Y., Xin, W., Jianhua, Y., 2007. Beijing aerosol: Atmospheric interactions and new trends. J. Geophys. Res. 112, D14314.

Hays, M.D., Cho, S.-H., Baldauf, R., Schauer, J.J., Shafer, M., 2011. Particle size distributions of metal and non-metal elements in an urban near-highway environment. Atmospheric Environment 45, 925–934.

Herner, J.D., Ying, Q., Aw, J., Gao, O., Chang, D.P.Y., Kleeman, M.J., 2006. Dominant Mechanisms that Shape the Airborne Particle Size and Composition Distribution in Central California. Aerosol Science and Technology 40, 827–844.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L., Puxbaum, H., 2006. Intercomparison of Thermal and Optical Measurement Methods for Elemental Carbon and Black Carbon at an Urban Location. Environ. Sci. Technol. 40, 6377–6383.

Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C., Vonmont, H., 2005. Chemical characterisation of PM2.5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment 39, 637–651.

IDAF-Aerosol [WWW Document], 2011. . URL http://idaf.sedoo.fr/spip.php?rubrique36 (accessed 1.7.13)

Iskander, F., 1985. Neutron activation analysis of an Egyptian cigarette and its ash. Journal of Radioanalytical and Nuclear Chemistry 89, 511–518.

Karanasiou, A.A., Sitaras, I.E., Siskos, P.A., Eleftheriadis, K., 2007. Size distribution and sources of trace metals and n-alkanes in the

Athens urban aerosol during summer. Atmospheric Environment 41, 2368–2381.

Kuloglu, E., Tuncel, G., 2005. Size Distribution of Trace Elements and Major Ions in the Eastern Mediterranean Atmosphere. Water, Air, and Soil Pollution 167, 221–241.

Li, X., Wang, L., Wang, Y., Wen, T., Yang, Y., Zhao, Y., Wang, Y., 2012. Chemical composition and size distribution of airborne particulate matters in Beijing during the 2008 Olympics. Atmospheric Environment 50, 278–286.

Ling, S., Van Eeden, S., 2009. Particulate matter air pollution exposure: role in the development and exacerbation of chronic obstructive pulmonary disease. Int J Chron Obstruct Pulmon Dis 4, 233–243.

Liousse, C., Galy-Lacaux, C., 2010. Urban pollution in West Africa. La Météorologie.

Liousse, C., Guillaume, B., Grégoire, J.M., Mallet, M., Galy, C., Pont, V., Akpo, A., Bedou, M., Castéra, P., Dungall, L., Gardrat, E., Granier, C., Konaré, A., Malavelle, F., Mariscal, A., Mieville, A., Rosset, R., Serça, D., Solmon, F., Tummon, F., Assamoi, E., Yoboué, V., Van Velthoven, P., 2010. Western african aerosols modelling with updated biomass burning emission inventories in the frame of the AMMA-IDAF program. Atmospheric Chemistry and Physics Discussions 10, 7347–7382.

Liousse, C., Penner, J.E., Chuang, C., Walton, J.J., Eddleman, H., Cachier, H., 1996. A global three-dimensional model study of carbonaceous aerosols. J. Geophys. Res. 101, 19411–19,432.

Lukács, H., Gelencsér, A., Hammer, S., Puxbaum, H., Pio, C., Legrand, M., Kasper-Giebl, A., Handler, M., Limbeck, A., Simpson, D., Preunkert, S., 2007. Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe. J. Geophys. Res. 112, D23S18.

Lyamani, H., Olmo, F.J., Alados-Arboledas, L., 2008. Light scattering and absorption properties of aerosol particles in the urban environment of Granada, Spain. Atmospheric Environment 42, 2630–2642.

Makkonen, U., Hellén, H., Anttila, P., Ferm, M., 2010. Size distribution and chemical composition of airborne particles in south-eastern Finland during different seasons and wildfire episodes in 2006. Science of The Total Environment 408, 644–651.

Manktelow, P.T., Carslaw, K.S., Mann, G.W., Spracklen, D.V., 2010. The impact of dust on sulfate aerosol, CN and CCN during an East Asian dust storm. Atmos. Chem. Phys 10, 365–382.

Marticorena, B., Chatenet, B., Rajot, J.L., Traoré, S., Coulibaly, M., Diallo, A., Koné, I., Maman, A., NDiaye, T., Zakou, A., 2010. Temporal variability of mineral dust concentrations over West Africa: analyses of a pluriannual monitoring from the AMMA Sahelian Dust Transect. Atmospheric Chemistry and Physics 10, 8899–8915.

Mazzoli-Rocha, F., Fernandes, S., Einicker-Lamas, M., Zin, W.A., 2010. Roles of oxidative stress in signaling and inflammation induced by particulate matter. Cell Biology and Toxicology 26, 481–498.

McTainsh, G.H., Nickling, W.G., Lynch, A.W., 1997. Dust deposition and particle size in Mali, West Africa. CATENA 29, 307–322.

Millero, F.J., Feistel, R., Wright, D.G., McDougall, T.J., 2008. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. Deep Sea Research Part I: Oceanographic Research Papers 55, 50–72.

Misra, C., Singh, M., Shen, S., Sioutas, C., Hall, P.M., 2002. Development and evaluation of a personal cascade impactor sampler (PCIS). Journal of Aerosol Science 33, 1027–1047.

Ozer, P., Laghdaf, M.B.O.M., Lemine, S.O.M., Gassani, J., 2006. Estimation of air quality degradation due to Saharan dust at Nouakchott, Mauritania, from horizontal visibility data. Water, Air, and Soil Pollution 178, 79–87.

Pakbin, P., Hudda, N., Cheung, K.L., Moore, K.F., Sioutas, C., 2010. Spatial and Temporal Variability of Coarse (PM10−2.5) Particulate Matter Concentrations in the Los Angeles Area. Aerosol Science and Technology 44, 514–525.

Pakkanen, T.A., Kerminen, V.-M., Korhonen, C.H., Hillamo, R.E., Aarnio, P., Koskentalo, T., Maenhaut, W., 2001. Urban and rural ultrafine (PM0.1) particles in the Helsinki area. Atmospheric Environment 35, 4593–4607.

Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B., Matos, M., 2011. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmospheric Environment 45, 6121–6132.

Pope, C.A., 3rd, Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. JAMA 287, 1132–1141.

Pope, C.A., Young, B., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association 56, 709–742.

Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H. ten, Tørseth, K.,

Wiedensohler, A., 2004. A European aerosol phenomenology—2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment 38, 2579–2595.

Querol, X., Alastuey, A., Viana, M.M., Rodriguez, S., Artiñano, B., Salvador, P., Garcia do Santos, S., Fernandez Patier, R., Ruiz, C.R., de la Rosa, J., Sanchez de la Campa, A., Menendez, M., Gil, J.I., 2004. Speciation and origin of PM10 and PM2.5 in Spain. Journal of Aerosol Science 35, 1151–1172.

Rasmussen, R.A., Rasmussen, L.E., Khalil, M.A.K., Dalluge, R.W., 1980. Concentration Distribution of Methyl Chloride in the Atmosphere. Journal of Geophysical Research 85, 7350–7356.

Rodríguez, S., Querol, X., Alastuey, A., Viana, M.-M., Alarcón, M., Mantilla, E., Ruiz, C.., 2004. Comparative PM10–PM2.5 source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain. Science of The Total Environment 328, 95–113.

Sandradewi, J., Prévôt, A.S.H., Weingartner, E., Schmidhauser, R., Gysel, M., Baltensperger, U., 2008. A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength Aethalometer. Atmospheric Environment 42, 101–112.

Sandroni, V., Smith, C.M.., 2002. Microwave digestion of sludge, soil and sediment samples for metal analysis by inductively coupled plasma–atomic emission spectrometry. Analytica Chimica Acta 468, 335–344.

Schmid, H., Laskus, L., Jürgen Abraham, H., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H., 2001. Results of the "carbon conference" international aerosol carbon round robin test stage I. Atmospheric Environment 35, 2111–2121.

Schnaiter, M., Horvath, H., Möhler, O., Naumann, K.-H., Saathoff, H., Schöck, O.W., 2003. UV-VIS-NIR spectral optical properties of soot and soot-containing aerosols. Journal of Aerosol Science 34, 1421–1444.

Sciare, J., Cachier, H., Oikonomou, K., Ausset, P., Sarda-Estève, R., Mihalopoulos, N., 2003. Characterization of carbonaceous aerosols during the MINOS campaign in Crete, July–August 2001: a multi-analytical approach. Atmos. Chem. Phys. 3, 1743–1757.

Sciare, J., Oikonomou, K., Favez, O., Markaki, Z., Liakakou, E., Cachier, H., Mihalopoulos, N., others, 2008. Long-term measurements of carbonaceous aerosols in the Eastern Mediterranean: evidence of long-range transport of biomass burning. Atmospheric Chemistry and Physics Discussions 8, 6949–6982.

Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric chemistry and physics: from air pollution to climate change, Wiley. New York.

Singh, M., Misra, C., Sioutas, C., 2003. Field evaluation of a personal cascade impactor sampler (PCIS). Atmospheric Environment 37, 4781–4793.

Skonieczny, C., Bory, A., Bout-Roumazeilles, V., Abouchami, W., Galer, S.J.G., Crosta, X., Stuut, J.B., Meyer, I., Chiapello, I., Podvin, T., Chatenet, B., Diallo, A., Ndiaye, T., 2011. The 7-13 March 2006 major Saharan outbreak : multiproxy characterization of mineral dust deposited on the West African margin. Journal of Geophysical Research. Atmospheres 116.

Sternbeck, J., Sjödin, Å., Andréasson, K., 2002. Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. Atmospheric Environment 36, 4735–4744.

Swami, K., Judd, C.D., Orsini, J., Yang, K.X., Husain, L., 2001. Microwave assisted digestion of atmospheric aerosol samples followed by inductively coupled plasma mass spectrometry determination of trace elements. Fresenius J Anal Chem 369, 63–70.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Malden, Mass. 122, 673–674.

Terzi, E., Argyropoulos, G., Bougatioti, A., Mihalopoulos, N., Nikolaou, K., Samara, C., 2010. Chemical composition and mass closure of ambient PM10 at urban sites. Atmospheric Environment 44, 2231–2239.

Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: a review. Sci. Total Environ. 400, 270–282.

Turpin, B.J., Lim, H.-J., 2001. Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. Aerosol Science and Technology 35, 602–610.

Val, S., Liousse, C., Doumbia, E.H.T., Galy-Lacaux, C., Cachier, H., Marchand, N., Badel, A., Gardrat, E., Baeza-Squiban, A., 2013. Physico chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells: description of a worrying situation. In review process on Particle and Fibre Toxicology.

Vinogradov, A.P., 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soft, Consultants Bureau. Inc., New york.

Watson, J.G., Chow, J.C., 2001. Source characterization of major emission sources in the

Imperial and Mexicali Valleys along the US/Mexico border. Science of The Total Environment 276, 33–47.

Weinstein, J.P., Hedges, S.R., Kimbrough, S., 2010. Characterization and aerosol mass balance of PM2. 5 and PM10 collected in Conakry, Guinea during the 2004 Harmattan period. Chemosphere 78, 980–988.

Yang, F., He, K., Ye, B., Chen, X., Cha, L., Cadle, S.H., Chan, T., Mulawa, P.A., 2005. One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai. Atmos. Chem. Phys. 5, 1449–1457.

Ye, S.-H., Zhou, W., Song, J., Peng, B.-C., Yuan, D., Lu, Y.-M., Qi, P.-P., 2000. Toxicity and health effects of vehicle emissions in Shanghai. Atmospheric Environment 34, 419–429.

Yu, J.Z., Tung, J.W.T., Wu, A.W.M., Lau, A.K.H., Louie, P.K.-K., Fung, J.C.H., 2004. Abundance and seasonal characteristics of elemental and organic carbon in Hong Kong PM10. Atmospheric Environment 38, 1511–1521.

CHAPITRE IV : ETUDE DES DIFFERENTES SOURCES DE L'AEROSOL A BAMAKO ET DAKAR

Introduction

Le chapitre précédent nous a permis d'obtenir des informations sur les caractéristiques physico-chimiques de chaque espèce mesurée dans l'aérosol à Bamako et à Dakar, leurs évolutions temporelles et les corrélations entre différents éléments. Cette connaissance préalable des sources des éléments est une étape indispensable à l'utilisation de modèles mathématiques de type statistique multivariée afin de faciliter l'interprétation des résultats.

Ce chapitre permet d'explorer les sources de particules d'aérosols qui influencent les sites de Bamako et de Dakar, d'identifier ces sources à l'aide de traceurs spécifiques et de déterminer leur importance relative, mais également de les quantifier.

La méthode choisie dans cette étude est l'application d'un modèle récepteur multivarié à chaque set de données sur la composition chimique de l'aérosol de chaque site. L'approche multivariée est basée sur l'idée que la dépendance temporelle d'une espèce chimique sur un site récepteur est la même pour toutes les espèces d'une même source. Les espèces de variabilité similaire sont groupées dans un minimum de facteurs, chaque facteur étant associé à une source ou à un type de source.

Cette étude a fait l'objet d'une publication en cours de soumission dans Atmospheric Environment **(Article A3)** et est présentée ici. Dans cet article, nous avons appliqué la démarche suivante :

- une première approche d'identification par Analyse en Composantes Principales (ACP) associée aux calculs de facteurs d'enrichissements (EF), l'analyse ACP est en effet très facile à mettre en œuvre, également la détermination des EF.
- une analyse plus avancée avec un modèle fourni par l'agence américaine pour la protection de l'environnent (USEPA): la Factorisation en Matrice Positive (PMF). L'ACP permet d'avoir une connaissance des facteurs (ici les sources) et de faciliter ainsi l'utilisation du modèle PMF, plus difficile à mettre en œuvre. Le modèle PMF permet d'extraire plus d'informations que l'ACP et d'aller ainsi plus loin dans l'exploration des données et donc d'atteindre une meilleure connaissance des sources.

IV.1. Modèles multivariés ACP et PMF

IV.1.1. ACP

L'ACP est une technique d'analyse multivariée dont le but est de ramener un nombre de variables intercorrélées (les constituants chimiques) à un plus petit ensemble de variables

indépendantes appelées «facteurs» ou «composantes principales» (**Hopke, 1991**). Chaque composante principale ou facteur est une combinaison linéaire des variables originales qui expliquent un maximum de la variabilité totale des données tout en étant non corrélé avec les autres composantes. Les coefficients de combinaisons linéaires appelés en anglais « loadings » représentent les degrés de corrélation entre les variables et le facteur. Par conséquent, les composés chimiques avec les plus grandes corrélations dans chaque facteur peuvent être interprétés comme une empreinte de la source. Cependant, l'analyse est pertinente si, avec un petit nombre de facteurs, on explique une grande partie de la variabilité des données originales. Pour le choix du nombre de facteur à retenir, plusieurs critères sont utilisés, à savoir: retenir autant d'axes qu'il le faut pour atteindre le seuil de variance expliquée désiré ou retenir les valeurs propres supérieures à 1 (critère de kaiser) ou le critère du Scree test fondé sur la courbe de décroissance des valeurs propres, le nombre de facteurs à retenir correspondant au premier point d'inflexion détecté sur la courbe. Ce dernier critère a été retenu dans cette étude (***Figure IV.1***). Les ACP ont été construites autour des concentrations des espèces chimiques (BC, OC, ions, éléments traces) mesurées dans les $PM_{2.5}$, PM_{10} et les TSP à Dakar et Bamako.

Toutefois, les limites de cette analyse sont que :

- en général, chaque élément n'est associé qu'à un facteur alors qu'un même élément peut être émis par plusieurs sources.

- l'ACP permet de connaître quels éléments sont corrélés avec quelle source mais ne permet pas directement d'extraire des profils de sources « physiquement » interprétables; ceci nécessite une transformation supplémentaire des données (Absolute Principal Component Analysis, Target Principal Component Analysis, …)

- l'ACP est sensible aux éléments « faibles » et donne le même poids à toutes les données alors que certaines sont plus « fiables » que d'autres. En effet, les valeurs en-dessous de la limite de détection et les valeurs manquantes qui ont été remplacées par la moyenne, devraient avoir moins d' «influence» que les données fiables.

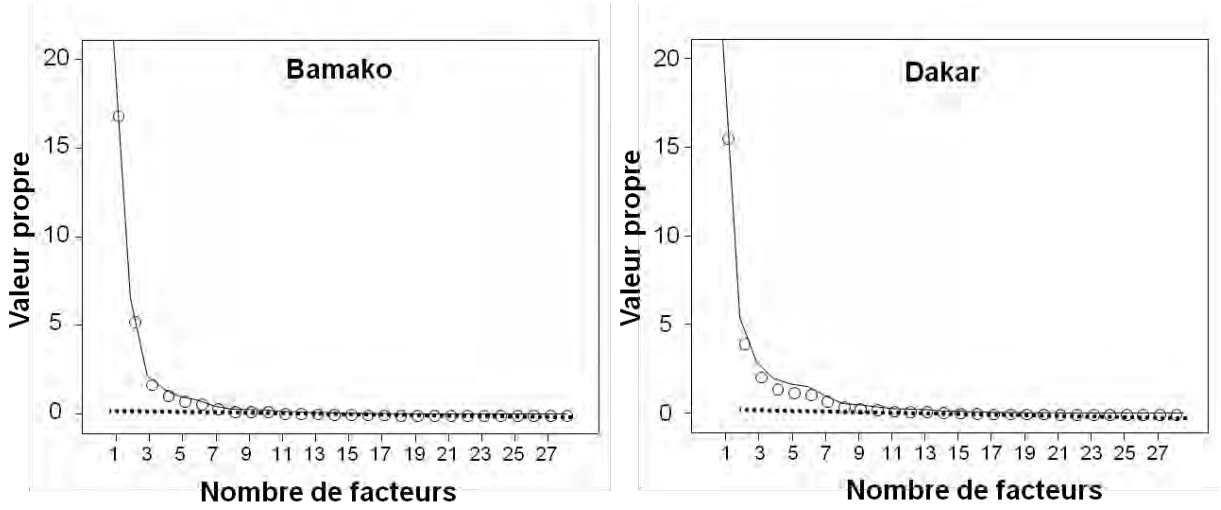


Figure IV.1: Courbe de décroissance des valeurs propres en fonction du nombre de facteurs : cas de Bamako et Dakar.

IV.1.2. PMF

La mise en œuvre de modèle PMF nécessite un bon choix des paramètres d'entrée du modèle et une connaissance a priori des sources facilitera l'interprétation des résultats. Les données appliquées au modèle PMF sont décrites dans le chapitre précédent.

IV.2. Présentation des principaux résultats

Le modèle PMF nous a permis d'obtenir des résultats satisfaisants pour l'ensemble des sources présentées dans cette étude. L'ACP ainsi que le modèle PMF ont permis d'estimer un nombre optimum de 5 sources à Bamako et 6 sources à Dakar. La comparaison des profils obtenus avec des profils donnés dans la littérature a permis d'identifier les 5 sources suivantes à Bamako (***Figure IV.2a***):

- La source la plus importante (51% des TSP, 28% des PM_{10} et 70% des $PM_{2.5}$), est liée aux combustions. Cette source regroupe à la fois les émissions par le trafic (véhicules et deux-roues) et les combustibles solides. Près de la moitié de la population de Bamako utilise les combustibles solides (bois, charbon de bois) pour la cuisine;
- La seconde source la plus importante est attribuée aux particules en resuspension issues du trafic. Elle représente entre 8 et 29% des émissions de particules d'aérosols à Bamako ;
- La source de poussières naturelles dans laquelle les éléments Al, Fe, et Ti sont fortement corrélés que ce soit dans les résultats de l'ACP ou du modèle PMF. Les tests de sensibilité effectués en enlevant les échantillons représentant l'épisode de poussière à Bamako n'ont pas permis aux deux modèles de distinguer les poussières locales (particules en resuspension) de

celles d'origines naturelles (poussières sahariennes). Cette source représente entre 11 et 16% de la masse des particules (TSP, PM_{10} et $PM_{2.5}$) ;

- La quatrième source, attribuée à l'usure des pneus et des garnitures de freins des véhicules, représente 5 à 13% et dont les éléments qui corrèlent le plus avec ce factor sont Sb, Cu et Zn ;
- La dernière source est probablement liée à la présence de lacs salés asséchés dans la région mais également à la proximité du site avec le fleuve Niger, puisque corrélé à des éléments principalement d'origines marines (Na^+, Mg^{2+}). Ce facteur est attribué aux sels inorganiques d'autant plus que les éléments Cl^-, SO_4^{2-} et NO_3^- y sont fortement présent. Sa contribution à la masse des aérosols à Bamako est estimée entre 3 et 9% ;
- La fraction non déterminée atteint 12% dans les TSP.

L'application du modèle PMF a permis de mettre en évidence 6 sources à Dakar (***Figure IV.2b***):

- La source trafic corrèle avec les éléments BC et OC (abondance relative de 64 et 76% respectivement) mais également avec les espèces Sb et Cu. Elle est la plus importante à Dakar (43 à 46% de la masse des TSP, PM_{10} et $PM_{2.5}$) ;
- Une source de poussière minérale repérée par les éléments Al, Fe et Ti. Elle contribue pour 28% des TSP, 18% des PM_{10} et 13% de la masse des $PM_{2.5}$;
- La source marine caractérisée par un ratio Na^+/Mg^{2+} proche de celui donné dans la littérature (8,4) et représente 15 à 21%. L'importance de cette source à Dakar s'explique par la proximité avec l'Océan Atlantique ;
- Une source liée à la production du ciment et aux activités de constructions avec une signature du Ca^{2+}, 13 à 18% de masse des particules sont attribués à ces émissions ;
- Une source attribuée à l'usure des garnitures de freins de voitures et qui génère entre 4 et 12% de la masse des aérosols à Dakar.
- La source de combustion de fuels lourds, associée aux activités dans le port de Dakar non loin du site, est tracée par l'abondance du Ni et du V. Cette source contribue pour 4 à 5% de l'aérosol ;
- La fraction non déterminée est plus faible à Dakar qu'à Bamako et représente environ 1% quelque soit le mode des particules.

Le modèle PMF a bien identifié les sources majeures à Bamako comme à Dakar mais a quelques difficultés à bien résoudre certaines sources considérées comme mineures.

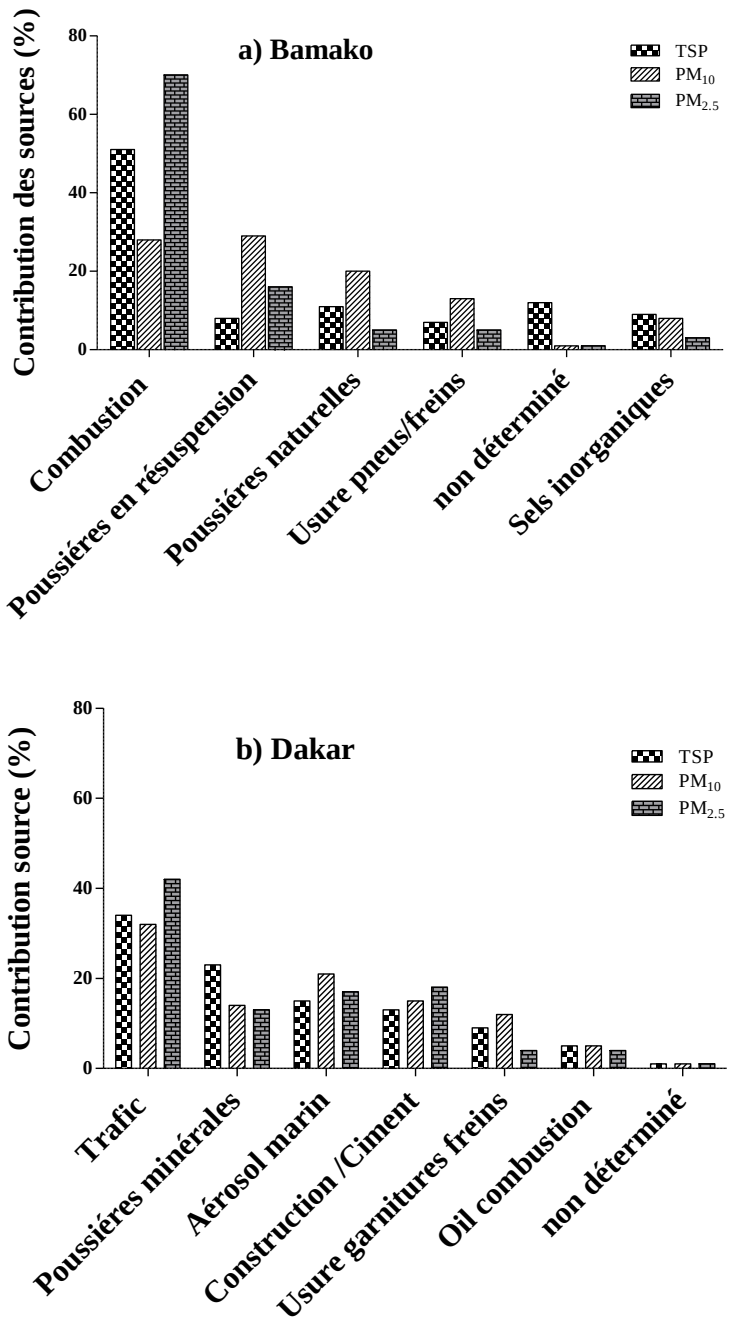


Figure IV.2 : Contribution des différentes sources aux TSP, PM_{10} and $PM_{2.5}$ à Bamako (a) et Dakar (b).

IV.3. Article A3

"Chemical composition and contributing sources of urban aerosol in Bamako (Mali) and Dakar (Senegal) during POLCA experiment"

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Soumis dans Atmospheric Environment

Abstract

This study aims at characterizing emission sources impacting West Africa traffic sites in Bamako (Mali) and Dakar (Senegal) during the dry season (January and December 2009, respectively) within the POLCA (POLlution des Capitales Africaines) program **(Liousse and Galy-lacaux, 2010 ; Doumbia et al., 2012a)**. Source apportionment of PM was performed using two receptor modeling techniques, Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF). In addition, enrichment factor (EF) calculations were analyzed. The speciated chemical PM data applied to these models came from analyze of 24-h samples. In this study, measurements of carbonaceous species (black carbon BC and organic carbon OC), water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+} and Mg^{2+}), and elements (Al, Mg, K, Ca, Ti, Tl, Be, V, Cr, Mn, Fe, Ni, Na, Rb, Cu, Zn, As, Se, Sb, Cd, Co and Pb) were used.

Both PCA and PMF analyses let appear 5 and 6 PM sources (TSP, PM_{10} and $PM_{2.5}$) in Bamako and Dakar, respectively. According to PMF, the Bamako site shows contributions of fuel combustion by vehicles (including two-wheel two-stroke vehicles) and solid fuel combustions by domestic fires (28-70%), crustal dust (5-20%), resuspended road dust (8-29%), tire and brake wear (5-13%) and inorganic salts (3-9%). Traffic emissions (32-42%), mineral dust (13-23%), construction and cement production (13-18%), marine aerosol (15-21%), oil combustion (4-5%) and brake wear (4-12%) are found in Dakar. Anthropogenic PM sources are predominant both at Bamako and Dakar sites, respectively, with relative contributions range of 67-81% and 61-68%.

Keywords: Particulate matter, West Africa, Source receptor models, Principal component analysis, Positive matrix factorization

1. Introduction

Identification and quantitative evaluation of the contributions of different aerosol sources are of interest for understanding their implication in health and environmental effects and mitigation. In developed countries, source characterization of atmospheric pollution has been systematically investigated for several years. Most generally this is far from being the case in developing countries with density populated regions such as in West Africa capitals. In these urban areas, quite a large proportion of atmospheric particles is attributable to anthropogenic sources such as traffic (vehicular and two-strokes), biomass and domestic burning (wood and charcoal), industries, … **(Arku et al., 2008 ; Kouassi et al., 2010 ; Weinstein et al., 2010 ; Dionisio et al., 2010 ; Assamoi and Liousse, 2010 ; Doumbia et al., 2012a)**. Also, Saharan dust aerosol is important during the dry season, with predominant North-Easterly trade winds (Harmattan) heavily loaded with dust **(Bertrand et al., 1974 ; Asubiojo et al., 1993 ; Eltayeb et al., 2001)**. In addition, mechanical processes such as resuspended of road particles remain a large source due to the high number of unpaved roads in theses cities. Consequently, rapid deterioration of air quality has now become a heavy challenge for the majority of capital cities in West Africa with an urgent need for the sources of this pollution to be quantified, in order to try reducing particulate matter (PM) pollution at source level. The more so that PM pollution levels in West Africa are comparable to concentrations observed in European, Asian and Unite State megacities **(Doumbia et al., 2012a)**, well above the international World Health Organization (WHO) recommendations.

Receptor-oriented source apportionment models are often used to identify aerosol sources and to estimate their contributions to measured concentrations **(Larsen and Baker, 2003 ; Yang et al., 2005 ; Xu et al., 2012)**. Some widely used multivariate models analyzing series of observations for the determination of the number of sources and elemental relative contributions are based on principal component analysis/absolute principal component scores (PCA/APCS) **(Gordon, 1988 ; Hopke, 1991)**, edge analysis (UMIX) **(Henry, 1997)**, chemical mass balance (CMB) **(Watson and Chow, 2002)**, and positive matrix factorization (PMF) **(Paatero and Tapper, 1993)**. The PCA/APCS approach consists in a source apportionment technique requiring minimal inputs from source characteristics, with an aim at quantitative information both upon source profiles and strength in terms of absolute concentrations. PCA alone is often used as an explanatory tool to identify the major sources of air pollutant emissions, while the other methods are used to quantify the contributions of all sources for all measured pollutants. Although UMIX and CMB methods have similar aims as

PMF, they follow different procedures, with UMIX not always able to resolve as many source factors as PMF **(Song et al., 2006)**. With CMB, the user must provide source profiles for mass apportionment. PCA/ACPS, CMB and PMF have already been compared in a number of studies. For example, **Callén et al., (2009)** have concluded that higher requirements for measurement uncertainty in PMF result in better results than in the two other models. Same conclusions were also obtained by **Miller et al. (2002)** when applying various models to simulated individual exposure data. PCA and PMF were used in this study due to their accessibility and relative easy use. Enrichment factor (EF) analyses are also extensively used to identify the major sources of air pollution and to quantify contributions of all sources of all measured pollutants **(Zhang et al., 2008)**. EF compares the ratios for various elements in measured atmospheric concentrations to the corresponding ratios in geological material **(Watson and Chow, 2002)**.

Preliminary identification of the main sources of particulate matter (PM) in Bamako and Dakar was previously discussed in **Doumbia et al. (2012b)**, and pointed out to strong mixing state of aerosol sources in these regions. In this study, a data set from intensive POLCA (POLlution des Capitales Africaines) **(Liousse and Galy-Lacaux, 2010 ; Doumbia et al., 2012a)** campaigns in Bamako (Mali) and Dakar (Senegal) (January 2009 and December 2009, respectively) was analyzed for a comprehensive description of aerosol source types, and their contributions to total PM using PCA and PMF techniques in association with enrichment factor (EF) analyses.

2. Methodology

2.1. Sampling and chemical analysis

The data discussed in this paper were obtained in the frame of the POLCA (POLlution des Capitales Africaines) program, dedicated to air quality and health studies in West Africa. A detailed description of the sampling and measurement procedures has been previously reported **(Doumbia et al., 2012b)**. Briefly, intensive field sampling took place at Bamako (Mali) between 20 January and 02 February 2009. Data were obtained at a downtown crossroad (***Figure 1***). This site is subject to intense human activities due to its position near the main Bamako market. It is heavily influenced by traffic (vehicles and motorcycles), and certainly by domestic fuel combustion and atmospheric dust. Another intensive field campaign was performed between 01 and 13 December 2009 at Dakar (Senegal). The site in this city (***Figure 1***) is heavily affected by intense traffic from several nearby roads. Thus,

traffic there is expected to be the major anthropogenic source for particulate pollution **(Doumbia et al., 2012a)**.

Daily aerosol samples were collected by filtration during the dry season at each site using IDAF PM collectors (**IDAF, 2011 ; Goix et al., 2011**). The system is designed to collect samples simultaneously using six lines, each with a vacuum pump at a average flow rate of 18 ± 7 lpm. TSP (total suspended particles), PM_{10} (particles with diameters smaller than 10µm) and $PM_{2.5}$ (particles with diameters smaller than 2.5µm) samples were collected on different filters. PM collection was carried out on 47mm diameter Teflon filters (Zefluor, Pall Corporation) and on 47mm diameter quartz filters (QMA, Whatman) for each particle mode.

TSP, PM_{10} and $PM_{2.5}$ were analyzed for particulate gravimetric masses, carbonaceous (black carbon BC and organic carbon OC), water-soluble ions and elemental composition. Extensive description of the analytical methods was previously published **(Val et al., 2013)**. Briefly, PM masses were determined by weighing Teflon filters before and after sampling at temperatures and relative ambient humidity using an electronic microbalance (1µg sensitivity). BC and OC were measured with DRI instrument using thermal-optical reflectance (TOR) technique **(Chow et al., 1993)**. The metal elements were determined by coupling microwave assisted digestion with induced coupled plasma-mass spectrometry (ICP-MS) **(Celo et al., 2010)** : over 40 elements were determined, only a part of them being retained for the sake of interpretation.

At each site, 39 samples (included TSP, PM_{10} and $PM_{2.5}$) were collected during the whole measurement period. A dust event has occurred on 23 January, 2009 at Bamako **(Val et al., 2013)**. The three dust event samples (one in each PM mode) were excluded from this analysis for the following reason: after many tests by **Song et al. (2006)**, the contributions due to dust episodes and to local dust resuspension could not be distinguished either by the PCA or the PMF techniques, so apportionment results could not be clearly explained. Therefore, our analysis was based on 39 samples for Dakar and 36 for Bamako (no dusty cases). Receptor models do not generally provide strict guidelines upon the minimal number of required samples. This is because the number of required samples also depends on the number of analyzed chemical species (source tracers in particular), quality of the data and number of contributing sources **(Chan et al., 2011)**. The PMF model can generally accommodate a minimal data set with a number of samples equal to the number of contributing sources (**e.g., Laupsa et al. (2009)** used ten samples).

In order to identify the optimal number of sources affecting aerosol concentrations and compositions at Bamako and Dakar sites, PCA was first performed using SPSS 15.0 software, then US EPA (Environmental Protection Agency) PMF v3.0 **(US EPA, 2008)** was used. PCA and PMF analyses involved the selection of 27 chemical variables (Al, Be, Ti, V, Mn, Co, Fe, Tl, K, As, Rb, Mg, Na, Ca, Ni, Se, Cr, Cu, Zn, Cd, Sb, BC, OC, Cl^-, SO_4^{2-} and NO_3^-). The basic criterion retained for PCA and PMF was that aerosol concentrations had to be above the detection limit for over 70% of all samples. In this study, the detection limit values were calculated as in **Alleman et al., (2010)**. Usually, data under the detection limit are rejected, but here, due to a limited number of samples, such data were not excluded. In the following, brief indications about PCA and PMF techniques are given, together with specific application to our data set.

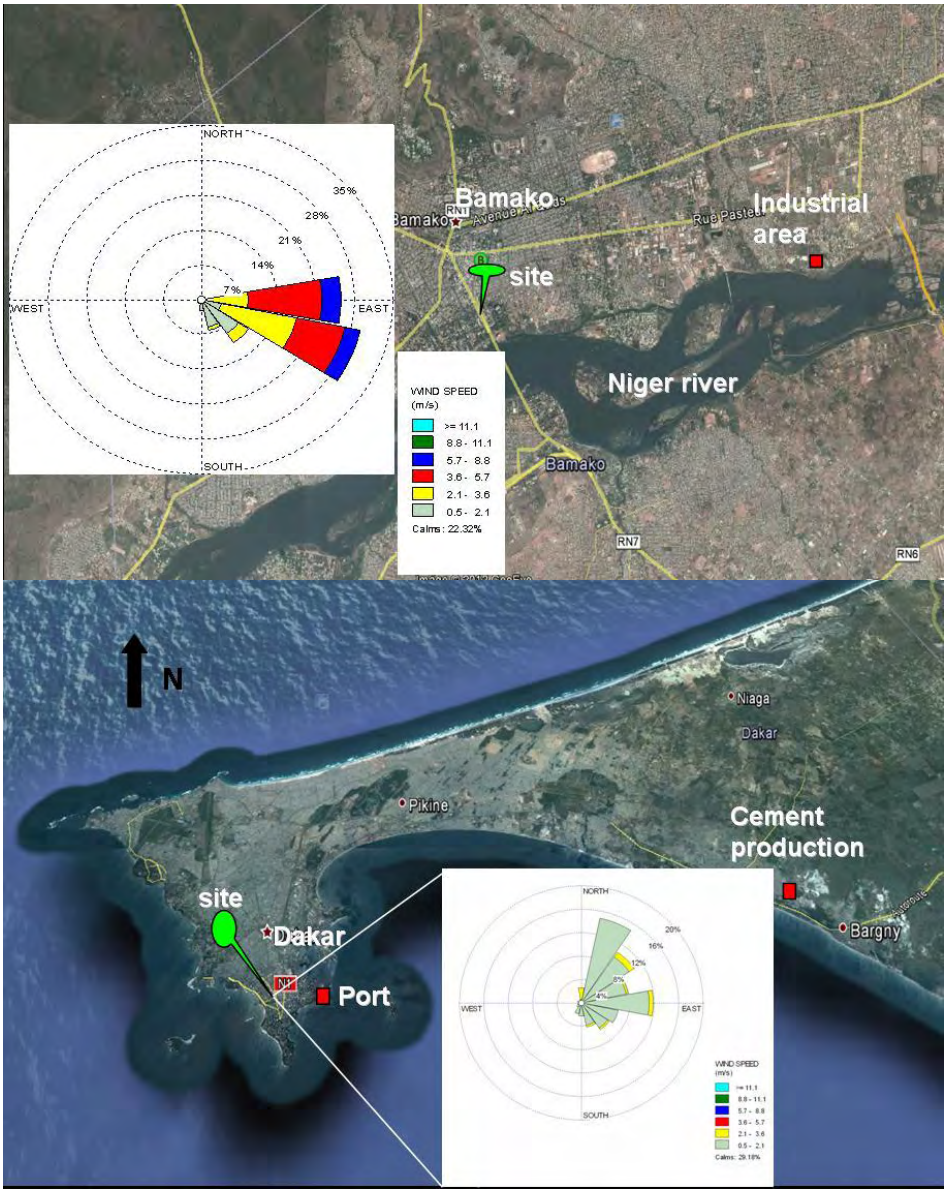

Figure 1: Maps of measurement sites with superimposed wind roses during the two field campaigns.

2.2. Principal component analysis (PCA)

The PCA technique was applied for source identification. One main objective of PCA is to reduce the number of variables to a smaller set of factors retaining maximal information from the original dataset **(Hopke, 1991)**. Due to the high variability of elemental concentrations, the chemical composition data are first transformed into a dimensionless standardized form. Assuming a linear relationship between variables (species concentrations) and a number of p factors (sources), PCA is expressed as:

$$Z_{ij} = \sum_{k=1}^{p} g_{ik} h_{kj}$$

where Z_{ij} is the reduced mass concentration of i th element in j th sample, $k = 1,....., p$ is the number of factors sources, while g_{ik} and h_{kj} respectively are factor loadings of the i th element to the k th component (source) and factor scores of the k th component (source) to the j th sample.

A VARIMAX rotation procedure is used to redistribute variances, so as to provide a more interpretable structure to factors. After rotation, species originating from the same source are linked to the same component with high weights (factor loadings), this component then being associated with this specific source.

The number of factors can be estimated using several methods. The "rule of one" (retained Eigenvalue that indicate the amount of variance explained by each factor greater than 1) and "scree test" usually allow to define the lower and the higher numbers of factors, respectively **(Henry, 2002)**. Here, the "scree test" method was applied to determine the number of factors for Bamako and Dakar datasets. This method looks for an elbow and leveling, large space between values sometimes difficult to determine the number of factors.

2.3. Positive Matrix Factorization (PMF) analysis

PMF 3.0 was used to apportion contributions from emission sources **(USEPA, 2008)**. Principles and usage of this technique are detailed in the US EPA user manual guide and in the literature (not repeated here). PMF uses both measured concentrations and uncertainty estimates to generate calculated chemical profiles and time series associated with each profile. PMF technique involves minimization of an objective cost function Q **(Paatero and Tapper, 1993 ; Paatero and Tapper, 1994 ; Polissar et al., 2001)**, given by:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{e_{ij}^2}{s_{ij}^2}$$

where e_{ij} is the residual associated with i th species concentrations measured in the j th sample, s_{ij} is an uncertainty estimate for i th species measured in the j th sample, n and m are respectively the numbers of samples and of species.

- *Input files*:

As seen earlier, the PMF 3.0 model requires two input files: one for the measured concentrations of species and one for estimated uncertainties. The selection of species to be included in the data matrix depends on the goal of the study and on the quality of available species measurements **(Reff et al., 2007)**. In the concentration file, missing values (denoted by the value of -999) were replaced by the median value of species with assigned uncertainty values four times the standard deviation. Any species, with a percentage of missing data over 70% was excluded from the data set, which is the case for Pb and NH_4^+. PMF requires estimated uncertainties for each species and for each sample in the dataset. Several authors **(Kim and Hopke, 2004 ; Reff et al., 2007 ; Alleman et al., 2010)** have estimated uncertainties in the measurement dataset based on various methods. In this study, uncertainties are calculated using the **Alleman et al. (2010)** methodology. When the measured concentrations are bellow the detection limit (DL), an adjustment is required, usually data below DL are replaced by DL/2, with an uncertainty given by 5 x DL/6 **(Polissar et al., 1998 ; USEPA, 2008)**.

Some authors include particle mass as a variable. Indeed, when the measured sum of chemical species is not close to measured PM, the PM measured mass time series would provide additional information to the PMF model **(Gupta et al., 2012)**. Hence, in such cases, PM mass is included as an explicit species with a large uncertainty, four times the concentrations **(Pekney et al., 2006 ; Bhanuprasad et al., 2008)**. Here, the mean difference between gravimetric particle masses and the sum of measured species were 46% and 36% mass in Bamako and Dakar, respectively. Consequently, particle measured mass is included as a variable.

- *PMF parameters*

Finding in PMF the best number of sources (the so called factors) is subjective, so various methods have been used **(Chueinta et al., 2000 ; Polissar et al., 2001 ; Kim and Hopke, 2004)**. Usually, minimization of the function Q is done through checking possible Q values

are versus various arbitrary numbers of factors. The PMF solution is obtained when Q values are closest to Q_{theory}, this latter being defined as the approximate data points in the matrix dataset (number of samples x number of species) **(Kim and Hopke, 2004 ; Reff et al., 2007)**. Thereafter, the model can be run with a selected maximum number of factors adequately describing the total particle mass concentrations while excluding a number of factors devoid of physical sense, such as duplicate factors or factors with unrealistic compositions or contributions. However, preliminary knowledge of possible sources in the area is crucial, since providing an answer when sources do not show clear separation.

After identifying the adequate number of factors (sources), the next step is to determine the optimal PMF solution. Because of the potential rotational ambiguity, PMF was run with different F_{peak} values to determine the range within which function Q (F_{peak}) remains low and relatively constant **(Paatero et al., 2002)**. F_{peak} parameter permits to examine how the rotation or linear transformation work on the solutions. More details on this parameter can be found in the PMF user guide. The optimal solution should lie in this F_{peak} range **(Alleman et al., 2010)**. Before using F_{peak}, the user should perform multiple base runs with no rotational forcing and choose one run as a starting point. Using this base-case run, the user should use several values of F_{peak} to evaluate different rotations. Note that, the F_{peak} parameter, not always required **(USEPA, 2008)**, allows to check the best rotation giving an adequate solution. In most studies **(Paatero et al., 2002 ; Gupta et al., 2012)**, model results were evaluated by checking multiple solutions within the range of F_{peak} values that yield an acceptable Q value.

3. Results and discussion

3.1. Species concentrations

Average mass concentrations for 28 species, including TSP, PM_{10} and $PM_{2.5}$ mass concentrations in Bamako and Dakar are given in ***Table 1***. Extensive description of aerosol chemical compositions at these two sites was given in **Doumbia et al. (2012b)**. Briefly, elemental concentrations widely vary between Bamako and Dakar sampling sites. Observed values are generally higher than generally reported in the literature, still highlighting quite high pollution levels for West African populations, notably, due to any regulation on air quality. OC, mainly emitted from burning sources such are coal combustion, biomass burning, and two-wheel vehicles emissions with gasoline and oil, or heterogeneous processes by

photochemical reactions, was the highest contributor (82.4-102.4 µg.m^{-3}, 15-37%) to TSP, PM_{10} and $PM_{2.5}$ in Bamako. While in Dakar, these contributions vary between 34.9 and 69.2 µg.m^{-3} (22-26%). Note that BC to OC ratio is relatively higher in Dakar (0.29-0.47) than in Bamako (0.23-0.26), suggesting probably more incomplete combustion emission in Bamako than in Dakar. Inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, K^+, Na^+, Ca^{2+} and Mg^{2+}) together contributed 15.7-24.1 µg.m^{-3}, or 3-6% of TSP, PM_{10} and $PM_{2.5}$ in Bamako. In Dakar however, this contribution is more important (21.5-38.9 µg.m^{-3}, 13-25%). These secondary products are primarily derived from the gaseous precursors SO_2 and NO_x and marine aerosol. Metal concentrations represent less than 12% (with concentrations between 34.3 and 46.3 µg.m^{-3}) in Bamako and only about 7% (8.4-20.2 µg.m^{-3}) in Dakar. ***Table 1*** also shows that 24-h mean European Union values of 50 µg.m^{-3} for PM_{10} mass and 25 µg.m^{-3} for $PM_{2.5}$ mass are largely exceeded both in Bamako and Dakar.

Table 1: Average 24-h concentrations for TSP, PM_{10}, $PM_{2.5}$ and associated elemental compositions in Bamako and Dakar. BC, OC and TC are determined by TOR method.

	Bamako			Dakar		
Species (µg.m^{-3})	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$
Mass PM	705.3 ± 99.3	503.6 ± 112.4	276.8 ± 94.7	274.9 ± 27.43	155.9 ± 15.7	138.2 ± 12.7
Cl^-	3.43	3.36	2.12	8.45	8.13	1.77
NO_3^-	1.87	1.87	1.18	2.06	2.31	0.97
SO_4^{2-}	4.44	4.29	2.98	6.18	7.49	4.75
Na^+	2.21	1.70	1.02	5.1	5.04	1.21
K^+	3.5	3.17	2.02	0.99	0.99	0.59
Mg^{2+}	0.87	0.75	0.49	0.72	0.71	0.28
Ca^{2+}	7.14	7.09	5.29	12.17	13.65	11.43
Inorganic ions	24.06	22.99	15.69	36.09	38.95	21.50
BC	23.34	18.85	27.11	20.14	16.41	15.88
OC	102.4	82.38	102.4	69.19	34.92	35.83
TC	125.74	101.23	129.51	89.33	51.33	51.71
Al	21.23	22.24	17.98	9.66	7.07	4.11
Fe	21.91	20.41	14.28	9.00	5.54	3.49
Ti	2.35	2.14	1.47	0.89	0.54	0.34
Mn	0.35	0.32	0.22	0.15	0.11	0.06
Zn	0.18	0.15	0.12	0.21	0.16	0.11
Cr	0.10	0.09	0.06	0.04	0.02	0.02
V	0.06	0.05	0.04	0.07	0.07	0.05
Cu	0.03	0.04	0.02	0.08	0.19	0.13
Ni	0.02	0.02	0.03	0.03	0.03	0.03
Pb	0.02	0.02	0.04	0.03	0.03	0.02
Rb	0.02	0.02	0.015	0.009	0.007	0.004
Co	0.009	0.008	0.005	0.004	0.002	0.0016
Sb	0.004	0.005	0.004	0.005	0.0044	0.0028
As	0.005	0.0045	0.003	0.003	0.0020	0.0014
Be	0.0008	0.0008	0.0005	0.0003	0.0002	0.0001
Cd	0.0007	0.0007	0.0008	0.0007	0.0006	0.0004
Se	0.0003	0.0003	0.0002	0.0007	0.0008	0.0005
Tl	0.0003	0.0003	0.0002	0.00005	0.00005	0.00003
Metals	46.29	45.53	34.29	20.18	13.78	8.38

3.2. Source identification

- PCA technique was used to primarily identify the number of sources and elemental associations.

- PMF is used for source apportionment through resolving the mixture of sources contributing to PM samples.

- Enrichment factor (EF) calculations were employed as a tool for interpretation of tracer selection in each source category especially for trace element contributions. Note that calcium, sodium, potassium, magnesium and chloride were included in their ionic forms, their elemental forms (obtained by microwave assisted digestion coupled to ICP-MS) being excluded to avoid double mass counting **(Reff et al., 2007 ; Gupta et al., 2012)**. The number of species used in PCA and PMF analysis amounts to 28, including particulate mass concentrations. This choice depends on the quality of available species measurements. The number of valid samples at Bamako and Dakar were 36 and 39, respectively.

3.2.1. Enrichment factor calculations

Enrichment factors (EF) of atmospheric elements were calculated using average PM concentrations for each measured element and the average upper-crust geological concentrations reported by **McLennan (2001)**. For element X in an aerosol sample, its EF relative to a reference element (E_{ref}) of the upper crust is:

$$EF = \frac{\left(\frac{X}{E_{ref}}\right)_{aerosol}}{\left(\frac{X}{E_{ref}}\right)_{crust}}$$

where X and E_{ref} respectively refer to the concentration (in ppb) of element X and the reference element. Many elements (Al, Ti, Si, Fe, Mn, Sr), mostly of soil origin are used as references **(Eltayeb et al., 2001 ; Dongarrà et al., 2007 ; Weinstein et al., 2010)**.

The results obtained for Bamako and Dakar are reported in ***Figures 2 and 3***, respectively. EF interpretations widely vary according to authors, due to the uncertainties associated with reference elements. In this study, EF calculations are made using different elements as references for comparison. Using Al, Fe or Ti as crustal references gives similar EF as shown in ***Figures 2 and 3***. A classification of sources depending on EF **(Alleman et al., 2010)** was adopted here. EF values less than 5 (Al, Co, Cr, Fe, K, Mg, Mn, Na, Rb, Ti, Be and Tl), regardless the reference element, were considered of natural origins, while elements with EF above 50 (Sb, Cd, Cu) were assumed of anthropogenic origins. Intermediate EF values could be affected both by natural and anthropogenic emissions (As, Ca, Ni, V, Zn).

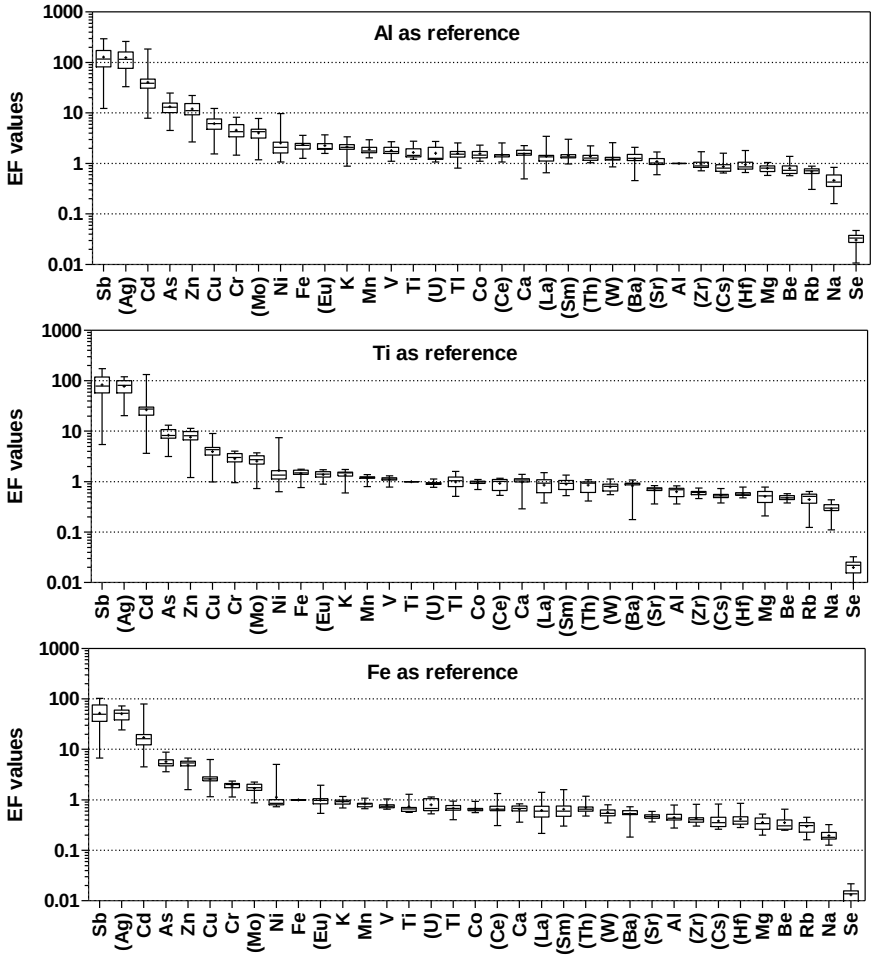

Figure 2: EF values calculated for PM using different reference elements in Bamako. Elements in parentheses are not discussed in this work, only given for information.

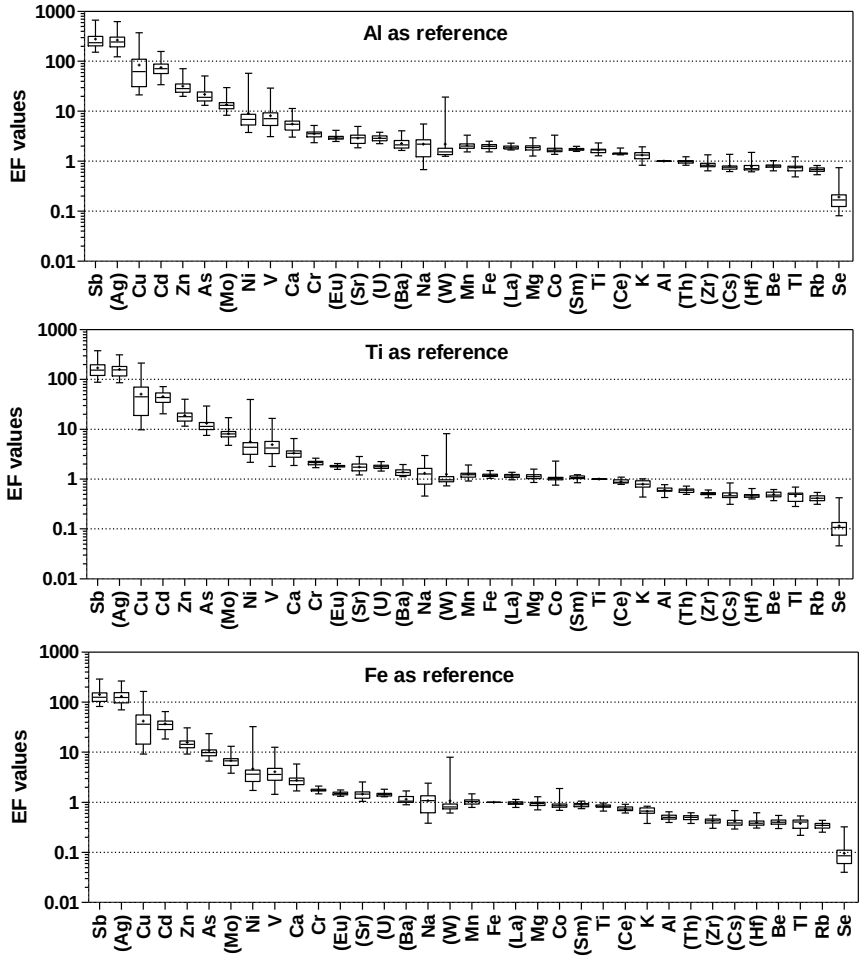

Figure 3: EF values calculated for PM using different reference elements in Dakar. Elements in parentheses are not discussed in this work, only given for information.

3.2.2. PCA

As previously seen, determination of the number of factors (i.e. sources) in PCA can be made using different methods. In this study, the scree test method associated with our general knowledge about sampling sites was applied to Bamako and Dakar samples to resolve the number of factors. Respectively, 5 and 6 factors were extracted, as reported in ***Table 2***. The VARIMAX rotated factor loading matrices for Bamako and Dakar and for the overall data set are displayed in ***Table 2.*** For the sake of interpretation, same categorization of factor loadings from **Nyanganyura et al., (2007)** is used here. Factor loadings with absolute values below 0.300 were considered as low, as moderate between 0.300 to 0.600, as moderately high when greater than 0.600 but smaller than 0.800 and finally, as high loadings for values above 0.800.

Table 2: VARIMAX rotated PCA factor loadings for PM collected at Bamako and Dakar (only those with values ≥ 0.600 are highlighted in bold characters, moderate factors (0.300-0.600) being underlined).

	Bamako						Dakar					
	F1	F2	F3	F4	F5		F1	F2	F3	F4	F5	F6
PM	**.684**	-.239	-.435	.086	-.391	PM	**.882**	.060	.046	-.132	-.355	-.056
Al	**.939**	.087	.058	-.152	.156	Al	**.938**	.190	.122	.054	.010	.149
As	**.746**	.365	.399	-.044	-.092	As	.526	.253	.304	-.237	-.057	**.619**
Be	**.963**	.129	-.122	-.112	.111	Be	**.938**	.124	.208	.083	.064	.144
Ca^{2+}	.521	**.690**	.050	-.333	.220	Ca^{2+}	.187	.103	**.888**	.153	-.009	.234
Cd	-.031	.078	**.698**	.088	.168	Cd	**.699**	.220	.584	-.044	.058	.008
Co	**.952**	.279	.041	-.020	.039	Co	**.920**	.163	.130	-.043	.290	.104
Cr	.589	.544	.479	.231	-.062	Cr	**.861**	.228	.052	-.137	.356	.082
Cu	.392	.524	.562	.130	-.035	Cu	-.106	.201	.255	**.815**	-.123	-.169
Fe	**.893**	.390	.187	.056	.020	Fe	**.932**	.274	.100	-.068	.010	.169
K^+	.049	**.889**	.299	.304	-.039	K^+	.499	.541	.595	.017	-.056	-.185
Mg	.226	**.917**	.195	.207	-.052	Mg	.288	**.931**	.131	.115	-.041	.070
Mn	**.963**	.238	.020	-.030	.062	Mn	**.910**	.292	.217	-.082	.031	.013
Na^{2+}	.334	**.905**	.117	.054	-.043	Na^{2+}	.248	**.949**	.134	.083	-.015	.050
Ni	.415	.054	.065	.145	**.812**	Ni	.179	-.068	.033	.034	**.944**	.002
Rb	**.661**	.285	.532	-.138	.210	Rb	**.937**	.223	.184	.038	-.050	.009
Sb	-.006	.251	**.854**	.216	-.144	Sb	**.633**	.344	.113	.443	.000	.063
Se	**.651**	.364	.501	.165	.129	Se	.330	.432	.115	**.625**	.258	.351
Ti	**.975**	.137	-.080	-.051	.080	Ti	**.950**	.203	.106	-.019	.033	.145
Tl	**.866**	.207	.316	.033	.163	Tl	**.895**	.118	.265	.196	.091	-.032
V	**.955**	.265	.078	-.021	.065	V	.572	.223	.267	.529	.229	.014
Zn	.264	.596	**.611**	.346	-.121	Zn	**.797**	.235	.293	.103	.294	.025
BC	-.184	.138	.120	**.878**	.168	BC	.504	.124	.475	-.577	.003	-.037
OC	-.039	.179	.257	**.901**	-.032	OC	**.722**	.194	.065	-.552	-.144	-.015
Cl^-	.161	**.877**	.344	.181	.038	Cl^-	.263	**.947**	.114	.053	-.029	.026
NO_3^-	.218	**.907**	.053	-.005	.139	NO_3^-	.174	**.658**	.369	.282	.140	.461
SO_4^{2-}	.501	**.836**	.103	-.076	.102	SO_4^{2-}	.274	.441	**.704**	.370	.187	.025

3.2.3. Application of PMF

To identify the adequate number of factors in each dataset, 20 random test runs were made, the one given the minimum estimated Q value being retained **(Paatero et al., 2002 ; USEPA, 2008)**. These tests were repeated for a number of factors between 3 and 12. Change of Q with the number of factors (***Figure 4***) show a reduction in Q when this number increases, with also the result that the eventual solutions were lead to agreement between estimated Q with its theoretical value (Q_{theory}). Solutions with factors 4, 5 and 6 for Bamako and factors 5, 6 and 7 for Dakar were carefully examined. Theoretically, Q_{theory} values (number of samples x number of species) for Bamako and Dakar were 980 and 1092, respectively. Q values for

factor numbers of 5 and 6, respectively for Bamako and Dakar are close to Q_{theory}, as shown in ***Figure 4***. Several studies report differences between Q and Q_{theory} values in the 1.5-3.5 range **(Polissar et al., 1998 ; Kim and Hopke, 2004)**. After extraction of factor numbers, many PMF solutions are possible, the F_{peak} parameter then helping to decide if the choice is optimal. No theoretical basis is available as for the choose of F_{peak}. However, it is important to examine the rotation of the original solution using different F_{peak} values (***Figure 5***). Minimized Q values for Bamako and Dakar were selected to be 728 and 1315, respectively, corresponding to F_{peak} values of 0.1 both in Bamako and Dakar.

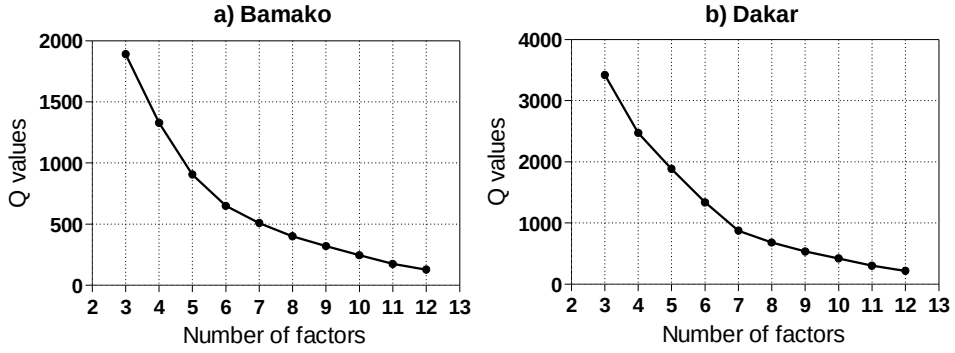

Figure 4: Plot of Q as a function of the number of factors for the PM data set in Bamako (a) and Dakar (b).

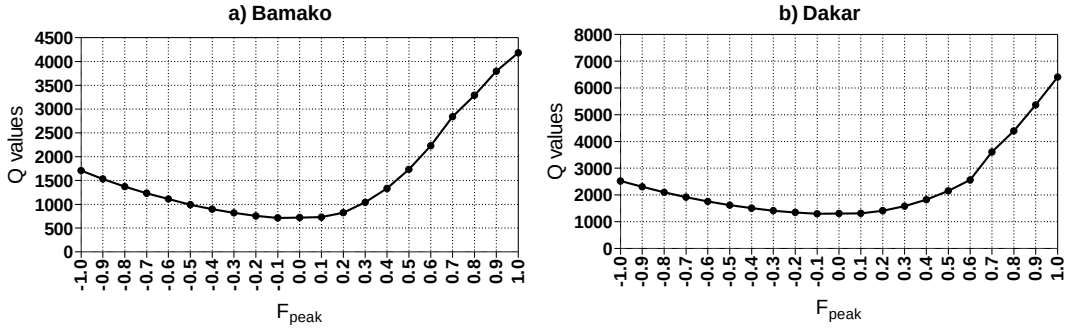

Figure 5: Plot of Q as a function of F_{peak} for the PM data set from Bamako (a) and Dakar (b).

3.2.4. Description of sources

3.2.4.1. Bamako

The optimal number of factors selected was 5. PCA results have shown that 5 factors were able to explain 90.8% of the total variance in the Bamako dataset, the first factor alone (F1)

explaining 56.7% of such variance against 3.4% for the last factor (F5). From PMF output, the comparison of reconstructed daily mean PM concentrations from all sources with measured PM concentrations shows that the identified factors effectively reproduce measured masses. The performance of PMF model was evaluated, with ***Table 3*** comparing the calculated values with measured concentrations for each species. The largest uncertainties such as 15% for Ni, 16% for BC and 14% for OC together with low correlation coefficients, can be imputed to data quality, since BC and OC missing values were replaced by their median values and associated uncertainties assigned to be four times the mean values. However, in general, good correlation coefficient was obtained between measured and calculated concentrations with significant correlation coefficients.

Table 3: Comparison between measured and PMF calculated concentrations (in ng.m^{-3}) except for PM (in µg.m^{-3}) in Bamako for studied chemical species.

Species	Measured	PMF modeled	r^2	Uncertainty
PM (µg.m^{-3})	430.01	380.67	0.25	11
OC	98295	84466	0.44	14
BC	24600	20765	0.35	16
Al	15457	15280	0.96	1
Fe	15423	15438	0.99	0
Ca^{2+}	5774	5775	0.98	0
SO_4^{2-}	3103	3078	0.97	1
K^+	2952	2934	0.99	1
Cl^-	2953	2902	0.94	2
NO_3^-	1649	1646	0.93	0
Na^+	1541	1542	0.99	0
Ti	1368	1335	1.00	2
Mg^{2+}	672	674	0.99	0
Mn	229	227	0.99	1
Zn	144	142	0.90	1
Cr	73	72	0.97	1
V	38	38	1.00	1
Cu	30	29	0.79	3
Ni	21	18	0.23	15
Rb	15	14	0.94	1
Co	6	6	0.99	1
Sb	4	4	0.67	3
As	3	3	0.85	3
Cd	1	1	0.26	1
Be	0.5	0.5	0.99	4
Se	0.3	0.3	0.94	0
Tl	0.2	0.2	0.92	4

Factor 1 was dominated by Al (52%), Be (70%), Fe (46%), Ti (75%), Mn (61%), V (57%) and Co (59%) in PMF outputs (***Figure 6***), most of them displaying high factor loadings in

PCA results (***Table 2***). This factor explains most of the variance (57%) in PCA results, most of these elements being considered as crustal tracer element **(Watson and Chow, 2001 ; Almeida et al., 2005)**. As expected, these elements display enrichment factors (EF) close to unity, whether Al, Fe or Ti being the crustal reference elements (***Figure 2***). Note that Tl, Ni, As and Cr show moderate factor loadings in PCA, against relatively high contributions in PMF (from 29% to 42% of total masses). Moreover, observed EF for Ni, As and Cr display relatively extended ranges (***Figure 2***), denoting their predominant anthropogenic origin. This suggests possible mixing of natural dust and anthropogenic sources in this factor. At Bamako site, this source likely results from resuspended unpaved road dust, dust from the Saharan desert becoming largely predominant in PM concentrations during dust storms.

Factor 2 shows higher factor loadings for Mg^{2+} (0.914), NO_3^- (0.908), Na^+ (0.905), K^+ (0.883), Cl^- (0.872) and SO_4^{2-} (0.834), in PCA results (***Table 2***). PMF outputs also denote high contributions of these elements in this factor (48% of Mg^{2+}, 38% of NO_3^-, 70% of Na^+, 44% of K^+, 45% of Cl^-, and 55% of SO_4^{2-}) (***Figure 6***). Mg^{2+}, Na^+ and Cl^- are generally associated with marine sources, though even if far from obvious in Bamako. In addition, examination of back trajectories and wind directions have not shown marine air mass impacting the Bamako site (not shown here). To assess this assumption, Na and K to Mg mass ratios were calculated and compared to typical values for sea water. Mass ratio of Na/Mg in this factor is 3.3, which is low compared to 8.4 in sea water **(Millero et al., 2008)**. Calculated K to Mg ratio in this factor is 4.1, higher than ones measured in sea water (0.31) **(Millero et al., 2008)**. However, Bamako site is very close to the Niger River (***Figure 1***) and obtained Na/Mg ratio is comparable to measured values in the Niger River water by **Camail et al. (1987)** and **Picouet (1999)**. All these comparisons let appear a possible contribution of various sources in this factor. This factor can be categorized as inorganic salts. Inorganic salts are locally present in Bamako environment, due to their presence in soils near the river **(Gillies et al., 1996)** and in rock salt quarries in northern Mali. In addition, chemical processes in dust well present in Mali (see previous paragraph) may lead to inorganic salts, since Bamako is located within a basin with observed low wind speeds and associated high temperatures favoring gas-to-particle conversion mechanisms **(Seinfeld and Pandis, 2006)** during the field campaigns.

Factor 3 was dominated by Cd (50%), Cu (50%), Sb (82%) and Zn (62%) in PMF (***Figure 6***), with also relatively high factor loadings for these elements in PCA (***Table 2***). Reported large

EF values (***Figure 2***) support the anthropogenic origin of these elements **(Alleman et al., 2010)**. This factor is identified as related to tire and brake wear, due to the enrichment in Zn, Cu and Sb **(Bukowiecki et al., 2010 ; Amato et al., 2011)** in both PCA and PMF results. High Cd and Sb contributions and relatively high contributions of As, Rb and Cr (range 37-38%) can be explained by mixture of other unclear sources in this factor. For example, Cr emissions from combustion oil and coal for power generation and refuse incineration are generally well established **(Weinstein et al., 2010)**. All such point sources were present near the site, with open waste burning occurring in Bamako practically all evenings.

Factor 4 shows high factor loadings (0.874-0.897) in PCA and high contributions (79-83%) in PMF, both for OC and BC, presumably in connection with combustion emissions **(Zheng et al., 2005)**. Several authors **(Guinot et al., 2007 ; Sandradewi et al., 2008 ; Pio et al., 2011)** have reported OC/BC mass concentration ratios of 1.1 for traffic emissions, 3.3 for secondary organic carbon formation, 6.6 for biofuel combustion and 12 for long range transport. For this factor, a OC/BC ratio of 4.3 is obtained, denoting probable mixtures of various combustion sources, including two-wheel two-stroke emissions (oil and gasoline) and domestic fires. Moderate factor loadings in PCA results (K^+ and Zn) and relative K^+ high contribution (38%), Mg^{2+} (32%) and Se (37%) in PMF could be due to additional, yet unclear for Mg^{2+} and Se, sources. Indeed, the presence of K^+ for this factor in both PCA and PMF, supports wood combustion **(Chow et al., 1993 ; Watson and Chow, 2001)** as a contributing source.

Factor 5 was characterized by large amounts of Ni and Rb (factor loadings of 0.761 and 0.406, respectively) in PCA results (***Table 2***) and relative high contributions to total aerosol masses from this source, about 62% for Ca^{2+} and 49% for Rb in PMF (***Figure 6***). Note that Ca^{2+} with higher contribution in PMF, is a tracer typical of the building sector including cement production, and crustal species or both **(Watson et al., 2004)**. This parameter permits us to conclude that this factor is probably related to resuspended road dust. BC is the third most abundant element in this factor, representing 20% of total BC. Similar values were obtained by **Watson and al. (2004)** for traffic source characterization using CMB, with abundances of 18 ± 5%. Moreover, Ni is a good indicator for residual oil combustion **(Chow and Watson, 2002)**. This source, highlighted in Bamako, seems to be linked to use of mixed bad quality oil and gasoline fuels for two-stroke engines.

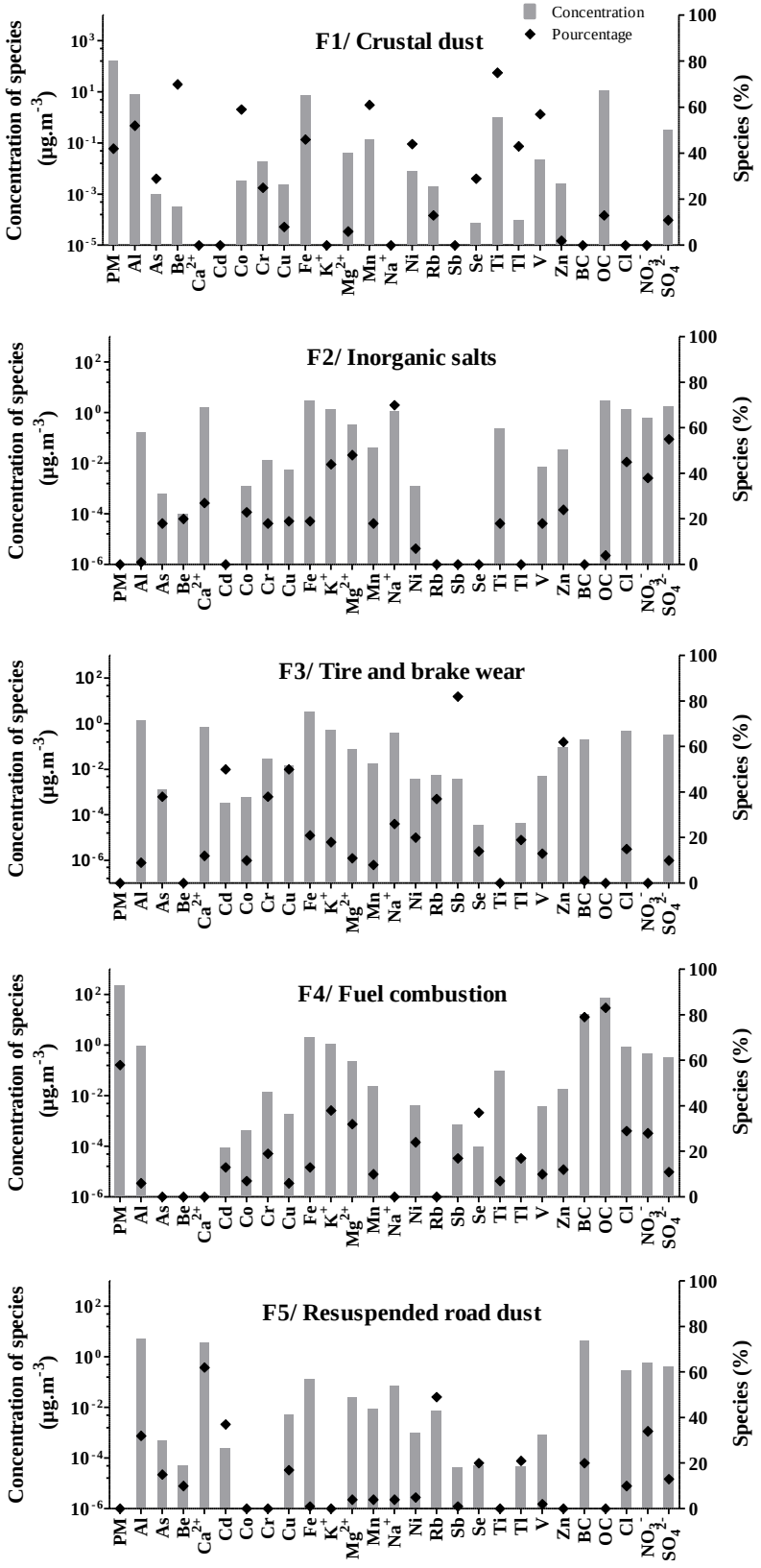

Figure 6: PM source profiles resolved from PMF (µg.m^{-3}) and species contributions (in %) for each source in Bamako.

3.2.4.2. Dakar:

In PCA results, 6 factors can explain 91.9% of total variance in the Dakar dataset, the first factor (F1) alone explaining 58.6% of the variance against 3.5% for the F6 factor. An optimal factor number of 6 also appeared in PMF. Comparison between daily mean reconstructed PM concentrations from all sources with measured PM concentrations shows that the identified factors effectively reproduce measured masses. ***Table 4*** shows the measured concentrations as compared to calculated ones in Dakar for every species. Uncertainties are generally low, the highest one being 10% for PM, as a result of the assumption including PM as a variable and assigning an uncertainty value 4 times the PM concentration values **(Pekney et al., 2006 ; Bhanuprasad et al., 2008)**. Significant correlation coefficients are also obtained between modeled and measured specie concentrations (***Table 4***).

Table 4: Comparison between measured and PMF calculated concentrations (in ng.m^{-3}) except for PM (in µg.m^{-3}) in Dakar for all chemical species.

Species	Measured	PMF modeled	r^2	Uncertainty
PM (µg.m^{-3})	170.36	189.67	0.82	10
OC	46057	47941	0.96	4
BC	17131	17042	0.70	-1
Ca^{2+}	12038	12189	0.83	1
Al	6934	7142	0.96	3
Cl^-	6074	6190	0.97	2
SO_4^{2-}	6073	6038	0.98	-1
Fe	5975	5979	0.98	0
Na^+	3765	3785	0.98	1
NO_3^-	1662	1683	0.78	1
K^+	829	835	0.92	1
Ti	583	586	0.98	1
Mg^{2+}	549	553	0.99	1
Zn	160	160	0.93	0
Cu	130	129	0.93	0
Mn	105	108	0.96	3
V	62	61	0.86	-2
Ni	26	28	0.78	7
Cr	24	24	0.84	-1
Rb	6	6	0.97	-5
Sb	4	4	0.73	3
Co	3	3	0.95	2
As	2	2	0.70	-5
Cd	1	1	0.85	-2
Se	1	1	0.83	1
Be	0.2	0.2	0.98	0
Tl	0.04	0.05	0.93	4

Factor 1 lets appear a large contribution from Al, Be, Fe and Ti, as demonstrated by high factors loadings in PCA, generally over 0.8 (***Table 2***) and high percentage contributions in PMF outputs, with individual contributions between 59 and 70% (***Figure 7***). These elements are usually considered of natural origin **(Eltayeb et al., 2001 ; Petaloti et al., 2006 ; Weinstein et al., 2010)**. Elements such are Rb, Co, Cr and Mn are highly present in this factor as shown in ***Table 2*** and ***Figure 7***: they are also tracers of natural soils **(Watson and al., 2004)**. This factor also contains elements usually issued from anthropogenic activities (Cd, Sb, Zn, K^+ and OC) **(Watson and al., 2004 ; Allen et al., 2001 ; Alleman et al., 2010)**. Some authors assume that particles from natural and anthropogenic sources form aggregates within the soil before being resuspended **(Sternbeck et al., 2002 ; Thorpe and Harrison, 2008)**. EF calculations (***Figure 3***) show values close to unity for Al, Ti, Be and Ti, confirming their natural origin, while Cd, Sb and Zn display higher EF suggesting anthropogenic sources. This result is coherent with the hypothesis of combined mineral dust and resuspended particles for this source.

Factor 2 was characterized by large amounts of Cl^-, Na^+ and Mg^{2+}, a signature of sea salt, with PCA results displaying high factor loadings for these elements (0.947 for Cl^-, 0.949 for Na^{2+} and 0.931 for Mg^{2+}) (***Table 2***). In addition, 92% of total Cl^-, 87% of total Na^+ and 72% of total Mg^{2+} are present in this factor (***Figure 7***). These three species account for 40%, 24% and 3% of the total mass of this aerosol source respectively, in close agreement with their corresponding percentages in seawater, namely 55%, 30% and 3% **(Goldberg, 1963)**. In order to still confirm the hypothesis of marine origin of these elements, Na^+ and K^+ to Mg^{2+} ratios were investigated. Na/Mg ratio obtained in this factor is 8.3, very close to 8.4 for sea water **(Millero et al., 2008)**. Values of 8.4 and 8.5 are also obtained by **Yuan et al., (2006)** and **Alleman et al., (2010)**, respectively. K/Mg ratio calculated for this factor (0.49) is also of the same order as in sea water (0.31) **(Millero et al., 2008)**. Species such as NO_3^-, SO_4^{2-} and K^+ also contribute to this source, for about 44, 20 and 23%, respectively (***Figure 7***). Marine aerosols are also sources of sulfate **(Watson et al., 2004)** and nitrate may from condensation processes. Both PMF model and PCA results clearly illustrate such conclusions, which are consistent with Dakar being a site surrounded on three sides by the Atlantic Ocean.

Factor 3 shows close associations between Ca^{2+} and SO_4^{2-}, with high factor loadings of 0.888 and 0.704, respectively (***Table 2***), and contributions to this factor for about 77% and 49% of total Ca^{2+} and SO_4^{2-}, respectively (***Figure 7***). Ca^{2+} is a typical tracer of the building sector

(Watson al., 2004), this factor here being probably related to emissions from the cement industry and open limestone quarry close to our Dakar site (about 20 km). There are also additional less contributing sources: EF for Ca calculated on the basis of Al, Ti and Fe varies between 2.8 and 5.6, suggesting a natural origin for Ca, probably a contribution of limestone quarry activities which provide calcium carbonate ($CaCO_3$) and sulfate. SO_4^{2-} in this factor may result also from heterogeneous processes in the presence of resuspended dust.

Factor 4 explains most part of Cu and Se, as shown by high factor loadings (0.888 and 0.625, respectively). PCA results also indicate that this factor contributes to a lesser extent to the observed concentrations of Sb, V, BC and OC, all with moderate factor loadings (***Table 2***). PMF outputs also show that 64% of total BC and 77% of total OC are present in this factor (***Figure 7***). These species are typical tracers of combustions, including road traffic emissions **(Allen et al., 2001 ; Watson et al., 2004)**. To confirm this hypothesis, the OC/BC ratio was calculated for this factor, with a 3.2 value obtained. This value is of the same order as previously reported, namely 2.1 ± 1.0 obtained from 13-stage impactor in Dakar **(Val et al., 2013)**. This value also compares with OC/BC values found for traffic diesel and gasoline emissions in **Sandradewi et al. (2008) ; Pio et al. (2011)**. Such results confirm this factor as being dominated by traffic emissions. In Dakar, more than 60% of public transports are associated with diesel old vehicles.

Factor 5 is characterized by high Ni loading, against moderate loadings for Cr, Se, and V (***Table 2***). PMF shows that 63% of total Ni and 57% of total V are present in this factor, while moderate contributions are observed for Se, NO_3^- and SO_4^{2-} (***Figure 7***). Oil combustion is expected to be the most important source for Ni and V **(Pacyna and Pacyna, 2001 ; Watson and al., 2004)**. Dakar is one of the major ports in West Africa, close to our sampling site (located around 2 km) (***Figure 1***). Therefore, this factor is probably connected with port activities.

Factor 6 displays significant loading for As, only moderate for Se and NO_3^- (***Table 2***). However, high Cu levels are retrieved in PMF (71% of total Cu), with associated consistent contributions of As and Sb (***Figure 7***). An anthropogenic origin is expected for these elements due to high observed EF values (***Figure 3***). Cu and Sb are elements widely used constituents of brake linings **(Bukowiecki et al., 2010 ; Amato et al., 2011)** and thus this factor can be attributed to brake wear source. Note that, PCA and PMF differently characterize this factor,

suggesting multiple contributions from other minor sources such are car repair garages activities, since our measurement site is close to the two biggest car parks in Dakar.

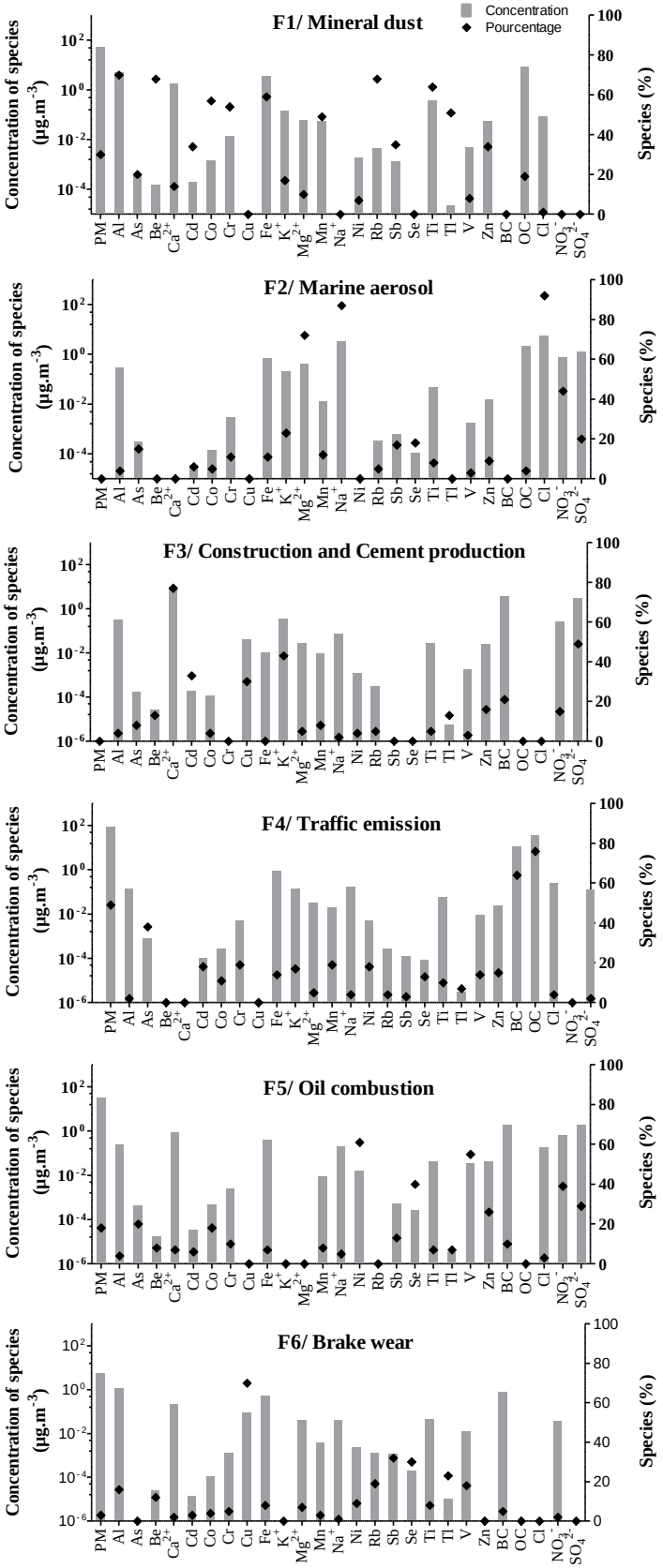

Figure 7: PM source profiles resolved from PMF (µg.m^{-3}) and species contributions (in %) for each source in Dakar.

3.2.5. Source apportionment

Estimated TSP, PM_{10} and $PM_{2.5}$ source contributions based on PMF in both Bamako and Dakar are displayed in ***Figure 8***. Error bars were the standard deviation of concentrations calculated in each factor. Fuel combustion, including vehicle, two-wheel two-stroke and wood burning emissions, is a major source in Bamako, accounting for 51% (94.4 $\mu g.m^{-3}$), 28% (44.7 $\mu g.m^{-3}$) and 70% (123.5 $\mu g.m^{-3}$) of TSP, PM_{10} and $PM_{2.5}$, respectively. This is related to the high proportion of the population using such vehicles and to fuel combustion for domestic energy. The second large contributor is crustal dust with contribution to TSP, PM_{10} and $PM_{2.5}$ ranged from 11 to 20% (20.5–32.9 $\mu g.m^{-3}$). Resuspended road dust contributed 8% (15.3 $\mu g.m^{-3}$), 29% (47.5 $\mu g.m^{-3}$) and 16% (27.8 $\mu g.m^{-3}$) for TSP, PM_{10} and $PM_{2.5}$, respectively. Two other sources were identified: one for inorganic salts contributing 3-9% (5.2–17.2 $\mu g.m^{-3}$) range to TSP, PM_{10} and $PM_{2.5}$ mass and a source linked to tire and brake wear with account for 5-13% (3.7–21.0 $\mu g.m^{-3}$). Finally, non resolved mass represent between 1% (1.3 $\mu g.m^{-3}$) and 12% (22.3 $\mu g.m^{-3}$) in Bamako (***Figure 8a***).

Traffic emission together with brake wear sources are most important in Dakar accounting for 43-46% (62.7–37.6 $\mu g.m^{-3}$) of the total TSP, PM_{10} and $PM_{2.5}$. Mineral dust contributes for 23% (33.4 $\mu g.m^{-3}$), 14% (14.7 $\mu g.m^{-3}$) and 13% (10.8 $\mu g.m^{-3}$) of TSP, PM_{10} and $PM_{2.5}$ respectively, while the building sector with cement production 13% (18.4 $\mu g.m^{-3}$), 15% (18.8 $\mu g.m^{-3}$) and 18% (14.8 $\mu g.m^{-3}$). The contribution of marine aerosol to PM mass range from about 15% (22.3 $\mu g.m^{-3}$) of TSP to 21% (21.6 $\mu g.m^{-3}$) of $PM_{2.5}$. The contribution of oil combustion source to TSP, PM_{10} and $PM_{2.5}$ at Bamako was about 4-5% (3.1–6.7 $\mu g.m^{-3}$). Finally, non resolved mass is ranged from 1 to 3% in Dakar (***Figure 8b***).

These results confirm that both in Bamako and Dakar, human activities (for range 67-81% and 61-68%, respectively) are the main emission sources determining high pollution levels in West Africa.

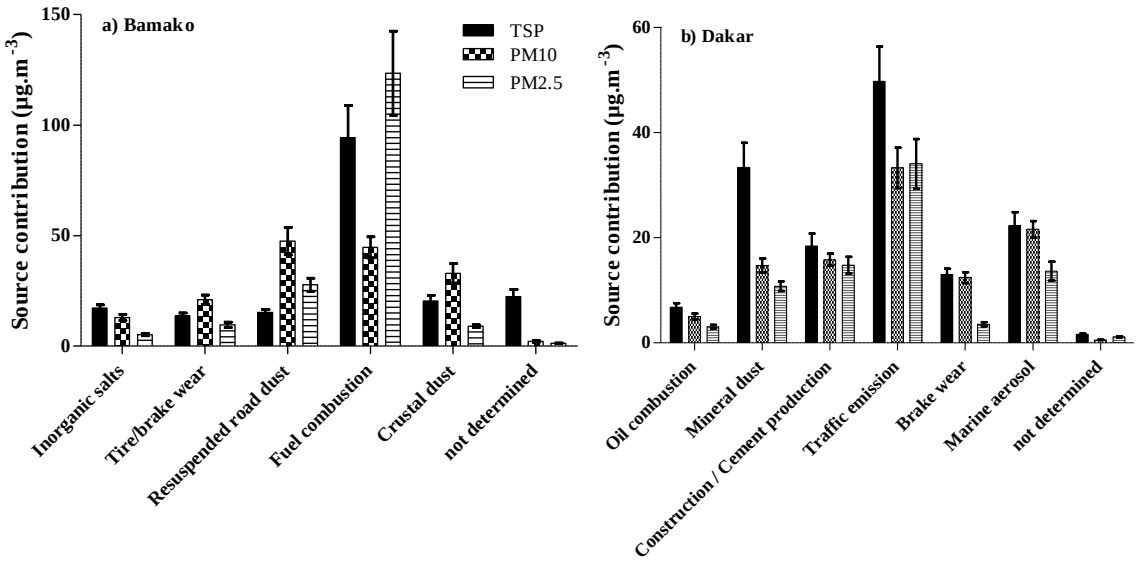

Figure 8: TSP, PM_{10} and $PM_{2.5}$ source contributions estimated by PMF in a) Bamako and b) Dakar.

4. Conclusions

Atmospheric aerosol sources determination was conducted at two urban traffic sites in West Africa, Bamako and Dakar. The complex mixture of particles from aerosol sources in this region constitutes a serious problem of individual identification.

In this study, a PMF receptor model calculation, in association with PCA and EF analyses was applied to the speciated PM data set collected during POLCA experiments at two sites in West Africa. Five and six main sources have respectively been identified for Bamako and Dakar. Bamako site shows contributions of sources to TSP, PM_{10} and $PM_{2.5}$ mass such as fuel combustion by two-wheel two-stroke vehicle and domestic fires (28-70%), crustal dust (5-20%), resuspended road dust (8-29%), tire/brake wear (5-13%) and inorganic salts (3-9%) within PM particles, against traffic emissions (32-42%), mineral dust (13-23%), construction and cement production (13-18%), marine aerosol (15-21%), oil combustion (4-5%) and brake wear (4-12%) in Dakar. Anthropogenic PM sources are expected to dominate both at Bamako and Dakar sites, respectively, with relative contributions range of 67-81% and 61-68%

Both PCA and PMF clearly depict the major sources in Bamako and Dakar, in spite of uncertainties, mainly due to limited numbers of samples. Note the difficulties of PMF to separate vehicles and two-stroke from domestic fire emissions in Bamako (i.e. factor 4 called fuel combustion), indicating that other methods are necessary to well apportion these sources. Finally, long-term monitoring is still required to further improve our knowledge of PM

sources, since PM pollution in West Africa, seasonally-variable and rather poorly documented, is a serious problem for human health and climate change.

References (A3)

Alleman, L.Y., Lamaison, L., Perdrix, E., Robache, A., Galloo, J.-C., 2010. PM_{10} metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. Atmospheric Research 96, 612–625.

Allen, J.O., Mayo, P.R., Hughes, L.S., Salmon, L.G., Cass, G.R., 2001. Emissions of size-segregated aerosols from on-road vehicles in the Caldecott tunnel. Environ. Sci. Technol. 35, 4189–4197.

Almeida, S.M., Pio, C.A., Freitas, M.C., Reis, M.A., Trancoso, M.A., 2005. Source apportionment of fine and coarse particulate matter in a sub-urban area at the Western European Coast. Atmospheric Environment 39, 3127–3138.

Amato, F., Pandolfi, M., Moreno, T., Furger, M., Pey, J., Alastuey, A., Bukowiecki, N., Prevot, A.S.H., Baltensperger, U., Querol, X., 2011. Sources and variability of inhalable road dust particles in three European cities. Atmospheric Environment 45, 6777–6787.

Arku, R.E., Vallarino, J., Dionisio, K.L., Willis, R., Choi, H., Wilson, J.G., Hemphill, C., Agyei-Mensah, S., Spengler, J.D., Ezzati, M., 2008. Characterizing air pollution in two low-income neighborhoods in Accra, Ghana. Science of The Total Environment 402, 217–231.

Assamoi, E.-M., Liousse, C., 2010. A new inventory for two-wheel vehicle emissions in West Africa for 2002. Atmospheric Environment 44, 3985–3996.

Asubiojo, O.I., Obioh, I.B., Oluyemi, E.A., Oluwole, A.F., Spyrou, N.M., Farooqi, A.S., Arshed, W., Akanle, O.A., 1993. Elemental characterization of airborne particulates at two Nigerian locations during the Harmattan season. Journal of Radioanalytical and Nuclear Chemistry Articles 167, 283 – 293.

Bertrand, J., Baudet, J., Drochon, A., 1974. Importance des aérosols naturels en Afrique de l'Ouest. Journal de Recherhce Atmosphérique 8, 845–860.

Bhanuprasad, S.G., Venkataraman, C., Bhushan, M., 2008. Positive matrix factorization and trajectory modelling for source identification: A new look at Indian Ocean Experiment ship observations. Atmospheric Environment 42, 4836–4852.

Bukowiecki, N., Lienemann, P., Hill, M., Furger, M., Richard, A., Amato, F., Prévôt, A.S.H., Baltensperger, U., Buchmann, B., Gehrig, R., 2010. PM_{10} emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland. Atmospheric Environment 44, 2330–2340.

Cachier, H., Brémond, M.P., Buat-Ménard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. Tellus Series B-Chemical and Physical Meteorology 41(B), 379–390.

Callén, M.S., de la Cruz, M.T., López, J.M., Navarro, M.V., Mastral, A.M., 2009. Comparison of receptor models for source apportionment of the PM10 in Zaragoza (Spain). Chemosphere 76, 1120–1129.

Camail, M., Mahamane, M., Pucci, B., Rigaud, J.P., 1987. Analyses chimiques des eaux du fleuve Niger à Niamey: Premiers résultats d'une campagne annuelle de mesures. Hydrol. continent 2, 87–99.

Celo, V., Dabek-Zlotorzynska, E., Mathieu, D., Okonskaia, I., 2010. Validation of simple microwave-assisted acid digestion method using microvessels for analysis of trace elements in atmospheric $PM_{2.5}$ in monitoring and fingerprinting studies. The Open Chemical & Biomedical Methods Journal 3, 141–150.

Chan, Y., Hawas, O., Hawker, D., Vowles, P., Cohen, D.D., Stelcer, E., Simpson, R., Golding, G., Christensen, E., 2011. Using multiple type composition data and wind data in PMF analysis to apportion and locate sources of air pollutants. Atmospheric Environment 45, 439–449.

Chow, J.C., Watson, J.G., 2002. Review of $PM_{2.5}$ and PM_{10} Apportionment for Fossil Fuel Combustion and Other Sources by the Chemical Mass Balance Receptor Model. Energy Fuels 16, 222–260.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The dri thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies. Atmospheric Environment. Part A. General Topics 27, 1185–1201.

Chueinta, W., Hopke, P.K., Paatero, P., 2000. Investigation of sources of atmospheric aerosol at urban and suburban residential areas in Thailand by positive matrix factorization. Atmospheric Environment 34, 3319–3329.

Dionisio, K.L., Rooney, M.S., Arku, R.E., Friedman, A.B., Hughes, A.F., Vallarino, J., Agyei-Mensah, S., Spengler, J.D., Ezzati, M., 2010. Within-Neighborhood Patterns and Sources of Particle Pollution: Mobile Monitoring and Geographic Information System Analysis in Four Communities in Accra, Ghana. Environmental Health Perspectives 118, 607–613.

Dongarrà, G., Manno, E., Varrica, D., Vultaggio, M., 2007. Mass levels, crustal component and trace elements in PM_{10} in Palermo, Italy. Atmospheric Environment 41, 7977–7986.

Doumbia, E.H.T., Liousse, C., Galy-Lacaux, C., Ndiaye, S.A., Diop, B., Gardrat, E., Zouiten, C.,

Candaudap, F., Rosset, R., 2012b. Urban West Africa aerosols concentration levels and differentiated PM characteristics at Bamako (Mali) and Dakar (Senegal). submit.

Doumbia, E.H.T., Liousse, C., Galy-Lacaux, C., Ndiaye, S.A., Diop, B., Ouafo, M., Assamoi, E.M., Gardrat, E., Castera, P., Rosset, R., Akpo, A., Sigha, L., 2012a. Real time black carbon measurements in West and Central Africa urban sites. Atmospheric Environment 54, 529–537.

Eltayeb, M.A.H., Injuk, J., Maenhaut, W., Van Grieken, R.E., 2001. Elemental composition of mineral aerosol generated from Sudan Sahara sand. Journal of atmospheric chemistry 40, 247–273.

Gillies, J.A., Nickling, W.G., Mctainsh, G.H., 1996. Dust concentrations and particle-size characteristics of an intense dust haze event: Inland Delta Region, Mali, West Africa. Atmospheric Environment 30, 1081–1090.

Goix, S., Point, D., Oliva, P., Polve, M., Duprey, J.L., Mazurek, H., Guislain, L., Huayta, C., Barbieri, F.L., Gardon, J., 2011. Influence of source distribution and geochemical composition of aerosols on children exposure in the large polymetallic mining region of the Bolivian Altiplano. Science of the Total Environment.

Goldberg, E.D., 1963. H.M. Hill (Ed.), Composition of sea Water, Comparative Oceanography, Vol.2 of the seaWiley. New York.

Gordon, G.E., 1988. Receptor models. Environ. Sci. Technol. 22, 1132–1142.

Guinot, B., Cachier, H., Sciare, J., Tong, Y., Xin, W., Jianhua, Y., 2007. Beijing aerosol: Atmospheric interactions and new trends. J. Geophys. Res. 112, D14314.

Gupta, I., Salunkhe, A., Kumar, R., 2012. Source Apportionment of PM_{10} by Positive Matrix Factorization in Urban Area of Mumbai, India. ScientificWorldJournal 2012.

Henry, R.C., 1997. History and fundamentales of multivariate air quality receptor models. Chemometrics and intelligent laboratory systems 37, 37–42.

Henry, R.C., 2002. Multivariate receptor models—current practice and future trends. Chemometrics and Intelligent Laboratory Systems 60, 43–48.

Hopke, P.K., 1991. An introduction to receptor modeling. Chemometrics and Intelligent Laboratory Systems 10, 21–43.

IDAF-Aerosol [WWW Document], 2011. URL http://idaf.sedoo.fr/spip.php?rubrique36 (accessed 1.7.13)

Kim, E., Hopke, P.K., 2004. Source apportionment of fine particles in Washington, DC, utilizing temperature-resolved carbon fractions. J Air Waste Manag Assoc 54, 773–785.

Kouassi, K.S., Billet, S., Garçon, G., Verdin, A., Diouf, A., Cazier, F., Djaman, J., Courcot, D., Shirali, P., 2009. Oxidative damage induced in A549 cells by physically and chemically characterized air particulate matter ($PM_{2.5}$) collected in Abidjan, Côte d'Ivoire. Journal of Applied Toxicology 310–320.

Larsen, R.K., Baker, J.E., 2003. Source Apportionment of Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere: A Comparison of Three Methods. Environ. Sci. Technol. 37, 1873–1881.

Laupsa, H., Denby, B., Larssen, S., Schaug, J., 2009. Source apportionment of particulate matter ($PM_{2.5}$) in an urban area using dispersion, receptor and inverse modelling. Atmospheric Environment 43, 4733–4744.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem. Geophys. Geosyst. 2, 1021–24.

Miller, S.L., Anderson, M.J., Daly, E.P., Milford, J.B., 2002. Source apportionment of exposures to volatile organic compounds. I. Evaluation of receptor models using simulated exposure data. Atmospheric Environment 36, 3629–3641.

Millero, F.J., Feistel, R., Wright, D.G., McDougall, T.J., 2008. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. Deep Sea Research Part I: Oceanographic Research Papers 55, 50–72.

Nyanganyura, D., Maenhaut, W., Mathuthu, M., Makarau, A., Meixner, F.X., 2007. The chemical composition of tropospheric aerosols and their contributing sources to a continental background site in northern Zimbabwe from 1994 to 2000. Atmospheric Environment 41, 2644–2659.

Paatero, P., Hopke, P.K., Song, X.-H., Ramadan, Z., 2002. Understanding and controlling rotations in factor analytic models. Chemometrics and Intelligent Laboratory Systems 60, 253–264.

Paatero, P., Tapper, U., 1993. Analysis of different modes of factor analysis as least squares fit problems. Chemometrics and Intelligent Laboratory Systems 18, 183–194.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111–126.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Reviews 9, 269–298.

Pekney, N.J., Davidson, C.I., Robinson, A., Zhou, L., Hopke, P., Eatough, D., Rogge, W.F., 2006. Major Source Categories for $PM_{2.5}$ in Pittsburgh using PMF and UNMIX. Aerosol Science and Technology 40, 910–924.

Petaloti, C., Triantafyllou, A., Kouimtzis, T., Samara, C., 2006. Trace elements in atmospheric

particulate matter over a coal burning power production area of western Macedonia, Greece. Chemosphere 65, 2233–2243.

Picouet, C., 1999. Géodynamique d'un hydrosystème tropical peu anthropisé: le bassin supérieur du Niger et son delta intérieur. (Thése sciences).

Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B., Matos, M., 2011. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmospheric Environment 45, 6121–6132.

Polissar, A.V., Hopke, P.K., Paatero, P., Malm, W.C., Sisler, J.F., 1998. Atmospheric aerosol over Alaska: 2. Elemental composition and sources. J. Geophys. Res. 103, 19045–19,057.

Polissar, A.V., Hopke, P.K., Poirot, R.L., 2001. Atmospheric Aerosol over Vermont: Chemical Composition and Sources. Environ. Sci. Technol. 35, 4604–4621.

Reff, A., Eberly, S.I., Bhave, P.V., 2007. Receptor modelling of ambient particulate matter data using positive matrix factorization: review of existing methods. J Air Waste Manag Assoc 57, 146–154.

Sandradewi, J., Prévôt, A.S.H., Weingartner, E., Schmidhauser, R., Gysel, M., Baltensperger, U., 2008. A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength Aethalometer. Atmospheric Environment 42, 101–112.

Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric chemistry and physics: from air pollution to climate change, Wiley. New York.

Song, Y., Xie, S., Zhang, Y., Zeng, L., Salmon, L.G., Zheng, M., 2006. Source apportionment of $PM_{2.5}$ in Beijing using principal component analysis/absolute principal component scores and UNMIX. Science of The Total Environment 372, 278–286.

USEPA, 2008. EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals and User Guide.

Val, S., Liousse, C., Doumbia, E.H.T., Galy-Lacaux, C., Cachier, H., Marchand, N., Badel, A., Gardrat, E., Baeza-Squiban, A., 2013. Physico chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells: description of a worrying situation. In review process on Particle and Fibre Toxicology.

Watson, J.., al., 2004. Desert Research Institute, Protocol for Applying and Validating the CMB Model for $PM_{2.5}$ and VOC. US Environmental Protection Agency, Air Quality Modeling Group.

Watson, J.G., Chow, J.C., 2001. Source characterization of major emission sources in the Imperial and Mexicali Valleys along the US/Mexico border. Science of The Total Environment 276, 33–47.

Watson, J.G., Chow, J.C., 2002. Particulate pattern recognition. In Introduction to Environmental Forensics, Murphy, B. L., Morrison, R., Eds. Academic Press: New York, NY 429–460.

Weinstein, J.P., Hedges, S.R., Kimbrough, S., 2010. Characterization and aerosol mass balance of $PM_{2.5}$ and PM_{10} collected in Conakry, Guinea during the 2004 Harmattan period. Chemosphere 78, 980–988.

WHO, 2000. World Health Organization. Air quality guidelines for Europe. [WWW Document].URL(http://www.euro.who.int/document/e71922.pdf.

WHO, 2006. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Global update 2005. Summary of risk assessment. [WWW Document]. URL http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf

Xu, L., Chen, X., Chen, J., Zhang, F., He, C., Du, K., Wang, Y., 2012. Characterization of PM_{10} atmospheric aerosol at urban and urban background sites in Fuzhou city, China. Environmental Science and Pollution Research 19, 1443–1453.

Yang, H., Yu, J.Z., Ho, S.S.H., Xu, J., Wu, W.-S., Wan, C.H., Wang, X., Wang, X., Wang, L., 2005. The chemical composition of inorganic and carbonaceous materials in $PM_{2.5}$ in Nanjing, China. Atmospheric Environment 39, 3735–3749.

Yuan, Z., Lau, A.K.H., Zhang, H., Yu, J.Z., Louie, P.K.K., Fung, J.C.H., 2006. Identification and spatiotemporal variations of dominant PM_{10} sources over Hong Kong. Atmospheric Environment 40, 1803–1815.

Zhang, R., Han, Z., Shen, Z., Cao, J., 2008. Continuous measurement of number concentrations and elemental composition of aerosol particles for a dust storm event in Beijing. Advances in Atmospheric Sciences 25, 89–95.

Zheng, M., Salmon, L.G., Schauer, J.J., Zeng, L., Kiang, C.S., Zhang, Y., Cass, G.R., 2005. Seasonal trends in $PM_{2.5}$ source contributions in Beijing, China. Atmospheric Environment 39, 3967–3976.

CHAPITRE V : DES EXPOSITIONS AUX DOSES D'AEROSOLS DEPOSES DANS L'APPAREIL RESPIRATOIRE: apport de la modélisation

Introduction

De nombreuses études ont montré que l'exposition à court et à long termes aux particules atmosphériques cause une morbidité et une mortalité importante **(WHO, 2000 ; Pope et al., 2009)**. Les chapitres précédents ont mis en évidence les niveaux très élevés de concentration de particules dans les villes d'Afrique de l'Ouest. Cette pollution peut affecter le système respiratoire (exacerbation de l'asthme et de la maladie pulmonaire obstructive chronique) et le système cardiovasculaire (déclencher l'arythmie, l'insuffisance cardiaque et les AVC) **(Delfino et al., 2009 ; Halonen et al., 2008 ; Pope et al., 2006 ; Brook, 2008 ; Lokken et al., 2009)**. Dans cette thèse, au delà de la caractérisation des effets toxicologiques des particules africaines, nous avons essayé de déterminer leur distribution en taille et de quantifier leur dépôt dans l'appareil respiratoire des populations ouest africaines. Pour ce faire, nous avons élaboré un module de dépôt, DEPCLUNG (DEPosition Clearance LUNG), afin de traduire les concentrations atmosphériques des polluants mesurés à Bamako et Dakar en doses dans les divers compartiments du système respiratoire, à savoir la région extra-thoracique (ET), les bronches (BB), les bronchioles (bb) et les alvéoles (Al). Ce module est une adaptation du modèle de dépôt des particules développé par la CIPR (Commission Internationale pour la Protection Radiologique) surtout appliqué aux populations caucasiennes et asiatiques **(ICRP, 1994)**. Ainsi donc, l'utilisation de DEPCLUNG nécessite la connaissance des paramètres physiologiques/morphologiques et respiratoires des populations étudiées. L'application du modèle aux populations ouest africaines est un sujet novateur qui s'avère compliqué puisque les paramètres physiologiques/morphologiques sont très mal renseignés pour les populations de l'Afrique de l'Ouest. En revanche, pour ce qui est des propriétés des particules utilisées comme données d'entrée du modèle, elles ont été obtenues à partir des mesures de terrain à l'occasion des campagnes POLCA (cf. chapitre III et IV). Ces travaux font notamment l'objet d'une publication, en cours de soumission, permettant de relier propriétés physico-chimiques de l'aérosol ouest africain et dépôt dans le système respiratoire de différents groupes de populations (hommes, femmes et enfants âgés de 10 ans).

V.1. Description de la méthodologie de calcul

Une description détaillée des équations utilisées dans le modèle se trouve dans l'article décrit au paragraphe V.3. Mon travail, a consisté dans un premier temps, à traduire le code du programme de base écrit avec un langage informatique ancien (Pascal) en un langage plus récent (Fortran 90) et plus accessible. Il a fallu également ajouter des équations permettant de calculer les doses mesurées connaissant les concentrations (expositions). Dans un second temps, un énorme travail de recherche de paramètres pertinents et/ou d'estimation de ces paramètres (physiologiques et respiratoires) pour les populations ouest africaines a été mené. J'ai par la suite effectué des tests de sensibilité en vue d'étudier l'impact de la variation de certains paramètres clés (volume tidal V_T, capacité résiduelle fonctionnelle FRC and flux respiratoire Q) d'entrée sur les résultats fournis par le modèle. Le ***Tableau V-1*** montre l'effet d'une variation de +30% du V_T, de la FRC et de Q sur le dépôt des particules dans les divers compartiments du système respiratoire chez l'homme adulte ouest africain respirant par le nez et en activité modérée. Le volume d'air couramment respiré ou V_T semble être déterminant dans le calcul de la fraction d'aérosol déposé dans les poumons, de même que le flux d'air respiré Q. On observe qu'une augmentation du V_T de 30% contribue à une augmentation du dépôt total d'une valeur moyenne de 15%. En revanche, cette augmentation est de 17% au niveau des alvéoles. On note cependant que ces variations sont plus importantes pour les particules de petites tailles (diamètre thermodynamique en dessous de 0,1 µm). En effet, pour ces particules nanométriques les processus de dépôt sont liés aux mouvements aléatoires des particules (diffusion) **(Heyder, 2004)**. L'ensemble de ces tests a permis de constater qu'une augmentation du volume tidal à flux respiratoire constant favorise la pénétration des fines particules jusque dans les alvéoles et donc une hausse de la fraction déposée.

J'ai par la suite appliqué à DEPCLUNG des concentrations de particules mesurées à Bamako (BK1 cas d'un épisode de poussière et BK2 après passage de cet événement) et à Dakar (DK) afin d'estimer l'exposition des populations, ainsi que les doses dans les cinq compartiments de l'appareil respiratoire.

Tableau V-1 : Effet de la variation de +30% du volume tidal (V_T), de la capacité résiduelle fonctionnelle (FRC) et du flux respiratoire (Q) sur le dépôt dans les divers compartiments de l'appareil respiratoire. Cas de l'homme ouest africain respirant par le nez et effectuant un exercice modéré.

	Homme adulte		
SE	**V_T-V_T***	**FRC-FRC***	**Q-Q***
ET1	**1**	**0**	**0**
BB	**2**	**1**	**3**
bb	**1**	**1**	**4**
Al	**17**	**2**	**12**
Total	**15**	**1**	**8**

SE : erreur standard (%), * Valeur de référence

V.2. Présentation des principaux résultats

Les résultats discutés dans l'**Article (A4)** en fin de ce chapitre intitulé «Estimation of aerosol particle deposition in the human respiratory tract of West African populations» s'articulent autour de trois points:

- L'estimation de la fraction déposée en fonction du diamètre des particules dans l'appareil respiratoire des populations ouest africaines montre globalement un dépôt faible dans la gamme de taille entre 0,1 et 1 µm (***Figure V-1***). Ce phénomène n'est pas surprenant, puisque déjà observé chez d'autres populations, avec d'autres modèles. D'une part, il est lié au fait que les particules de ces tailles sont trop grosses pour que le mécanisme de diffusion soit important et trop petites pour que l'impaction et la sédimentation aient un effet. D'autre part, on peut aussi l'attribuer à la difficulté des modèles à bien représenter les mécanismes entrant en jeu dans cette gamme de tailles de particules (0.1-1 µm) intermédiaires. La figure indique également que les particules de taille comprise entre 0,01 et 0,1 µm se déposent majoritairement dans la région alvéolaire, tandis que celles de diamètre inférieur à 0,01 µm se retrouvent principalement dans les régions extra-thoraciques (ET) et trachéo-bronchiques (BB, bb). Ceci est lié à un mécanisme de diffusion plus important à ces tailles d'aérosols. Par contre, précisons que les particules de grosses tailles (> à 2,5 µm) ont un maximum de dépôt dans ET, suggérant un processus de sédimentation et d'impaction dominant. Il est intéressant de souligner que le dépôt régional est identique chez les hommes et les femmes, un peu différent chez les enfants.

- La comparaison entre le dépôt chez populations ouest africaines et caucasiennes présente des résultats similaires, sauf chez les enfants de 10 ans pour qui on note un écart maximal d'environ 26% en ce qui concerne le dépôt dans les alvéoles. Ceci peut s'expliquer par plusieurs faits : d'une part, les incertitudes liées aux données respiratoires sur les enfants d'Afrique en général. Il n'existe que très peu de publications dans ce domaine, ce qui nous a poussé vers une estimation allométrique de certains de ces paramètres en se basant sur des facteurs d'échelle (caucasien/ouest africain) entre certains paramètres physionomiques, tels que la taille ou le poids, mais également sur quelques caractéristiques respiratoires telle la capacité respiratoire totale (Total Lung Capacity, TLC), s'ils sont connus. Ces méthodes connues sous le terme « scaling factor » ont déjà été utilisées par d'autres auteurs **(James et al., 1991 ; Yamada et al., 2007)**. D'autre part, la différence pour les enfants peut être également liée aussi à l'écart entre les valeurs du volume tidal (V_T) reportées dans le ***Tableau 3*** de l'**Article A4**. Ce tableau montre un V_T plus important chez les enfants ouest africains (écart de 11%) par rapport aux Caucasiens, alors que le ***Tableau V-1*** indique une augmentation du dépôt dans les alvéoles en moyenne de 17% lorsque le V_T augmente de 30%, à flux respiratoire Q constant. En résumé, à Q fixe, une hausse de 30% du V_T implique un écart moyen de 17%, alors qu'à Q variable, l'augmentation de 11% du V_T fournit un écart maximal de 26% dans les Al. Par conséquent, cette grande différence du dépôt entre enfants ouest africain et caucasien s'explique en partie par la variabilité des paramètres Q et V_T chez les deux groupes de population.

- Afin d'investiguer l'influence des différents paramètres (masse, taille et composition chimique) sur le dépôt des particules collectées à Bamako et Dakar dans les voies respiratoires, trois scénarios ont été testés pour les paramètres d'entrés de DEPCLUNG: 1) un cas où l'on considère l'inhalation d'une masse donnée de $1 \mu g/m^3$; 2) un cas où différentes distributions en masse par classe de tailles (BK1, BK2 et DK) sont introduites dans DEPCLUNG ; 3) un cas où les compositions chimiques par classe de tailles (BK2 et DK) sont données en entrée.

a) L'application des distributions en tailles des concentrations d'aérosol mesurées à Bamako (événement de poussière BK1, suivi de BK2) et Dakar (DK) en entrée du modèle DEPCLUNG, montre une large modification des courbes d'entrées en sortie du modèle. Les trois cas d'aérosols considérés représentent des particules provenant de sources différentes et

donc offrent des caractéristiques variées (taille/chimie). Les résultats obtenus mettent en évidence une prédominance de l'effet de la taille sur les dépôts dans les poumons par rapport à l'effet de masse. La taille des particules est donc plus pertinent pour la détermination de l'efficacité du dépôt dans les divers compartiments de l'appareil respiratoire, mais également dans l'étude des mécanismes de toxicité **Val et al. (2013)**.

b) L'effet de la composition chimique sur le dépôt régional des particules dans l'appareil respiratoire des populations ouest africaines a été aussi testé. Comme pour la distribution granulométrique, nous avons utilisé cette fois ci en entrée du modèle les données d'observations obtenues à nos deux sites (comme prévisible) les particules d'origines naturelles telles que les poussières (essentiellement des grosses particules) se déposent majoritairement dans les voies supérieures de la région extra-thoracique, tandis que les particules issues des activités humaines, principalement composées de particules fines, se déposent plus profondément notamment dans les alvéoles (cf. **Article A4**). A Bamako et Dakar, ces petites particules composées en grande partie de matières carbonées (organique et élémentaire, cf. **Article A4**) seront difficilement éliminées (totalement ou partiellement) par l'organisme puisqu'elles sont présentes en grand nombre dans les fines particules (particules de diamètre inférieur à 0.1 µm ou $PM_{0.1}$) (***Tableau V-1***). La solubilité de ces espèces peut également influencer leur dépôt dans l'arbre respiratoire, mais n'est pas encore totalement intégré dans DEPCLUNG. Notons également, qu'il existe des différences entre flux de dépôt entre les sites d'échantillonnages qui se traduisent par une différence au niveau des caractéristiques physico-chimiques des particules.

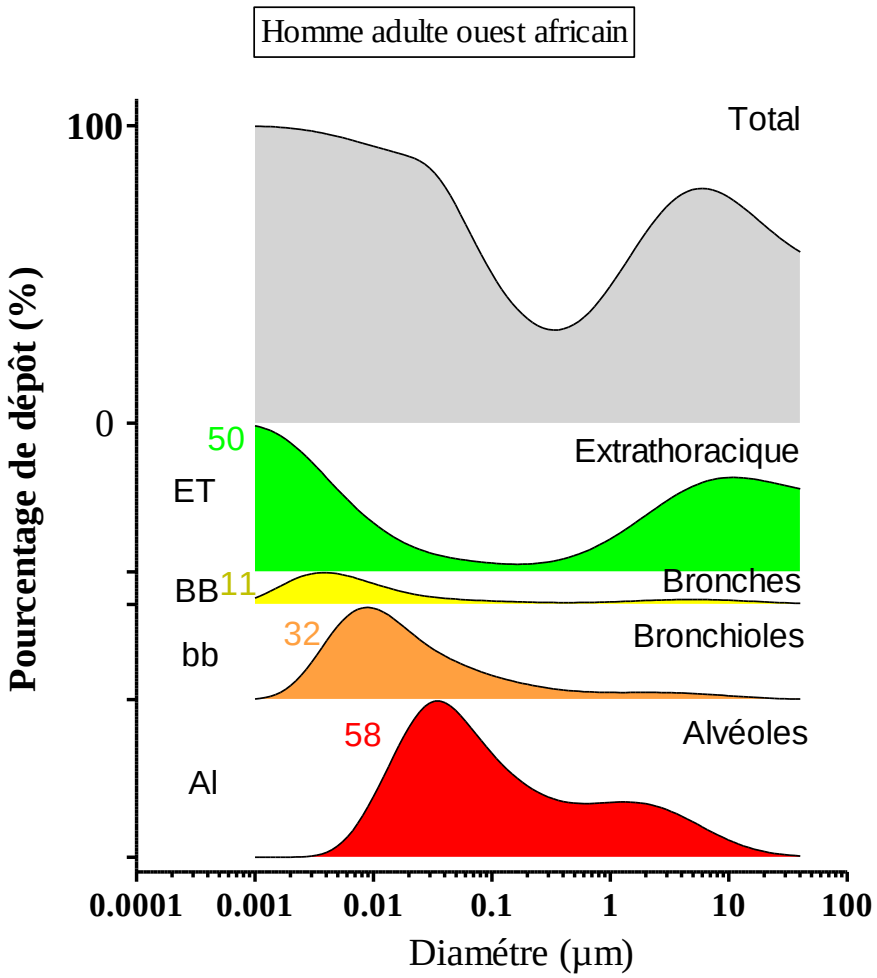

Figure V-1 : Fraction déposée dans les divers compartiments de l'appareil respiratoire. Cas de l'homme ouest africain respirant par le nez et effectuant un exercice modéré.

V.3. Article A4

"Estimation of aerosol particle deposition in the human respiratory tract of West African populations"

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Soumis dans Environmental Research

Abstract

Toxicological and epidemiological studies have shown associations between fine particles and human health effects **(e.g. Pope and Dockery, 2006)**, with exposure to high levels of particulate matter increasing the rate of respiratory diseases at short and long terms. However it is possible that inhaled particles would be different than particles within the respiratory system. Therefore, it is important to assess particle deposition in human respiratory tract. In this study, the DEPosition Clearance LUNG (DEPLUNG) model derived from the International Commission on Radiological Protection, Publication 66 (ICRP66) was used to estimate compartmental particle deposition for West African people of different ages and genders. For West African adults (males and females), 31 ± 9% (36 ± 12%) of predicted particulate deposition occurs in the extra-thoracic region (ET1 - ET2), 3 ± 1% in the bronchial region (BB), 6 ± 5% in the bronchiolar region (bb) and 24 ± 15% in the alveolar region (Al). Results show that the deposition fractions (DF) for West Africans are rather close to Caucasian references, though with larger differences between children. A real case has been also tested related to exposures measured at Bamako (with or without dust event), and in Dakar at traffic sites in the frame of POLCA **(Liousse and Galy-Lacaux, 2010 ; Doumbia et al., 2012a).** DEPCLUNG was used to evaluate the role and effects of particle sizes and chemical compositions deposited in human respiratory tracts. Differences in size distributions affect particle deposition in lung compartments, highlighting the prominent role of this parameter. Aerosol chemical composition has also been shown to be important. This has strong implications for in vitro studies in which differences in regional deposition are to be considered.

Keywords: Aerosol, size distribution, chemical composition, health, DEPCLUNG model, lung deposition, West Africa

1. Introduction

Epidemiological studies have shown associations between daily levels of $PM_{2.5}$ (particles with diameters under 2.5µm), hospital admissions and mortality in developing countries, as elsewhere in the world **(Dockery et al., 1993 ; Pope et al., 2006 ; Ostro et al., 2007; WHO, 2012)**, in spite of the paucity of such dedicated analyses in those regions. Toxicological studies have particularly implicated fine and ultrafine particles (< 1µm in diameter), since first they are the most numerous and secondly, they display increased toxicity relatively to larger particles due to higher surface to volume ratios **(Happo et al., 2008 ; Huang et al., 2002 ; Val et al., 2013)**. More generally, definitive conclusions on the mechanisms and associated effects of particulate matter (PM) are still to be drawn. Aerosol size distributions, concentrations and chemical speciation are all required information to decipher the health effects of PM. For risk estimations, it is essential to have as good as possible a description of the whole chain of processes at play, the complexity of such processes both requiring experimental data and modeling. Moreover, it is to be expected that inhaled aerosol doses differ critically from those measured deeply in the respiratory tract. Particle sizes are largely determinant for deposition location of aerosols in the human respiratory tract **(Raabe et al., 1986)**. The estimation of inhaled aerosol doses selectively deposited in the successive compartments of the respiratory tract also relies on human exposure to particle concentrations and their physical and chemical properties, together with lung morphologies and breathing parameters which are dependent on individual characteristics **(Jaques and Kim, 2000 ; Brown et al., 2002 ; Löndahl et al., 2007)**. It is also expected that the deposited dose rates vary significantly between healthy and ill people, the more so with increasing severity of the disease **(Löndahl et al., 2012)**.

The International Commission on Radiological Protection **(ICRP, Publication 66, Bailey, 1994 ; Bair and al., 1994)** has developed successive model versions for particulate depositions and clearance within and from the human respiratory tract, with a main objective of providing lung doses for a large variety of populations of different ages and gender. In addition to this primary goal, provisions have been made for dealing with environmental pollution and smoking by including possible flow distortions due to lung diseases **(Bair, 1995)**.

The objective of our study is to investigate particle deposition in respiratory tracts of West African people using DEPCLUNG model (DEPosition Clearance LUNG). Such a work requires experimental data to be associated with modeling. In this way, results of POLCA

(POLlution des Capitales Africaines) experiments at Bamako and Dakar **(Liousse and Galy-Lacaux, 2010 ; Doumbia et al., 2012a)** were used to assess concentrations, together with physical and chemical properties of particles and deposition in lungs. The ICRP model historically referred only to Caucasian and Asiatic people. In this work, our derived model DEPCLUNG has been specifically adapted to West Africa populations.

Here, a first investigation is made to extract biometry and associated lung capacities for West African populations from existing data, in view of their application to DEPCLUNG. Differences in compartmental deposition fractions (DF) for adults and children between West Africans and Caucasians were analyzed. Also, estimations of size speciated chemical concentrations among five lung compartments were performed using atmospheric particle measurements performed in Bamako and in Dakar during POLCA experiments.

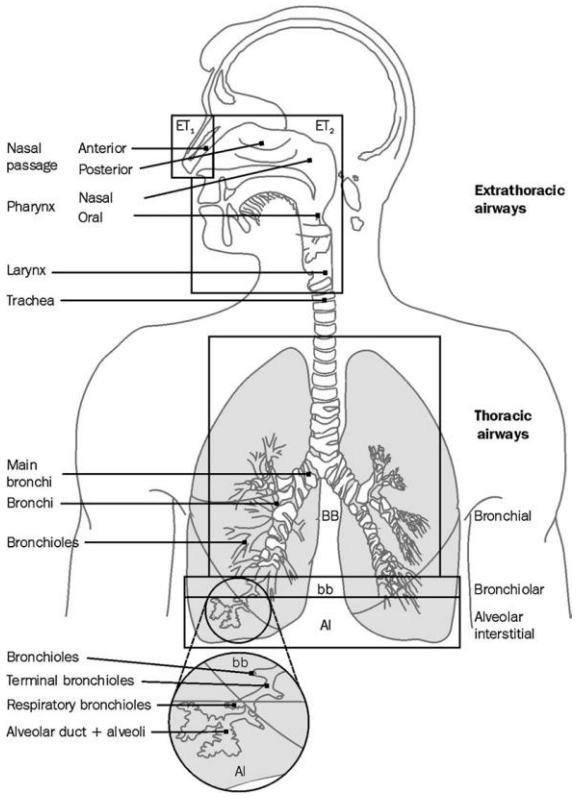

Figure 1: The extrathoracic region consists in the anterior nasal (ET1), and posterior nasal passage, pharynx, larynx and mouth (ET2). The thoracic region comprises the bronchial region (BB), the bronchiolar region (bb), and the alveolar-interstitial region (Al). (ICRP, 1994).

2. Methodology

2.1. Deposition fraction DF calculations

2.1.1. Model description

The DEPCLUNG model describes particle distributions amongst the five lung main regions **(ICRP, 1994)**: two extra-thoracic regions, the anterior nasal (ET1) and the posterior nasal passage with pharynx larynx and mouth (ET2), and three thoracic regions, the bronchial region (BB) consisting of the trachea and bronchi from which deposited material is cleared by micro-ciliary action, the bronchiolar region (bb) with bronchioles and terminal bronchioles and, the alveolar region (Al) comprising the respiratory bronchioles, the alveolar ducts and sacs and interstitial tissue (***Figure 1***). The respiratory tract model can be thought to consist of a number of linearly connected filters, the output of one filter serving as input to the next one.

With this scheme, the deposition fraction (DF) in each region is expressed as a function of the efficiency (η) of the equivalent filter, with additional terms allowing for the volumetric fractions (ϕ) of preceding filters in the series **(James et al., 1991)**. η are expressed as functions of particle physical characteristics and ventilation parameters. ϕ describe the effects on regional deposition of tidal volume (volume of air breathed in and out without conscious effort) and variation of airway volumes.

The deposition fractions (DF) in each region of the respiratory tract are given by the equations in ***Table 1***.

Table 1: Deposition fractions DF in the different lung regions.

Region	Deposition fraction DF
ET1	$DF(ET1) = F_n \eta_l \eta(ET1)[1 + (1 - \eta(ET))(1 - DF(T)/\eta_l)]$
BB	$DF(BB) = \eta_l \psi(ET)(1 - \eta(ET))\eta(BB)$
bb	$DF(bb) = \eta_l \psi(bb)(1 - \eta(ET))(1 - \eta(BB))\eta(bb)$
Al	$DF(Al) = \eta_l \psi(Al)(1 - \eta(ET))(1 - \eta(BB))(1 - \eta(bb))\eta(Al)$

where

- F_n is the nasal fraction of ventilating air. For oral breathing, this fraction (F_m) is calculated as $F_n = 1 - F_m$. A default value of F_n for light exercise is 1 **(ICRP, 1994)**.
- η_I is the inhalability. It is assumed in DEPCLUNG that the efficiency with which particles in ambient air enter the nose or mouth (not influenced by breathing rate or nose or mouth dimensions) is given as:

$$\eta_I = 1 - 0.5\left[1 - \left(7.6\times10^{-4} d_{ae}^{2.8} + 1\right)^{-1}\right] \quad (1)$$

This equation is applicable to any subject and under all conditions **(James et al., 1991)**.

- $\eta(R)$ are the deposition efficiency expressed by a combination of aerodynamic and thermodynamic terms in lung region R. Indeed, $\eta(R)$ are evaluated for larger (d_{ae} > 1µm) aerodynamic particles (η_{ae}) deposited by impaction and gravitational settling and for smaller (d_{th} < 0.1µm) thermodynamic particles (η_{th}), deposited by diffusion processes. ***Table 2*** resumes $\eta(R)$ formulations, both aerodynamic (η_{ae}) and thermodynamic (η_{th}). These η values are influenced by the volumetric flow rates (ϕ) via the residence time (τ) a pollutant spends in a region during the breathing cycle. The ϕ equations are also given in ***Table 2***.

Table 2: Deposition efficiencies η and volumetric fractions ϕ in the different lung regions.

Region	Deposition efficiency η	Volumetric fraction ϕ
ET1	$\eta_{ae} = 1 - (3\times10^{-4} d_{ae}^2 * Q * SF_t^3 + 1)^{-1}$ $\eta_{th} = 1 - \exp\left[-18D^{1/2}(Q * SF_t)^{-1/8}\right]$	1
BB	$\eta_{ae} = 1 - \exp\left[-4x10^{-6} SF_t^{2.8}(Q * d_{ae}^2)^{1.15}\right]$ $\eta_{th} = \psi_{th}\left\{1 - \exp\left[-16SF_t(D * \tau(BB))^{1.15/2}\right]\right\}$	$1 - \frac{V_D(ET)}{V_T}$
bb	$\eta_{ae} = 1 - \exp\left[-\left(0.009 + 0.165\tau(bb)^{1.5}\right)d_{ae}^{\tau(bb)^{-0.25}}\right]$ $\eta_{th} = 1 - \exp\left[-\left(70 + 12SF_{bb}^5\right)(D * \tau(bb))^{1.05/2}\right]$	$1 - \frac{V_D(ET) + V_D(BB)[1 + V_T / FRC]}{V_T}$
Al	$\eta_{ae} = 1 - \exp\left[-0.14SF_{Al}\left(d_{ae}^2 * \tau(Al)\right)^{2/3}\right]$ $\eta_{th} = 1 - \exp\left[-(-450 + 1000SF_{Al})(D * \tau(Al))^{2/3}\right]$	$1 - \frac{V_D(ET) + [V_D(BB) + V_D(bb)][1 + V_T / FRC]}{V_T}$

where the scaling factor SF_R, is the ratio between airway dimensions of region R for Caucasians versus West Africans ; $\tau(BB)$ a time constant for air conduction through the trachea and bronchi ; V_D is the "dead volume" (air volume not participating in the breathing process), Q is the inspiratory flow rate including both inhalation and exhalation, V_T is the tidal volume, FRC is the functional residual capacity. All these terms have been defined in **ICRP (1994)**.

$$\tau(BB) = \frac{V_D(BB)}{Q}\left(1 + \frac{0.5V_T}{FRC}\right); \quad (2)$$

$\tau(bb)$, a time constant for air conduction through the bronchioles

$$\tau(bb) = \frac{V_D(bb)}{Q}\left(1 + \frac{0.5V_T}{FRC}\right); \quad (3)$$

$\tau(Al)$ is a time constant for air residence in the alveolar airways

$$\tau(Al) = \frac{V_T - V_D(ET) - [V_D(BB) + V_D(bb)][1 + (V_T/FRC)]}{Q}; \quad (4)$$

D, the diffusion coefficient of particles in air;

$$D = \frac{C(d_{th})KT}{3\pi\mu d_{th}}; \quad (5)$$

where $K = 1.38066 \times 10^{-23} JK^{-1}$ is Boltzmann's constant, $T = 310K$, a typical temperature, and $\mu = 1.90 \times 10^{-4} g.cm^{-1}s^{-1}$, air dynamic viscosity **(Bair and al., 1994)**.

ψ_{th} is an empirical correction factor.

$$\psi_{th} = 1 + 80\exp\left\{-\left[\log_{10}\left(80 + 10/d_{th}^{0.6}\right)\right]^2\right\}; \quad (6)$$

In DEPCLUNG, for expressing DF as a function of d_{ae} and d_{th}, it was assumed that the geometric standard deviations (σ_g) have typical values slightly above 1 for small particles (d_{th}), against 2.5 for larger particles (d_{ae}). Without specific knowledge on σ_g, a practical formula is used:

$$\sigma_g = 1 + 1.5\left[1 - \left(100d^{1.5} + 1\right)^{-1}\right] \quad (7)$$

Since aerodynamic and thermodynamic processes act competitively to remove particles, the resulting deposition fraction in region R is given by:

$$DF_R = \left(\eta_{ae}^2 + \eta_{th}^2\right)^{1/2} \tag{8}$$

In practice, particles are considered either as a monodisperse (same diameter) or polydisperse. Conversely, particles in a polydisperse aerosol display a range of diameters, e.g. size particles distributed log normally **(ICRP, 1994)**. In DEPCLUNG, particle deposition is evaluated for polydisperse aerosols in the diameter range 1nm to 50µm. Note that thermodynamic and aerodynamic diameters are related through the equation:

$$d_{ae} = d_{th}\left[\frac{\rho C(d_{th})}{\chi \rho_0 C(d_{ae})}\right] \tag{9}$$

where ρ is particle density, ρ_0 unit density, and χ, the shape factor. The function $C(d)$ is the Cunningham slip factor **(Hinds, 1982)**

$$C(d) = 1 + \frac{\lambda}{d_c}\left(2.514 + 0.800e^{-0.55d_c/\lambda}\right) \tag{10}$$

where $\lambda = 0.0683\mu m$ is the mean free path of air molecules, and $d_c = d\left(1 + 3e^{-2200d}\right)$ is a correction for diameters.

2.1.2. Input parameters

Uncertainties in particulate deposition due to input parameters, breathing patterns, gender and age of subjects have been reported by several authors **(Harvey and Hamby, 2002 ; Bolch et al., 2001 ; Fritsch, 2006)**. However, the highest uncertainties were observed within the lower parts of lungs for the smallest and the largest aerosol sizes, mainly due either to particle density or to their aerodynamic diameter **(Fritsch, 2006)**. Such uncertainties are even higher for West Africans due to additional significant lack of knowledge about morphology and respiratory parameters for these populations, apart a few data on spirometry. For our study, specific West African anatomical and physiological parameters are required. Spirometric values published for African people from Senegal **(Dufetel et al., 1989 ; Seck et al., 1990)**, Togo **(Dufetel et al., 1990)**, Nigeria **(Onyedum et al., 2010)** will be used, assumed to be representative of West African populations. Moreover, these parameters vary highly between subjects, thus strongly affecting particle deposition in the respiratory tract. Additionally, differences in exercise levels and breathing scenarios affect DF calculations **(Bartley and**

Vincent, 2011): only light exercise conditions and nasal breathing were selected here, still in the absence of pertinent published data, especially for children.

Table 3 summarizes the main parameters for population used in DEPCLUNG for adult males, adult females and 10-year old children, both for healthy West Africans and Caucasians. ***Table 3*** comprises all values for Caucasians from ICRP66, together with data extensively collected in the literature for West African populations. In case of no available data, scaling factor for airways dimensions **(James et al., 1991 ; Yamada et al., 2007 ; Pichelin et al., 2012)** was applied for estimating surrogates. Briefly, one-dimensional parameters such as trachea diameters were calculated from scaled values according to body-height ratios between Caucasians and West Africans. For three-dimensional parameters such as V_D or FRC, the total lung capacity (TLC) ratios were selected as surrogates. For example, dead volumes for West African adult males are calculated by multiplying dead volume values for Caucasians by a factor 0.808 (5.64/6.98, cf. ***Table 3***). Respiratory parameters (Q, V_T) or ventilation rate (VR) were also estimated for West Africans using scaling factors based on TLC.

Table 4 summarizes the different parameters for particles in DEPCLUNG. Particle density (ρ) is assumed in the range from 1 to 10 g.cm^{-3} with a mode of 3 g.cm^{-3}, shape factors range between 1 and 2 **(ICRP, 1994)**. Sensitivity tests have been conducted for different ρ and shape factors χ. ***Figure 2*** compare total DF obtained with varying ρ and χ. It is observed that DF is independent of the density and shape factor for larger d_{ae} particles. Conversely, DF varies with ρ for smaller particles (d_{th}). In our tests, with density increasing from 1 to 5 g.cm^{-3} results a maximum difference of 53% in DF for 0.1µm diameter particles. So, a value of 2 g.cm^{-3} was assigned in DEPCLUNG for Bamako and Dakar, based on knowledge on dominant material at our sites **(Sloane, 1983 ; D'Almeida et al., 1991)**. The shape factor was 1.5, the ICRP66 default value. Geometric standard deviations (σ_g) were obtained from our experiment results.

The variation of +30% of other key parameters such as Q, V_T and FRC was also tested (not shown here). It appears that the tidal volume (V_T) mostly influences the deposition on lung with a maximum uncertainty of 17% in the alveolar region.

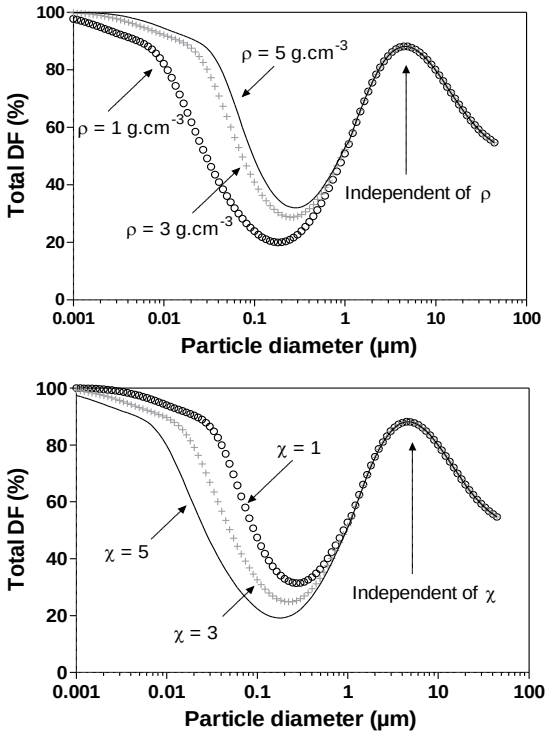

Figure 2: Total DF values through varying parameters: a) particle densities (ρ) and b) shape factor (χ) for an adult male, light exercise and nasal breathing.

2.1.3. Other deposition calculations

Mass depositions were calculated with the following relationship:

$$DM_i = DF_i * N(t) * V_T * VR$$

where DM is deposited mass per unit exposure per unit time per person, DF is deposition fraction, N aerosol concentrations (in $\mu g.m^{-3}$ or $particle.m^{-3}$), V_T tidal volume (in ml), VR ventilation rate (in $m^3.h^{-1}$), t is time and i refers to lung compartment. This deposited mass can also be expressed in other forms. For example, DW is obtained when "per person" is replaced by "per body weight". Such a definition is important since when inhaled aerosol is removed from the lung and cleared in the body, body weight plays a significant role as concerns health effects **(Yamada et al., 2007)**. Another deposition index DL (deposition lung volume) is obtained when replacing "per person" by "per lung volume" or total lung capacity (TLC). Finally, a pertinent deposition metric is the standardized deposition mass rate (SDMR in $\mu g.h^{-1}.m^{-2}$), which both includes specific lung target areas and exposure duration. SDMR is thus expressed in unit duration exposure per unit area. Appropriate indexes can be selected according to the particular kind of study, e.g. for exposure or dose determination. For example, it was expected that for exposure studies (in vitro experiments), the most suitable

metric is particle mass or number per volume (µg.ml^{-1} or particle/ml), whereas for dose studies, adequate metric could be deposition mass rates. Detailed discussions upon governing indexes can be found in **Paur et al. (2011)**.

Table 3: Typical biometry and lung volumes for Caucasians and West African populations: H height, W weight, TLC Total Lung Capacity, FRC Fractional Residual Capacity, VC Vital Capacity, V_D dead volume, Q inspiratory flow rate, V_T tidal volume and VR ventilation rate.

	Adult males			Adult females			10-year old children		
Parameter	Caucasians[a]	West African	Ratio	Caucasians[a]	West African	Ratio	Caucasians[a]	West African	Ratio
H (cm)	176	177[b]	1.006	163	165[b]	1.012	138	136[c]	0.985
W (kg)	73	68[b]	0.932	60	63[b]	1.050	33	28[c]	0.848
TLC (L)	6.98	5.64[e]	0.808	4.97	3.95[e]	0.795	2.87	2.17[d]	0.756
FRC (L)	3.30	2.6[f]	0.788	2.68	1.82[f]	0.679	1.48	1.12*	-
VC (L)	5.02	4.20[b]	0.837	3.55	3.00[b]	0.845	2.33	1.71[c]	0.734
V_D (ET) (ml)	50	40.4*	-	40	31.8*	-	25	18.3*	-
V_D (BB) (ml)	49	39.6*	-	40	31.8*	-	26	19.1*	-
V_D (bb) (ml)	47	38.0*	-	44	35.0*	-	26	19.1*	-
Light exercise									
Q (ml.s^{-1})	833	673*	-	694	552*	-	317	325[d]	-
VT (L)	1.25	1.01*	-	0.99	0.79*	-	0.58	0.65[d]	-
VR (m^3.h^{-1})	1.5	1.2b	0.800	1.25	0.96*	-	1.12	0.792*	-

[a] ICRP publication 66, [b] **Dufetel et al., 1989** and **Dufetel et al., 1990**, [c] **Seck et al., 1990**, [d] **Miller et al., 1977**, [e] **Lapp et al., 1974**, [f] **Roy et al., 1991**.

[*] estimated value

Table 4: Particle parameter options and default parameters from ICRP66.

	Diameter type	Diameter size	Shape factor χ	Density ρ	σ_g
Range/choices	d_{th} , d_{ae}	0.001 – 50 µm	1 - 2	1 – 10 g.cm^{-3}	formula or custom value (< 1)
Default	d_{ae}	5 µm	1.5	3.0 g.cm^{-3}	formula

2.2. Application of DEPCLUNG to real cases during POLCA experiment

DEPCLUNG was applied to three measurements samples in West Africa issued from POLCA experimental results. Detailed information about particle sampling and analytical methods are reported in **Val et al., (2013)**. Only a brief summary is given here. Atmospheric aerosol

measurements are performed at two West African traffic sites (Dakar, Senegal and Bamako, Mali) during two intensive field campaigns, respectively in January 2009 and in December 2009 at the dry season when the pollution is maximum **(Liousse and Galy-Lacaux, 2010) ; Doumbia et al., 2012a).** Size-resolved particle samples at BK were collected during two distinct periods: BK1, during a typical dust event and BK2 following this event and representative of the rest of the campaign. BK1 took place from January 22 to 24 and BK2, from January 27 to 29. In DK, 48h size-resolved particulate matter samples were collected from December 5 to 7, typical of particulate pollution close to traffic sources at this period of the year.

A 13-stage electrical low pressure cascade impactor (ELPI, Dekati Ltd., Finland) and a 5-stage impactor (SIOUTAS) were used to derive size speciated chemical aerosol. This ELPI combines both possibilities of size-resolved particle collection on filters for subsequent chemical analysis and real time size distribution measurements of particle masses, numbers, diameters and areas. Raw data were acquired with Dekati's ELPIVI software 4.0 for particle diameters and geometric standard deviation (σ_g) determination. The ELPI works at a flow rate of 30 $l.min^{-1}$, with nominal cut size aerodynamic diameters between 3nm and 10µm. The SIOUTAS works at a flow rate of 9 $l.min^{-1}$, with cut size in the ranges < 0.25µm, 0.25-0.50, 0.50- 0.10, 0.10-2.5 and 2.5-10µm. The ELPI, mounted with 25mm diameter polycarbonate Nucleopore filters (1µm porosity), was devoted to water-soluble ion analyses using ionic chromatography (IC) **(Adon et al., 2010)** and gravimetric measurements (using a Mettler Microbalance MC21S with 1µg sensitivity). The SIOUTAS, mounted with 25mm diameter quartz filters (QMA, Whatman), was dedicated to carbonaceous aerosol measurements (black carbon BC and organic carbon OC) using Desert Research Institute (DRI) analyzer **(Chow et al., 1993)**. For coherence and simplification, chemical analyses results are displayed in the same size ranges as the SIOUTAS impactor.

3. Results and Discussion

3.1. Particle deposition fractions

3.1.1. West African populations

Deposition fraction calculations were performed with DEPCLUNG for polydisperse aerosol particles in the diameter range 0.001-50µm, for light exercise and a nasal breathing scenario. Results on compartmental depositions in the extra-thoracic regions (ET1 and ET2), tracheo-bronchial regions (BB and bb) and alveolar region (Al) for adult males, adult females and 10-

year old children from West Africa are shown in ***Figure 3***. DF in the extra-thoracic regions, which is the first line of body defense against inhaled air pollutants, shows two modes, with high deposition values up to 40%, both for the uppermost and lowermost particle sizes. This corresponds to the two dominant deposition mechanisms in these lung regions, namely diffusion for particles below 0.1µm and inertial impaction for particles above 0.1µm **(Cheng, 2003)**. In the rest of the respiratory tract (BB, bb and Al regions), DF reduces to only one mode with peaks in the particle thermodynamic diameters under 0.1µm. In this size range, DF peak increases from BB to Al regions, reaching maximum values of 60% in the Al region. This means that small particles mainly deposit in the Al region. Total DF, the sum of all regional DF, is close to 100% in the thermodynamic (< 0.1µm) and the aerodynamic (> 1µm) size range. Similar DF for adult males and females are found for fine and coarse particles. This is not in agreement with the experimental studies of **Kim and Hu, (2006)** which show that DF are consistently greater for women than for men for coarse particles (diameters of 3 and 5 µm), regardless of inspiratory flow rates. Let us specify that this latter study was based only on monodisperse aerosols. For 10-year old children, DF are higher than for adults, especially in the Al region and for the particle size range 0.03 to 1µm. Maximum DF in the Al region were 58% for 10 year old children, 52% for adult males and 49% for adult females. Total DF for 10-year old children are high, with a 35% maximum for 0.5 µm particles, more than for adult males and females (***Figure 3***), highlighting that children would suffer from more severe health risks than adults through exposure to atmospheric PM. **Asgharian et al. (2004)** have also found that particle lung deposition as a function of age results for children, particularly infants, in stronger risks.

For adults (males and females), as an average, 31 ± 9% (36 ± 12%) of particulate matter is deposited in the extra-thoracic region ET1 (ET2), 3 ± 1% in the bronchial region (BB), 6 ± 5% in the bronchiolar region (bb) and 24 ± 15% in the alveolar region (Al). Note that, the percentages of particles deposited in the Al region are higher than in the extra-thoracic region for < 0.5µm particles (31-44% in the Al region against 22-24% in the ET region).

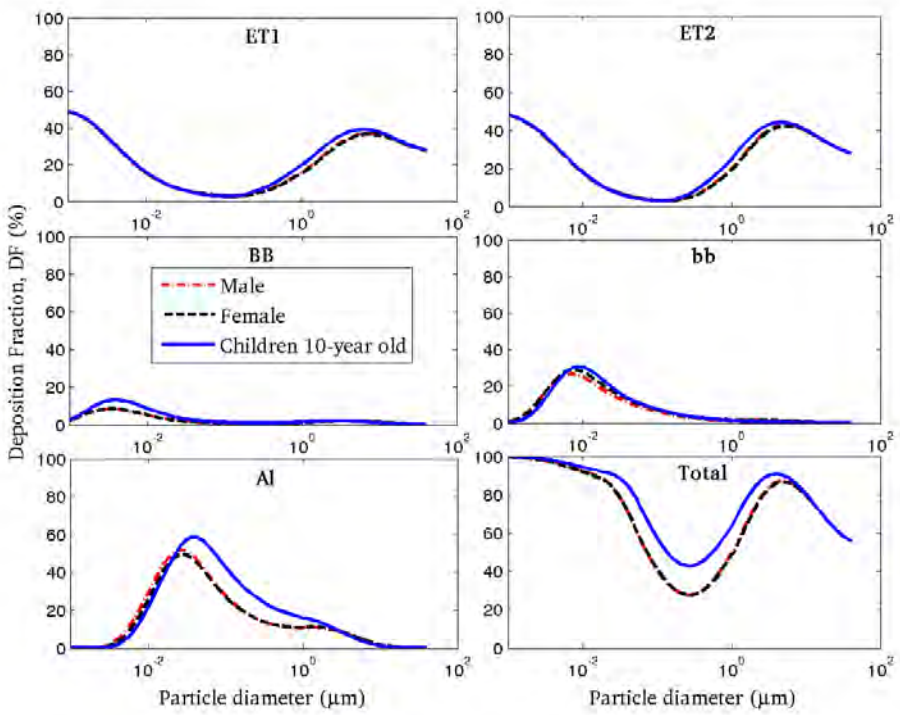

Figure 3: Particle deposition fractions in the extrathoracic (ET1 and ET2), bronchial (BB), bronchiolar (bb) and alveolar (Al) regions for adult males, adult females and 10-year old children from West Africa, in conditions of nasal breathing and light exercise.

3.1.2. DF comparisons between West Africans and Caucasians

Figure 4 shows a comparison in deposition fractions between West African and Caucasian adult males (***Figures 4a, 4b***) and for 10-year old children (***Figures 4c, 4d***). Box (25^{th} and 75^{th} percentiles) and whisker (5^{th} and 95^{th} percentiles) plots are used to depict uncertainties. DF patterns for adult males from West Africa are quite similar to those for Caucasians. A 2% maximum difference only is shown in ***Figures 4a, 4b***, with similar aerosol sizes for maximum DF (not shown here). These values are close to the 3% difference between Japanese and Caucasians from **Yamada et al. (2007)**. This implies that ethnic differences between West Africans, Caucasians and Japanese adults are only weakly reflected in DF values, despite larger differences (from 19 and 26%) in lung capacities between West African and Caucasian populations as shown in ***Table 3***. The patterns are quite different for 10-year old children, since DF differences between West Africans and Caucasians strongly vary between compartments, reaching 27% in the Al region (***Figure 4c, 4d***), with 26% maximum difference in lung capacities (***Table 3***). This result denotes that on average 10-year old Caucasian children have lung capacities more developed than West African ones, with less deposition in the Al region as a response to air contaminant exposures. Such a difference still needs to be

further confirmed. First, differences in DF between adults and 10-year old children are mainly observed in the 0.1µm to 1µm particle size range. Several studies have revealed modeling difficulties to characterize deposition in human lungs in this size range **(Bartley and Vincent, 2011)**, due to this range being intermediate between thermodynamic and aerodynamic particle diameters. Secondly, uncertainties in input parameters such as lung capacities and respiratory characteristics require further documentation, since they are very poorly documented for African people in general, and particularly for children.

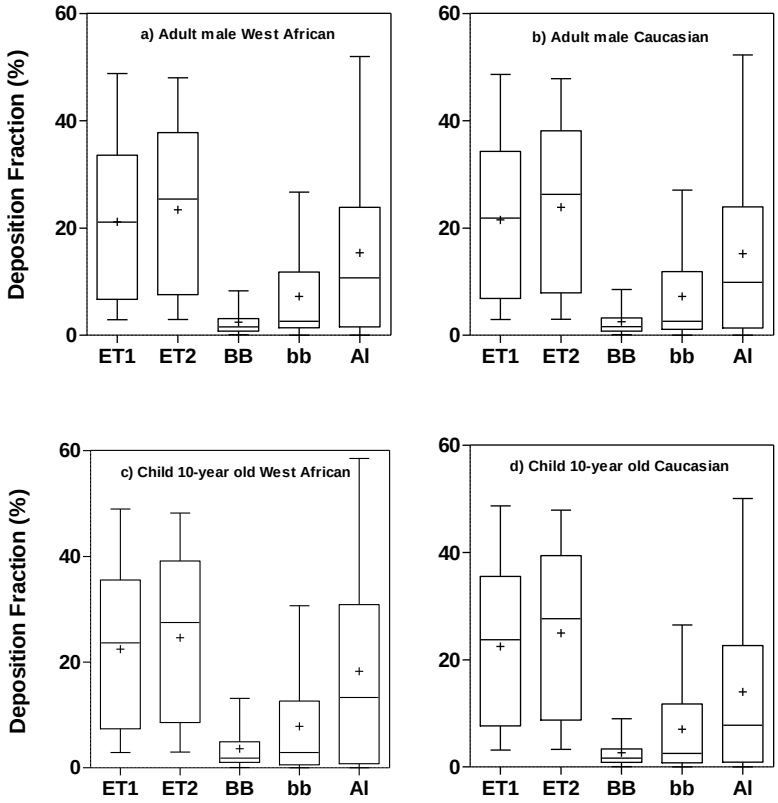

Figure 4: Compartmental DF values, comparison between West Africans and Caucasians (light exercise and nasal breathing) for: a) West African adult males, b) Caucasian adult males, c) West African 10-year old children, and d) Caucasian 10-year old children.

3.2. Particle mass deposition

Three scenarios have been considered to evaluate the impact of mass deposition on the respiratory tract: 1) in the first one, aerosol inhalation of 1 $\mu g.m^{-3}$ concentrations is assumed, 2) in the second one, it is assumed that following inhalation, the input particle size distributions are the ones measured in BK and DK during POLCA, and 3) in the third one, a chemical speciation is analyzed based on measured chemical mass distributions.

3.2.1. Estimated lung depositions after inhalation of 1 µg.m^{-3} particle concentrations

Results of compartmental particle size-dependent mass deposition for factors such as DM, DW and DL are shown in ***Figure 5***. DM patterns show clear differences between adult males, adult females and 10-year old children. In the Al region for example, maximum DM was 0.623 µg.h^{-1} for adult males, 0.474 µg.h^{-1} for adult females and 0.463 µg.h^{-1} for 10 year old children. Maximum DM for West African adult males was 0.795 (0.623/0.784) times the ones for Caucasians (not shown). For adult females and 10-year old children, the ratios were 0.750 (0.474/0.632) and 0.825 (0.463/0.561), respectively. The DM differences then were 21% between adult males, 25% for adult females and 18% for 10-year old children. These differences are close to the ones found for lung capacities between West Africans and Caucasians (adult males and females only), respectively 19% and 23% (***Table 3***), suggesting that such DM differences are due to lung capacity differences (Caucasian values are generally over those for West Africans), the two groups being submitted to similar exposures. However, for 10-year old children, the differences in lung capacities (26%) are over 18%. Previous DF comparisons, except for 10-year old children, have shown that despite large differences in lung capacities, the West African and Caucasian groups display rather similar DF. However, at the difference of DF values, DM ones do not support such comparison.

DW curves differs from DM ones (***Figure 5***). 10-year old children display higher depositions, peaking at 0.0165 µg.h^{-1}.kg^{-1} in the Al region. In the same region, maximum depositions for adult males and females are 0.0092 and 0.0075 µg.h^{-1}.kg^{-1}, respectively. In comparison with Caucasians, ratios of maximum DW for 10-year old children are 0.970 (0.0165/0.0170). For adult males and females, these ratios are 0.860 (0.0092/0.0107) and 0.714 (0.0075/0.0105), respectively. As for DM, differences between West Africans and Caucasians are observed, amounting to 3% for 10-year old children, 14% for adult males and 29% for adult females. For children, this difference exactly corresponds to the difference in inspiratory flow rates Q. These flow rates characterize breathing intensity in human lung ventilation, i.e. the volume of air inspired or exhaled per unit time. Deposition of inhaled particulates is significantly influenced by this flow rate, which varies with individual activity levels and ages. This result still highlights the major influence of body-weight as for lung deposition.

Deposited masses per unit exposure time per lung volume (DL curves) (***Figure 5***) are similar to those for DW, as regards gender and age. Maximum deposition in the Al region for 10-year old children from West Africa is 0.214 µg.h^{-1}.L^{-1}, thus 1.78 times as large as the 0.120 µg.h^{-1}.L^{-1} for adult females, the same ratio as between their total lung capacity (TLC)

1.82 (3.95/2.17). For adult males, maximum DL is 0.111 µg.h^{-1}.L^{-1}, close to ones for females. For this deposition index, West African to Caucasian ratio is 0.911 for 10 year old children, 0.945 for adult females and 0.991 for adult males. This corresponds to range differences from 1 to 9% between all groups. This is again coherent with TLC ratio variations. Clearly, deposition levels are strongly correlated to changes in indexes, suggesting that it could be important to take into account this parameter for threshold determinations.

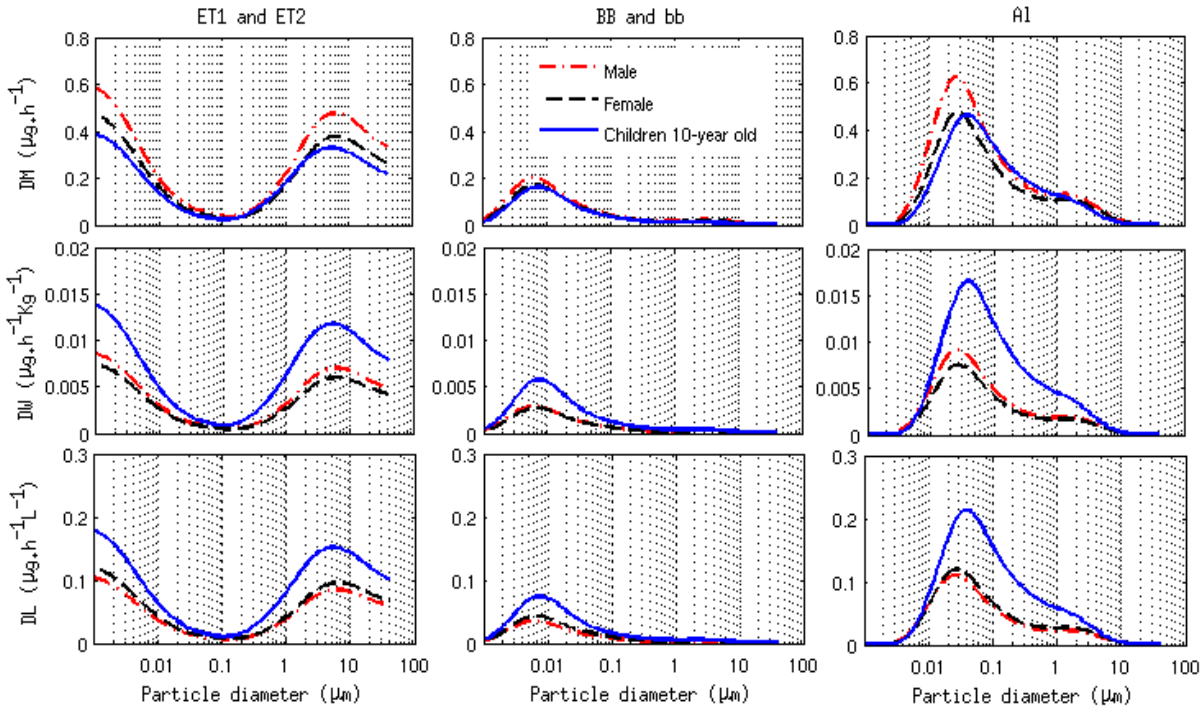

Figure 5: Compartmental particle mass depositions (DM, DW and DL) for West Africans, for light exercise and nasal breathing conditions.

3.2.2. Estimated deposition in lungs as a function of size speciated particle mass concentrations measured in Bamako and Dakar

Figure 6A shows the size distribution patterns for measured particle mass concentrations in BK1, BK2 and in DK during POLCA. These results show that measured mass distributions of particles are highly different during the three sampling periods. Bulk mass concentrations measured in BK1 and BK2 samples are 210.3 and 151.6 µg.m^{-3} respectively, whereas a value of 33.0 µg.m^{-3} was obtained for DK sample. This large variability can be related to the dust episode which occurred during BK1 measurements, in addition to the strong influence everywhere of resuspended particles. Note that in DK lower concentration were observed

(Doumbia et al., 2012a). BK1 sample displays a single mode distribution with peak concentrations in the 4-5µm particle range, implying a large contribution of natural source such as mineral dust from both the Sahara desert and downtown particle resuspension from unpaved roads. BK2 and DK samples show identical bimodal mass distributions (accumulation mode in the 0.01-1µm range and coarse mode for particle diameters over 2.5µm). However, in BK2 sample, the accumulation mode displays the same peak as the coarse mode, 8 times more than observed in DK sample, suggesting similar contribution of natural and anthropogenic sources to BK1 sample. These particles size distribution patterns highlight the mixed state of aerosols in these samples and therefore show different aerosol physical properties which can impact their deposition in the respiratory tract. Values of geometric standard deviation (σ_g) from ELPI results are respectively 1.12 for BK1, 1.75 for BK2 and 1.89 for DK.

The estimated deposition mass DM, for mass distribution measured in Bamako and Dakar using the DEPCLUNG model, and relative to the alveolar region of West African adult males, adult females and 10-year old children, at light exercise and in nasal breathing scenarios, are shown in ***Figure 6B***. These results clearly show that measured particulate distributions input have been modified in the output issued through the DEPCLUNG model, with particles in the accumulation mode (0.01-1µm diameter range) relatively more important in the alveolar region than at nose level. This confirms that fine particles more deeply penetrate into the respiratory tract than larger ones. This is coherent with the conclusions of **Val et al. (2013)**, in which BK and DK aerosols induce a clear pro-inflammatory response of the airway epithelium, especially for the finest particles (< 1µm). Peak of fine to coarse ratios are changed a lot comparing input and output data: 1) for BK2 sample, an input ratio of 0.96 (24.1/25.2) was measured, which becomes 3.01 (2.99/9.01) at the output; 2) for DK sample, an input ratio of 0.43 (3.1/7.2) was measured, while model output gives a ratio 4 times higher (1.65 = 1.15/0.70) for adult males; 3) BK1 sample displays a single input coarse mode, while the model displays a wide peak covering both fine and coarse modes. Comparing the maximum mass concentrations for BK1 (dust event, 42.9 µg.m^{-3}) and BK2 samples (25.2 µg.m^{-3}) (***Figure 6***, cf. scales), a peak ratio of 1.70 was obtained as an input to DEPCLUNG, whereas the output gives a ratio 4 times lower (0.45 = 4.14/9.22), denoting low significance of mass concentration in deposition. The same observations are obtained when comparing BK and DK samples. All these results illustrate the predominant role of particle characteristics (mostly size distributions and standard deviations) over particle mass on particle deposition

calculation in the respiratory tract system, with subsequent quite large implications for aerosol health effects. No clear difference in estimated deposition mass concentrations has been found between adult males, adult females and 10-year hold children, despite large differences in breathing patterns among these different groups.

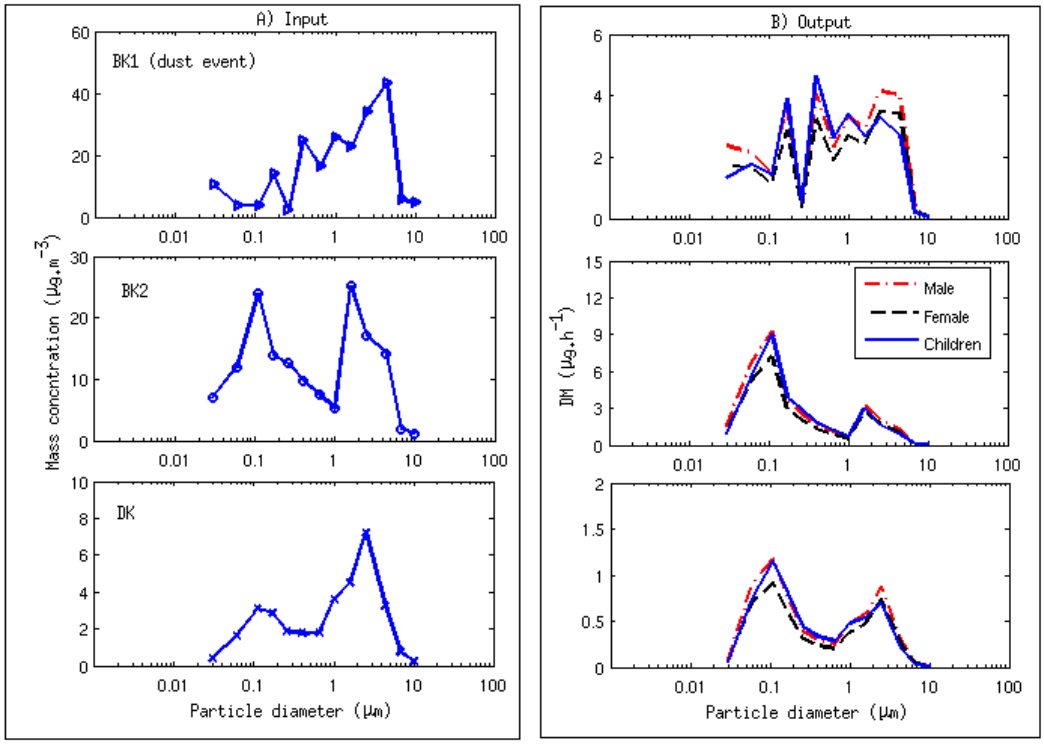

Figure 6: A) inhaled measured concentrations versus B) estimated deposited masses DM in alveolar region for West African adult males (dash-dot), adult females (dash) and 10-year old child (lines), in case of light exercise and nasal breathing.

3.2.3. Estimated lung depositions as a function of measured size speciated chemical aerosol distributions in Bamako and Dakar

Aerosol chemical characteristics are of key interest regarding particle deposition in lungs, due to significant particle differences between aerosol components. This section investigates the influence of aerosol components in terms of deposited mass rates per unit surface (SDMR). ***Figure 7*** shows particle size speciated aerosol chemistry (particulate organic matter POM, black carbon BC, sulfate, nitrate, chloride and estimated mineral dust) from BK2 and DK samples. An extensive description of chemical composition of aerosols in BK and DK has been discussed in **Val et al. (2013)**. POM, the most abundant aerosol component in BK2 sample, was expected to have the higher toxicological effects as compared to BK1 and DK (**Val et al., 2013**). BC is relatively more important in DK than in BK2. Our results also

display high composition variability between particle classes of sizes. Generally, POM and BC sizes in both BK2 and DK samples display bimodal distributions, with smaller peaks in the larger particle diameters (> 1.0µm) and the higher peaks in the small particle diameters range (0.25-0.50µm). Therefore, carbonaceous aerosols would have strong implications for inhalation exposure due to their sizes. **Morawska et al. (2005)** also demonstrate that combustion aerosols (diesel, oil and tobacco smoke) show significant differences in total deposition in lungs between these three aerosol types due to differences in aerosol median diameters. Dust aerosols, sulfate, nitrate, and chloride size distributions peak at large particle diameters (2.5-10µm), both in BK2 and DK samples, with dust mass concentrations higher in BK2 than in DK.

Lung deposition patterns for aerosol components measured in BK2 and DK, within the different compartments of the respiratory tract of West African adult males were estimated using the measured size speciation as input data for DEPCLUNG (***Figure 7***). It appears that each component is distributed differently in the compartments of the respiratory tract. Species which display peak concentration below 1µm particle diameters are strongly deposited deeply in the respiratory tract (for example in the Al region). Moreover, when looking at relative component abundances in the Al region, deposited mass rates in this region for BK2 sample (in the particle fraction below 0.5µm diameter) has mean values of 60% for POM and 52% for BC. Same amounts for DK sample displays mean values of 50% for POM and 59% for BC. Such high percentages also underline the most likely negative effect of carbonaceous aerosols on public health **(Mauderly and Chow, 2008**).

Table 5 shows estimated doses of the different aerosol components for BK2 and DK samples as a function of particles sizes in the Al region. Recently, **Paur et al. (2011)** have underlined the difference between in-vitro dose levels and realistic in-vivo fine particle (< 0.1µm) doses in the lung. The authors reported that when considering average ambient urban exposure at 5000 $\mu g.m^{-3}$ as the boundary of human exposure, the corresponding upper-limit range of fine particle flux delivered to the lung tissue ranged between 3E-05 and 5E-03 $\mu g.h^{-1}.cm^{-2}$. As shown in ***Table 5***, this range is reached for POM component and in a less extent for BC for both BK2 and DK results. These results show the importance of chemical aerosol composition (linked to the main source difference here between BK2 and DK), which highly affect deposition processes. Nevertheless, deposition of large particles in the upper airways has also health implications. Dust aerosols are mostly deposited in the ET and BB regions (for more than 80%), probably due to their large diameters, suggesting the efficiency of gravitational settling process and removal before reaching the bb and Al regions. It was also

expected that other elements such as NO_3^-, SO_3^{2-} and Cl^- are mainly deposited in the upper respiratory tract. This has consequences, because mineral dust, for example, mainly deposited in the extra-thoracic region can be one cause of bacterial meningitis (**Yaka et al., 2008**). However, BK1 results (not shown here) typical of dust event show that dust more deeply deposited in the respiratory tract due to higher content of smaller particles. These preliminary results highlight the importance to put links between aerosol chemical composition and deposition within the respiratory tract.

Table 5: Estimated doses of BK2 and DK aerosol components in the Al region as a function of particle sizes.

BK2	POM	BC	SO_4^{2-}	Cl^-	NO_3^-	Dust
Particle size (µm)	Dose in alveolar region (µg.h^{-1}.cm^{-2})					
<0.25	9E-05	1E-05	1E-05	2E-06	6E-07	2E-05
0.25-0.5	7E-05	2E-05	6E-07	1E-06	3E-07	9E-06
0.5-1.0	5E-05	1E-05	7E-07	6E-07	2E-07	1E-05
1.0-2.5	5E-05	1E-05	1E-06	9E-07	2E-07	3E-05
>2.5	1E-05	2E-06	6E-07	5E-07	2E-07	2E-05

DK	POM	BC	SO_4^{2-}	Cl^-	NO_3^-	Dust
Particle size (µm)	Dose in alveolar region (µg.h^{-1}.cm^{-2})					
<0.25	3E-05	1E-05	3E-06	7E-07	3E-07	2E-06
0.25-0.5	4E-05	2E-05	1E-06	2E-07	3E-07	1E-06
0.5-1.0	3E-05	1E-05	8E-07	6E-07	6E-07	3E-06
1.0-2.5	3E-05	6E-06	1E-06	2E-06	1E-06	7E-06
>2.5	1E-05	3E-06	1E-06	3E-06	7E-07	1E-05

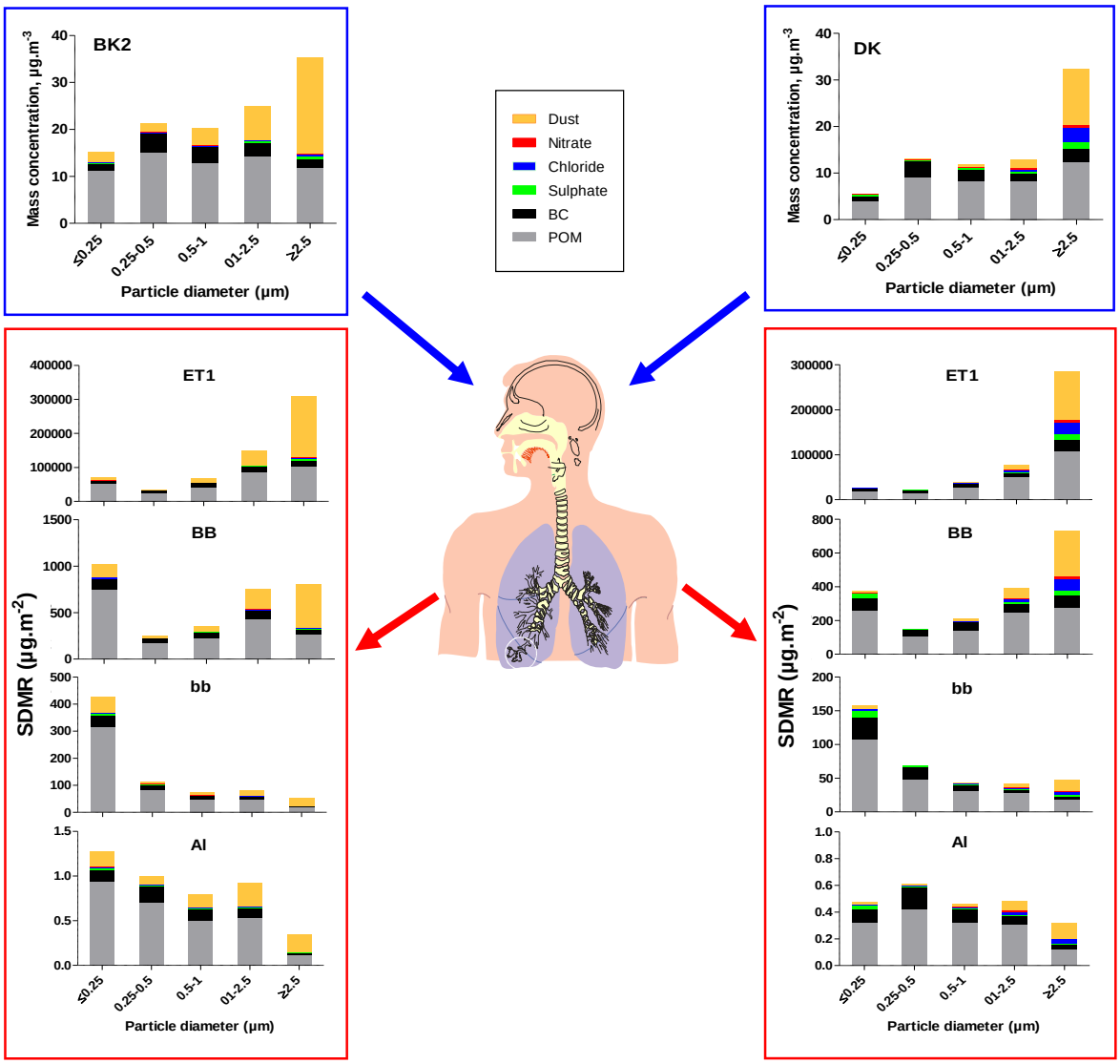

Figure 7: Compartmental particle deposition expressed in Standard Deposition Mass Rate (SDMR) for West African adult males, for light exercise and nasal breathing (BK2 on left side and DK on right side).

4. Conclusions

This study, the first one of this type in West Africa, was devoted to the evaluation of particle deposition in the respiratory tract of West African populations (males, females and children) using the DEPCLUNG model. Our results highlight particle deposition in lungs as being strongly dependent upon population age, lung characteristics and respiratory capacities. Indeed, differences in deposition were observed between males, females and children, whatever deposition parameter considered. Deposition fractions (DF) are rather similar for adult West Africans and Caucasians. For 10-year old children, differences have appeared between these two population groups, probably due to greater tidal volume (V_T) in West African children than in Caucasian ones. This can also be explained by inherent uncertainties and variability in input parameters, along with general lack of data about lung capacities for Africans, particularly for children: much more investigations are needed. This study shows that lung particle depositions do not depend only on size distribution, but also on chemical composition. Our results illustrate the predominant role of particle characteristics, mostly size distributions over particle mass, on lung deposition. Therefore, depending on the predominant sources at site of study, different input and output chemical compositions have been determined. Such distributions will still be modified when more thoroughly introducing particle solubility/hygroscopicity characteristics in DEPCLUNG. Indeed, we can project that more OC solubility will result in increased deposition before reaching the Al region. Depending on the predominant sources, not the same inhaled species that will reach the alveoli regions.

Such results will allow to better link toxicological and physico-chemical studies. Indeed up to now, alveoli cells are mixed to inhaled studies atmospheric aerosols for toxicological studies. This study shows the need to take into account the differences (both in size/chemistry/mass) occurring between inhalable particles and respiratory tract particles.

References (A4)

Adon, M., Galy-Lacaux, C., Yoboué, V., Delon, C., Lacaux, J.P., Castera, P., Gardrat, E., Pienaar, J., Al Ourabi, H., Laouali, D., others, 2010. Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers. Atmos. Chem. Phys 10, 7467–7487.

Asgharian, B., Ménache, M.G., Miller, F.J., 2004. Modeling age-related particle deposition in humans. J Aerosol Med 17, 213–224.

Bair, W.J., 1995. The ICRP Human Respiratory Tract Model for Radiological Protection. Radiat Prot Dosimetry 60, 307–310.

Bair, W.J., al., 1994. Human Respiratory Tract Model for Radiological Protection. volume 24 of Annals of the ICRP: ICRP Publication 66, Pergamon Oxford.

Bartley, D.L., Vincent, J.H., 2011. Sampling Conventions for Estimating Ultrafine and Fine Aerosol Particle Deposition in the Human Respiratory Tract. Annals of Occupational Hygiene 55, 696–709.

Bolch, W.E., Farfán, E.B., Huh, C., Huston, T.E., Bolch, W.E., 2001. Influences of parameter uncertainties within the ICRP 66 respiratory tract model. Health Physics 81, 378–394.

Brown, J.S., Zeman, K.L., Bennett, W.D., 2002. Ultrafine Particle Deposition and Clearance in the Healthy and Obstructed Lung. Am. J. Respir. Crit. Care Med. 166, 1240–1247.

Cheng, Y.S., 2003. Aerosol Deposition in the Extrathoracic Region. Aerosol Science and Technology 37, 659–671.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The dri thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies. Atmospheric Environment. Part A. General Topics 27, 1185–1201.

D'Almeida, G.A., Koepke, P., Shettle, E.P., 1991. Atmospheric Aerosols: Global Climatology and Radiative Characteristics. A. Deepak, Hampton, Va. 561.

Dockery, D.W., Pope, C.A., 3rd, Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Jr, Speizer, F.E., 1993. An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med. 329, 1753–1759.

Doumbia, E.H.T., Liousse, C., Galy-Lacaux, C., Ndiaye, S.A., Diop, B., Ouafo, M., Assamoi, E.M., Gardrat, E., Castera, P., Rosset, R., Akpo, A., Sigha, L., 2012a. Real time black carbon measurements in West and Central Africa urban sites. Atmospheric Environment 54, 529–537.

Dufetel, P., Pigearias, B., Lonsdorfer, J., Derossi, G., Diaine, C., Faltot, P.J., 1989. Spirometric Reference Values in Senegalese Black Adults. Eur Respir J 2, 352–358.

Dufetel, P., Sambiani, K., Togbey, K., Kolani, M., 1990. Characteristics of lung volume and expiratory flow seen in black Africans adults. Rev Mal Respir 7, 215–222.

Fritsch, P., 2006. Uncertainties in aerosol deposition within the respiratory tract using the ICRP 66 model: a study in workers. Health Physics 90, 114–126.

Happo, M.S., Hirvonen, M.-R., Halinen, A.I., Jalava, P.I., Pennanen, A.S., Sillanpaa, M., Hillamo, R., Salonen, R.O., 2008. Chemical compositions responsible for inflammation and tissue damage in the mouse lung by coarse and fine particulate samples from contrasting air pollution in Europe. Inhal Toxicol 20, 1215–1231.

Harvey, R.P., Hamby, D.M., 2002. Age-specific Uncertainty in Particulate Deposition for 1 µm AMAD Particles Using the ICRP-66 Lung Model. Health Physics 82, 807–816.

Hinds, W.C., 1982. Aerosol technology: properties, behavior, and measurement of airborne particles.

Huang, S.-L., Hsu, M.-K., Chan, C.-C., 2002. Effects of Submicrometer Particle Compositions on Cytokine Production and Lipid Peroxidation of Human Bronchial Epithelial Cells. Environmental Health Perspectives 111, 478–482.

ICRP, 1994. Human Respiratory Tract Model for Radiological Protection, Annal of the international Commission on Radiological Protection (ICRP). Pergamon Press, Oxford, UK.

James, A.C., Stahlhofen, W., Rudolf, G., Egan, M.J., Nixon, W., Gehr, P., Briant, J.K., 1991. The Respiratory Tract Deposition Model Proposed by the ICRP Task Group. Radiat Prot Dosimetry 38, 159–165.

Jaques, P.A., Kim, C.S., 2000. Measurement of total lung deposition of inhaled ultrafine particles in healthy men and women. Inhal Toxicol 12, 715–731.

Kim, C.S., Hu, S.-C., 2006. Total respiratory tract deposition of fine micrometer-sized particles in healthy adults: empirical equations for sex and breathing pattern. J Appl Physiol 101, 401–412.

Kuloglu, E., Tuncel, G., 2005. Size Distribution of Trace Elements and Major Ions in the Eastern Mediterranean Atmosphere. Water, Air, and Soil Pollution 167, 221–241.

Lapp, N.L., Amandus, H.E., Hall, R., Morgan, W.K.C., 1974. Lung volumes and flow rates in black and white subjects. Thorax 29, 185–188.

Löndahl, J., Massling, A., Pagels, J., Swietlicki, E., Vaclavik, E., Loft, S., 2007. Size-Resolved Respiratory-Tract Deposition of Fine and Ultrafine Hydrophobic and Hygroscopic Aerosol Particles During Rest and Exercise. Inhalation Toxicology 19, 109–116.

Mauderly, J.L., Chow, J.C., 2008. Health Effects of Organic Aerosols. Inhalation Toxicology 20, 257–288.

Miller, G.J., Saunders, M.J., Gilson, R.J.C., Ashcroft, M.T., 1977. Lung function of healthy boys and girls in Jamaica in relation to ethnic composition, test exercise performance, and habitual physical activity. Thorax 32, 486–496.

Morawska, L., Hofmann, W., Hitchins-Loveday, J., Swanson, C., Mengersen, K., 2005. Experimental study of the deposition of combustion aerosols in the human respiratory tract. Journal of Aerosol Science 36, 939–957.

Onyedum, C.C., Chukwuka, J.C., Onwubere, B.J.C., Ulasi, I.I., Onwuekwe, I.O., 2010. Respiratory symptoms and ventilatory function tests in Nigerians with HIV infection. African health sciences 10.

Ostro, B., Feng, W.-Y., Broadwin, R., Green, S., Lipsett, M., 2007. The effects of components of fine particulate air pollution on mortality in california: results from CALFINE. Environ. Health Perspect. 115, 13–19.

Paur, H.-R., Cassee, F.R., Teeguarden, J., Fissan, H., Diabate, S., Aufderheide, M., Kreyling, W.G., Hänninen, O., Kasper, G., Riediker, M., Rothen-Rutishauser, B., Schmid, O., 2011. In-vitro cell exposure studies for the assessment of nanoparticle toxicity in the lung—A dialog between aerosol science and biology. Journal of Aerosol Science 42, 668–692.

Pichelin, M., Caillibotte, G., Katz, I., Martonen, T., 2012. Categorization of Lung Morphology Based on FRC and Height: Computer Simulations of Aerosol Deposition. Aerosol Science and Technology 46, 70–81.

Pope, C.A., Young, B., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association 56, 709–742.

Raabe, O.G., Howard, R.S., Cross, C.E., 1986. Aerosol considerations in asthma. Bronchial asthma. M. E. Gershwin. Orlando, FL, Brune & Stratton, Inc. 495–514.

Roy, M., Becquemin, M.H., Bouchikhi, A., 1991. Ventilation rates and lung volumes for lung modelling purposes in ethnic groups. Radiation Protection Dosimetry, Nuclear Technology Publishing 38, 49–55.

Seck, G., Kane, M., Fall, M., Faltot, P.J., 1990. Abaques de Références Anthropo-spirométriques chez les Sénégalais âgé de 3 à 23 ans, in: Symposium on Nouvelles Acquisitions Sur l'Asthme Bronchique. Ferrara, Italie.

Sloane, C.S., 1983. Optical properties of aerosols: Comparison of measurements with model calculations. Atmospheric Environment 17, 409–416.

Val, S., Liousse, C., Doumbia, E.H.T., Galy-Lacaux, C., Cachier, H., Marchand, N., Badel, A., Gardrat, E., Baeza-Squiban, A., 2013. Physico chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells: description of a worrying situation. In review process on Particle and Fibre Toxicology.

WHO | Air quality and health [WWW Document], 2012. WHO. URL http://www.who.int/mediacentre/factsheets/fs313/en/index.html

Yaka, P., Sultan, B., Broutin, H., Janicot, S., Philippon, S., Fourquet, N., 2008. Relationships between climate and year-to-year variability in meningitis outbreaks: A case study in Burkina Faso and Niger. Int J Health Geogr 7, 34.

Yamada, Y., Fukutsu, K., Kurihara, O., Momose, T., Miyabe, K., Akashi, M., 2007. Influences of Biometrical Parameters on Aerosol Deposition in the ICRP 66 Human Respiratory Tract Model: Japanese and Caucasians. Earozoru Kenkyu 22, 236–243.

CHAPITRE VI : ETUDE D'IMPACT TOXICOLOGIQUE DE L'AEROSOL A BAMAKO ET DAKAR

Introduction

POLCA, consacré d'une manière générale à la caractérisation physico-chimique complète de la pollution atmosphérique gazeuse et particulaire en zone urbaine africaine et de son impact sur la santé, permet de mieux renseigner sur les niveaux élevés des polluants mais également leur toxicité.

Le volet impact sanitaire des particules urbaines africaines a consisté à étudier leurs effets biologiques à court terme. Ce volet constitue l'un des objectifs du programme POLCA tout en soulignant le caractère pluridisciplinaire de nos travaux. Différents laboratoires ont été impliqués dans la collecte des échantillons et leurs analyses. La ***Figure VI-1*** schématise le rôle joué par chacun d'eux. Avec mon laboratoire (LA/OMP), j'ai réalisé la collecte des particules d'aérosols par classes de tailles, leur caractérisation physico-chimique (distribution en tailles, masse, ensemble des mesures chimiques exceptés les HAPs, les analyses biologiques et les organiques solubles), et j'ai analysé, avec les différentes équipes impliquées, les résultats obtenus. Cette partie a fait l'objet d'un **Article (A5)** en cours de révision intitulé « Physico-chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells », et qui est présenté à la fin de ce chapitre.

Les pays d'Afrique de l'Ouest sont confrontés à des niveaux de pollutions du même ordre de grandeur que les grandes mégalopoles européennes, asiatiques et américaines comme vu précédemment. Pourtant, il n'existe pratiquement pas de réglementation pour lutter efficacement contre cette pollution, elles sont toutes au plus très limitées. Ce défaut institutionnel ne prend pas en compte les dégâts engendrés en terme de santé publique et donc de coût financier. De ce fait, il est plus que nécessaire que des études dans ce sens soient réalisées. Depuis peu, des initiatives ont cependant été prises dans certaines villes d'Afrique de l'Ouest. C'est le cas notamment à Dakar où le CETUD (Conseil Exécutif des Transports Urbains de Dakar), sous la tutelle du gouvernement du Sénégal et en partenariat avec le Fond Nordique de Développement, a mis en place un Centre de Gestion de la Qualité de l'Air (CGQA). Le programme POLCA en est également une illustration.

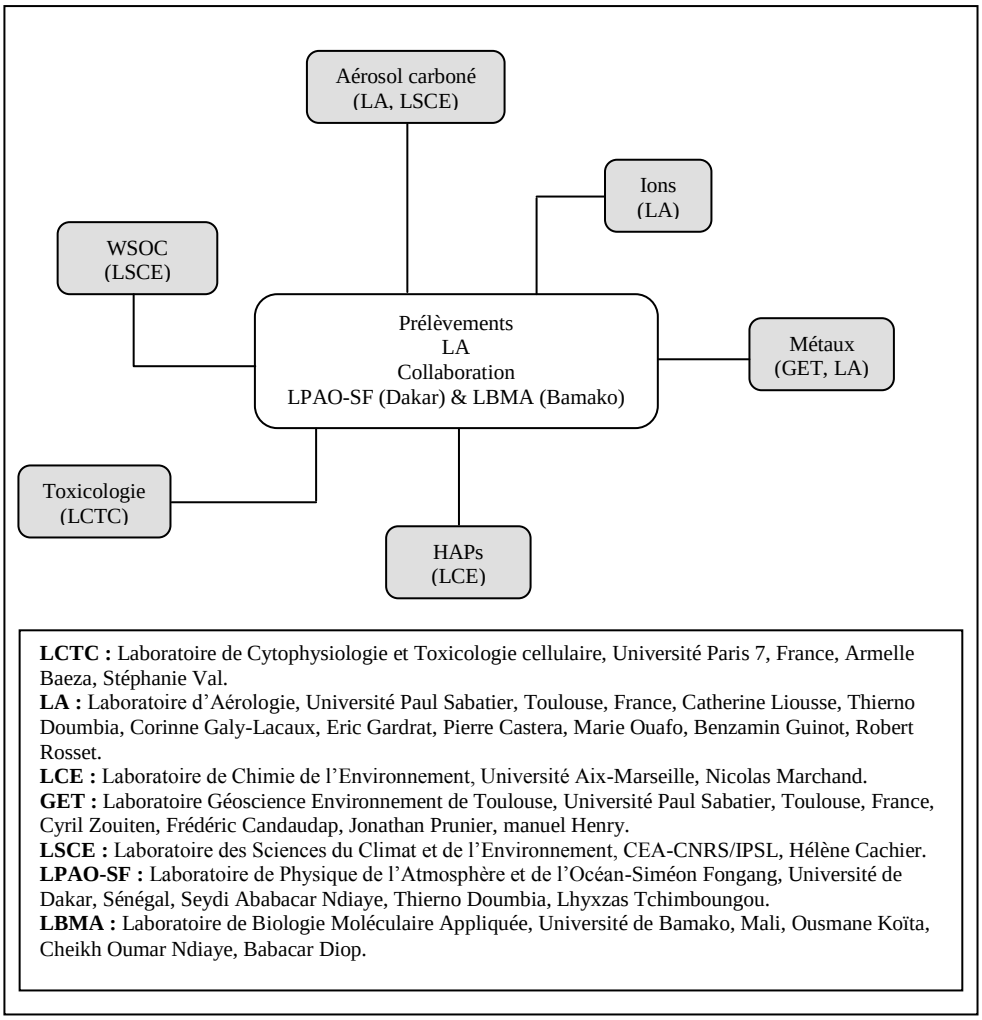

Figure VI-1 : Organigramme des différents laboratoires qui ont contribué aux mesures et aux analyses.

VI.1. Description de la méthodologie

VI.1.1. Echantillonnage des aérosols pour analyses toxicologiques

Les prélèvements, par classes de tailles, de l'aérosol Ouest Africain ont été réalisés à Bamako et Dakar en plein carrefour, au cours de campagnes intensives de terrain décrites au chapitre II de ce manuscrit.

Le prélèvement par impaction des aérosols destinés aux analyses biologiques a été réalisé avec un impacteur basse pression de type DEKATI/ELPI à 13-étages. Il fonctionnait en parallèle avec d'autres impacteurs pour les analyses physico-chimiques : 1 DEKATI réservé à la mesure des espèces ioniques, métaux traces et de la gravimétrie, 1 SIOUTAS 5-étages pour la détermination de l'aérosol carboné, mais également des composés organiques solubles, et un impacteur haut volume de type STAPLEX pour la mesure des HAPs totaux.

Les impacteurs DEKATI et SIOUTAS collectent les particules à des classes de tailles différentes. Par souci de cohérence, trois classes de tailles ont été définies : les ultrafines (UF) de tailles entre 0,03 et 0,17 µm, les fines (F) de 0,17 à 0.65 µm et les particules grossières (G) de 0,65 à 10 µm. La ***Figure VI-2*** montre le regroupement effectué à partir des deux instruments. Trois cas typiques des mélanges caractéristiques de l'aérosol africain ont été étudiés : à Bamako lors d'un événement de poussière (BK1), après le passage de cet épisode (BK2) et à Dakar (DK).

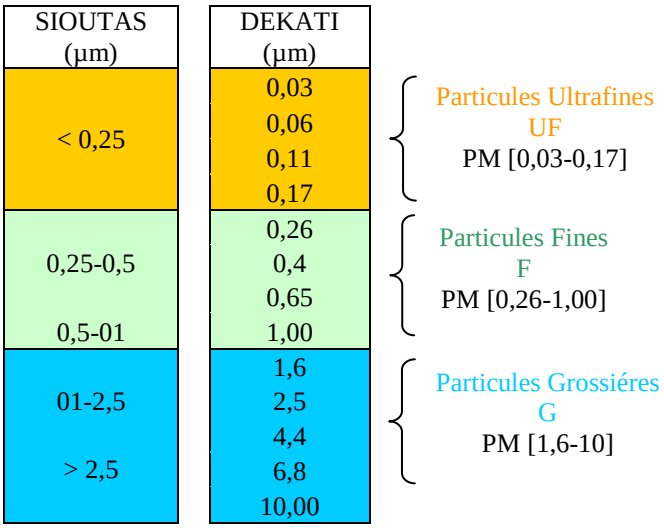

Figure VI-2 : Classification par classes de tailles des étages d'impaction des deux types d'impacteurs (DEKATI et SIOUTAS).

VI.1.2. Description des analyses toxicologiques en laboratoire

Afin de pouvoir utilisé les particules regroupés par classe de tailles sur les cellules épithéliales bronchiques étudiées (lignée 16HBE), les particules sont extraites des membranes suivant la méthodologie décrite par **Ramgolam et al. (2009)**, présentée dans l'article A5, avant traitement.

Les analyses biologiques consistent à caractériser la réponse des cellules 16HBE à l'exposition à court terme à différentes concentrations de particules. Le potentiel pro-inflammatoire des particules a été déterminé en étudiant la sécrétion des GM-CSF et des IL-6 et IL-8 induite par les particules, cytokines exprimées par les cellules 16HBE (**Ramgolam et al., 2009 ; Val et al., 2009**). Le dosage des CYP1A1 a été également effectué, bio-marqueur dont l'expression est induite spécifiquement par les hydrocarbures aromatiques polycycliques (HAPs) (**Seagrave et al., 2006**). La caractérisation de l'effet des particules sur les gènes

activés par des xénobiotiques mesurés a été menée. Il s'agit de l'enzyme anti-oxydante hème oxygénase-1 (HO-1) dont le rôle est de limiter les dommages faits à la cellule lors d'un stress oxydant et du facteur de croissance, l'amphiréguline (AREG) bio-marqueur dont la sensibilité aux PM a été observée (**Rumelhard et al., 2007**). Les particules extraites des filtres sont exposées sur les cellules pendant 24h afin de quantifier la réponse pro-inflammatoire provoquée à court terme mais également pour différentes fractions granulométriques et différentes doses de particules (1, 5 puis 10 µg/cm^2). Une description plus détaillée est donnée dans l'**Article A5** en fin de ce chapitre.

Notons que la caractérisation de l'effet des particules collectées à Bamako sur la sécrétion des mucus par une autre lignée de cellules (NCI-H292) a fait l'objet d'un sujet de stage de master et que les résultats ne sont pas intégrés dans la publication. En effet, cette étude ne portant que sur l'échantillon de Bamako, ne fera pas l'objet d'une discussion détaillée.

VI.2. Présentation des principaux résultats

VI.2.1. Caractérisation physico-chimique de l'aérosol à Bamako et Dakar

La physico-chimie de l'aérosol à Bamako et Dakar montre des caractéristiques variées (***Figure VI-3***). En effet, les particules de BK1 essentiellement composées de poussières provenant du Sahara, sont caractéristiques de l'événement de poussière observé le 22 Janvier 2009 mais également de particules en resuspension comme le montrent les **Articles A2** et **A3**. Plus de la moitié de cet aérosol se retrouve dans la fraction grossière (***Figure VI-3***). Par contre, les échantillons BK2 et DK sont dominés par les espèces carbonées (BC et POM) et se retrouvent principalement dans les fractions F et UF, indiquant une influence accrue des sources anthropiques. Il ressort également que les particules à Bamako ont un caractère plus solubles (WSOC est plus important à Bamako qu'à Dakar) tandis que les hydrocarbures aromatiques polycycliques (HAPs) sont beaucoup plus élevés dans les échantillons de Dakar.

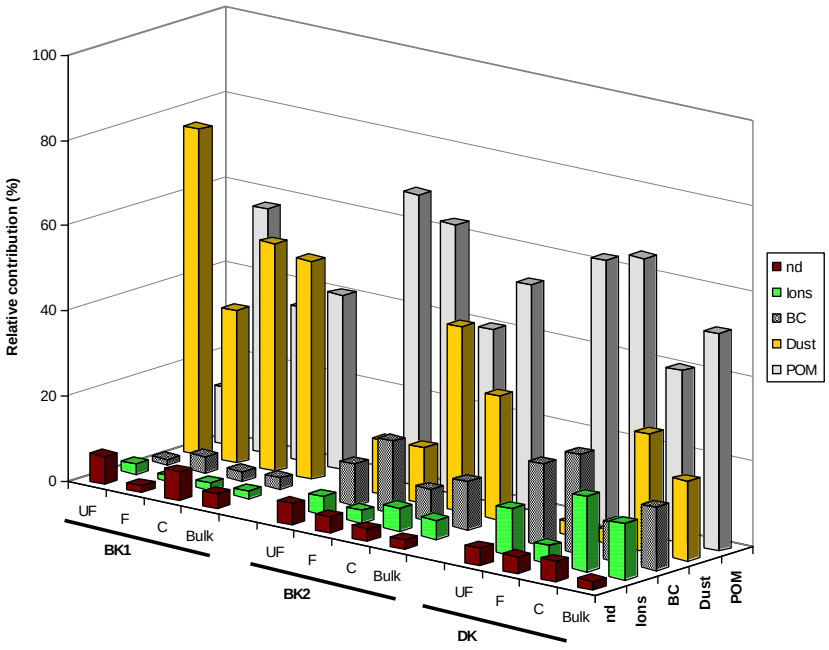

Figure VI-3: Composition chimique de l'aérosol par classe de taille à Bamako (BK1 cas d'un épisode de poussière et BK2 hors événement de poussière) et à Dakar (DK).

VI.2.2. Relation entre physico-chimie des aérosols et réponse pro-inflammatoire

La toxicité de l'aérosol en Afrique de l'Ouest est étudiée sous deux aspects : 1) la réponse des cellules épithéliales bronchiques (16HBE) à des concentrations progressives de 1 à 10 µg/cm^2 de particules à BK1, BK2 et DK (effet dose-réponse) pour différentes classes de tailles ; et 2) la corrélation entre espèces chimiques analysées et la sécrétion de cytokines.

1) Les résultats obtenus montrent un effet dose-réponse positif, c'est à dire que pour des particules de même taille, l'expression des bio-marqueurs augmente avec la concentration en particules mises en contact avec les cellules. Cependant, pour une même concentration, l'expression de l'ensemble des bio-marqueurs est la plus importante pour les particules fines (F) et ultrafines (UF). Selon des études similaires à Paris (**Ramgolam et al., 2009**), ce résultat serait en partie lié à la proportion en masse de la fraction F et UF, beaucoup plus importante. Ce qui n'est pas le cas l'aérosol Ouest Africain où l'on obtient une prédominance de la fraction grossière (F et UF) dans l'aérosol collecté à BK1, BK2 et DK. Les grosses particules regroupent donc la majorité de la masse de l'aérosol et pourtant, elles n'induisent que faiblement l'expression de cytokines. Il est donc clair que la forte induction produite par les particules UF et F repose sur leurs propriétés spécifiques, notamment du fait qu'elles offrent une plus grande surface de réactivité. A titre d'exemple, le ***Tableau VI-1*** indique que les

particules de ces tailles là présentent des surfaces importantes. A masse égale, la comparaison entre les trois prélèvements montre que les réponses pro-inflammatoires (sécrétion de GM-CSF par exemple) sont plus importantes pour BK2 par rapport aux échantillons de BK1 et DK. Ce résultat suggère que les particules collectées lors de l'échantillonnage de BK2 sont plus toxiques que celles prélevées pendant BK1 et en DK. Ceci pourrait s'expliquer par un mélange d'aérosols composé de particules de caractéristiques diverses pouvant influencer la sécrétion de cytokines. En effet, l'aérosol de BK2 contient plus d'organique soluble (cf. **Article A5**), ce qui suggère une perte de leur forme initiale et de leurs propriétés physiques une fois en contact avec les cellules. Dans ce cas, la réponse cellulaire dépend de la composition et du nombre de particules. Comme on le voit dans le ***Tableau VI-1***, le nombre de particules est plus élevé à BK2, quelle que soit la fraction considérée. Précisons que pour les particules insolubles, c'est plutôt la surface des particules qui détermine la réponse physiologique (**Löndahl et al., 2007**). La comparaison avec les résultats obtenus à Paris **(Ramgolam et al., 2009**) souligne également le potentiel oxydant de l'aérosol africain, indiquant probablement des effets sanitaires plus importants pour les populations ouest africaines.

Tableau VI.1 : Nombre et surface des particules mesurées à l'aide d'un ELPI à Bamako (BK1 et BK2) et Dakar (DK) pour différentes classes de taille.

	Nombre de particules (cm^{-3})			Surface ($\mu m^2/cm^3$)		
Diamètre (µm)	BK1	BK2	DK	BK1	BK2	DK
PM [0,03-0,17]	18264	27334	21655	373	714	517
PM [0,26-1,00]	4259	14696	4511	1216	4772	1231
PM [1;6-10,00]	229	136	37	3389	1885	641

2) L'analyse de la spéciation chimique de l'aérosol en fonction des bio-marqueurs étudiés montre de meilleures corrélations entre d'une part les différentes espèces chimiques et le GM-CSF et d'autre part entre les différents bi-marqueurs et l'aérosol carboné (BC et POM). La ***Figure VI-4*** présente des exemples de courbes dose-réponse entre concentration de cytokine GM-CSF et de matière organique (POM) pour les particules fines de BK1 (épisode de poussière), BK2 (après l'épisode de poussière) et DK. Les courbes dose-réponses montrent des réponses plus marquées pour l'échantillon BK2 et DK par rapport à BK1, avec une meilleure réponse pour BK2 comparé à DK. Ce résultat serait-il lié au caractère soluble de l'aérosol organique (POM) de BK2 comme la montré **Ramgolam et al., 2009** pour les

échantillons parisiens ? Ceci pourrait être une explication car il y'a plus d'organique soluble à Bamako qu'à Dakar comme on le voit sur le ***Tableau 4*** de l'**Article A5.** Par ailleurs, il semble que les sources de nature incomplète à Bamako (notamment des deux-roues et des feux domestiques) auraient un impact plus important que les sources de type diesel à Dakar. Cependant, la sensibilité de certaines cytokines aux particules produites par les sources naturelles n'est pas négligeable malgré les faibles corrélations observées.

Finalement, les résultats décrits dans ce chapitre mettent en évidence la capacité de l'aérosol africain à provoquer de manière forte, par rapport à d'autres types de particules, la sécrétion de biomarqueurs impliqués dans l'aggravation de certaines pathologies respiratoires. Il est donc urgent que les autorités compétentes prennent conscience du degré de toxicité des particules émises dans les villes d'Afrique de l'Ouest et que des décisions soit prises en vue de limiter ces émissions.

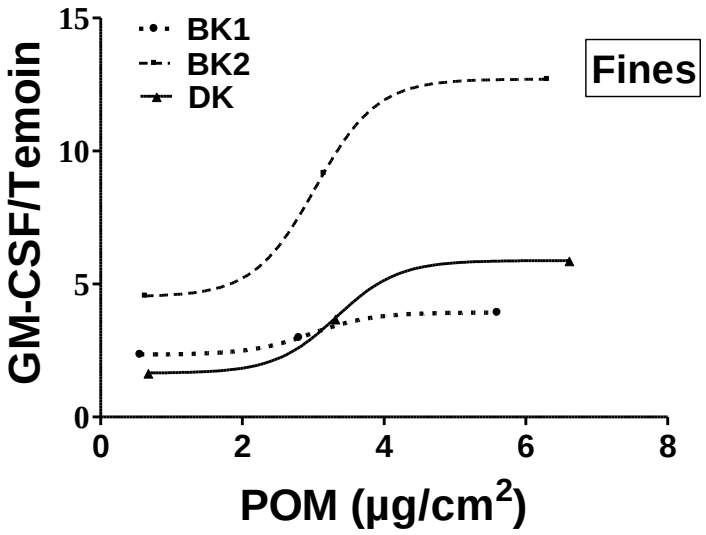

Figure VI-4: Sécrétion de GM-CSF en fonction de la concentration des fines particules de POM pour les échantillons de BK1, BK2 et DK.

I.3. Article A5

"Physico-chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells"

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En cours de révision dans Particle Fiber Toxicology

Abstract

Background: The involvement of particulate matter (PM) in cardiorespiratory diseases is now established in developed countries whereas in developing areas such as Africa with a high level of specific pollution, PM pollution and its effects are poorly studied. Our objective was to characterize the biological reactivity of urban African aerosols on human bronchial epithelial cells (16HBE) in relation to PM physico-chemical properties to identify toxic sources.

Methods: Size-speciated aerosol chemical composition was analyzed in Bamako (BK, Mali, 2 samples with one having dust event BK1) and Dakar (DK; Senegal) for Ultrafine UF, Fine F and Coarse C PM. PM reactivity was studied in human bronchial epithelial cells investigating six biomarkers (oxidative stress responsive genes and pro-inflammatory cytokines).

Results: PM mass concentrations were mainly distributed in coarse mode (60%) and were impressive in BK1 due to the dust event. BK2 and DK samples showed a high content of total carbon characteristic of urban areas. The DK sample had huge PAH quantities in bulk aerosol compared with BK that had more water soluble organic carbon and metals. Whatever the site, UF and F PM triggered the mRNA expression of the different biomarkers whereas coarse PM had little or no effect. The GM-CSF biomarker was the most discriminating and showed the strongest pro-inflammatory effect of BK2 PM. The analysis of gene expression signature and of their correlation with main PM compounds revealed that PM-induced responses are mainly related to organic compounds. The toxicity of African aerosols is carried by the finest PM as with Parisian aerosols, but when considering PM mass concentrations, the African population is more highly exposed to toxic particulate pollution than French population. Regarding the prevailing sources in each site, aerosol biological impacts are higher for incomplete combustion sources (two-wheel vehicles, domestic fires) than for diesel vehicles (Dakar). Dust events seem to produce fewer biological impacts than anthropogenic sources.

Discussion Our study shows that combustion sources contribute to the high toxicity of F and UF PM of African urban aerosols, and underlines the importance of emission mitigation and the imperative need to evaluate and to regulate particulate pollution in Africa.

Keywords: 16HBE, particle, lung, inflammation, metabolism, oxidative stress, organic compounds, traffic emissions, domestic fires, dust event.

Background

A number of epidemiological studies have now established associations between exposure to particulate pollution and increased morbidity and mortality for respiratory and cardiovascular diseases **[1]**. Toxicological investigations in animals and humans have shown that the major short term effect of particle exposure is a lung inflammation even a systemic inflammation **[2]** that in chronic condition is suspected to contribute to the exacerbation of chronic inflammatory diseases such as asthma and chronic obstructive pulmonary disease (COPD), particularly among vulnerable populations **[3]**. The fine and ultrafine fractions of the aerosol are now recognized as the more prone to induce biological effects due to their ability to reach the distal lung together with specific compositions including transition metals and organic compounds **[4, 5, 6]**. Particle toxicity results from their ability to trigger intracellular production of reactive oxygen species (ROS) in epithelial cells and macrophages, the first cells encountered by particles in the respiratory tract. This oxidative stress activates signalling pathways leading to the release of pro-inflammatory mediators (interleukins IL-8, IL-6; granulocyte macrophage colony stimulating factor GM-CSF….) **[7]**.

The effects of particles on health have been studied extensively in developed countries leading to specific regulations. Only a few studies have been conducted in developing countries such as in Africa **[8, 9]**. This is in spite of the very high levels of pollution (both for gases – NO_2, SO_2 and particles) observed in African cities being at same levels as in Asian megacities **[10, 11, 12, 13]** and well above WHO (world health organization) international norms. Such somewhat unexpected pollution is due to the explosive development of African megacities with largely unregulated traffic emissions including intensive use of 2 stroke vehicles **[14]** and very old vehicles, widespread domestic fires using wood, charcoal or animal waste, and finally in some countries by industries without norms or regulations. Such problems are expected to increase further in the near future due to the prolonged absence of any regulations since urbanization rates are known to be among the highest in the world. Moreover, this anthropogenic pollution is enhanced by desert dust particles and biomass burning (savanna fires) gases and aerosols, the impacts of which have been already underlined in Western African cities **[9, 11]**. Improved knowledge of aerosol compositions, size and related biological reactivities are urgently needed since these sources which are associated with the intense photochemistry prevailing in Africa, are expected to generate pollution specificities and impacts, quite different from those in developed countries. Such studies could contribute to the proposal of mitigation options through identifying sources of concern.

In this context, the POLCA (Pollution des Capitales Africaines=African Capital Pollution) program has been jointly developed between African and French universities and institutes. One aim was to characterize atmospheric particulate pollution and to determine the toxic potential of particles according to their sizes (coarse, fine and ultrafine particles). Two traffic sampling sites were selected in African megacities: Bamako (Mali) and Dakar (Senegal). The sites differ in terms of the vehicle fleet, fuel type, road quality, domestic fires, dust events and biomass burning impacts.

In this paper, we display for the first time (i) results of an exhaustive size-differentiated physico-chemical characterization of African aerosols in these two cities exhibiting various specific sources of pollution, (ii) and characterization of the toxicity of three size-segregated aerosols in order to correlate their toxicities to specific sources. Three specific situations were scrutinized: Bamako with (BK1) and without (BK2) a dust event and Dakar (DK).

In order to screen size speciated aerosol compositions, coarse, fine and ultrafine PM from the two African cities have been sampled with different stage impactors for analysis of their total mass, organic and black carbon content, ion contents and trace elements. In addition, organic compounds such as polyaromatic hydrocarbons (PAH), polar compounds, water soluble organic carbon (WSOC) and light absorbing organic carbon (humic-like substances) were measured in bulk aerosol samples. In parallel, the toxicity of coarse, fine and ultrafine PM has been studied *in vitro* in human bronchial epithelial cells as relevant target cells. PM biological reactivities were characterized measuring the expression of a panel of biomarkers. Cytochrome P450 1A1 (CYP1A1) and NADPH quinone oxydoreductase (NQO-1), two xenobiotic metabolising enzymes (XME) were investigated as exposure biomarkers to identify the ability of cells to metabolize PM organic components. Heme oxygenase 1 (HO-1), an antioxidant enzyme, GM-CSF and IL-6, two pro-inflammatory cytokines and amphiregulin (AREG), a growth factor were used as effect biomarkers for the occurrence of oxidative stress and pro-inflammatory response respectively. African aerosol reactivities have been compared to urban traffic aerosols in Paris in which ultrafine and fine PM were shown to be the most reactive fractions **[15, 16]**.

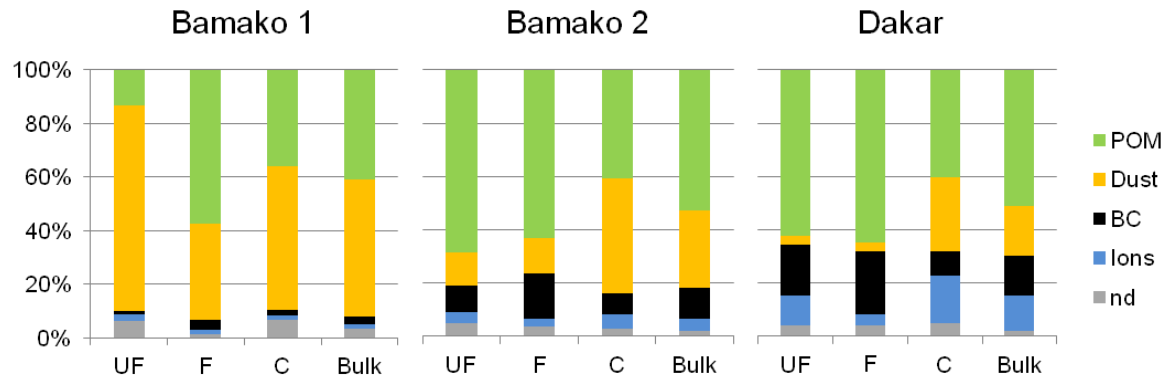

Figure 1: Chemical mass closure for the 3 class fractions of PM for Bamako and Dakar samples. For each site, the PM chemical composition of the 3 size fractions was totally determined by different analyses and results are presented as relative chemical abundance. Data are represented for Ultrafine PM (UF [0.03 µm-0.17 µm]), fine PM (F [0.17 µm-1 µm]), coarse PM (C [1 µm-10µm]) and bulk aerosol. BC: Black Carbon; POM: Particulate Organic Matter; n.d.: not determined.

Results and discussion

In cities of developed countries, the health effects of particulate pollution are related to the finest particles which are mainly generated by traffic. By contrast the size dependent effect of PM from developing megacities devoid of specific regulations is still unknown. The high level of particulate pollution and the presence of multiple sources, some of which are absent in occidental cities could induce a different pattern of toxicity. Our study is the first one attempting to provide an extensive physico-chemical characterization of size-segregated aerosol samples in two different African megacities in association with a comparison of their biological reactivity towards human bronchial epithelial cells.

African aerosols were sampled at crossroads near the traffic and in two cities exhibiting different emission sources and geographical characteristics. Both cities, like the rest of African capitals, have rapid population grown (5% per year), which is known to be an important factor influencing pollution levels.

Table 1: Gravimetric and source characteristics of Bamako and Dakar samples.

Samples		**Bamako 1 (BK1)**	**Bamako 2 (BK2)**	**Dakar (DK)**
Concentration µg.m^{-3} (Mass %)	UF	18.0 (8.7%)	14.6 (12%)	6.0 (7.4%)
	F	57.1 (27.8%)	43.8 (35.9%)	24.1 (30%)
	C	130.7 (63.5%)	63.7 (52.1 %)	50.5 (62.6%)
	Bulk	205.8	122.1	80.7
Main sources		traffic, biomass burning, dust		traffic , biomass burning
		Dust event	No dust event	No dust event

Physico-chemical characterization of the aerosols

In Bamako city, traffic was dominated by gasoline and oil fuel vehicles especially motorcycles and domestic burning using fuel wood, charcoal and animal wastes. Moreover, Bamako is often exposed to Saharan dusts and is also impacted by trash burning and aerosols from unpaved roads. Dakar exhibited different traffic sources, mostly due to bigger vehicles such as minibuses using bad quality diesel. Dakar is also impacted by combustion aerosols coming from biomass burning, especially in winter. Note that Bamako is located in a basin in which the dispersion of pollutants is limited, while Dakar is a coastal site influenced by marine air masses that favour the dispersion of pollutants. Bamako and Dakar were characterized by high bulk PM concentrations as shown in ***Table 1***. A higher concentration was obtained for the BK1 sample (205.8 µg/m^3) regardless of the size fraction that was linked to dust event influence. BK2 concentrations (122.1 µg/m^3) were higher than DK concentrations (80.7 µg/m^3). All these samples were composed mainly of coarse particles which comprised about 60% of the aerosol, compared with 10% for UF and 30% for F. Note that the concentrations of UF and F from DK were similar to $PM_{2.5}$ concentrations found by the study of Dieme et al. **[8]**.

As expected in BK1, dust concentrations are higher in the coarse (76.8 µg/m^3) than in the UF (13.4 µg/m^3) and F (22.1 µg/m^3) modes. However, as shown in ***Figure 1***, for the BK1 sample, the UF mode was largely dominated by mineral dust particles (76%), which was surprisingly much more important than in the coarse fraction, in which dust accounted for 53%. Particulate organic matter (POM) was the major component in the F mode, but dust still contributed significantly (36%). Black carbon (BC) and ions combined, represented 5% of the total aerosol mass. Note that the importance of dust was expected in BK1 due to a dust event occurrence during sampling. This scheme was very different for BK2 aerosol which was characterized by an important proportion of POM in both UF and F fractions (68 and 63%, respectively), while C mode mainly contained POM and dust (41 and 43 %, respectively). As shown in ***Table 2***, BC/OC ratio was relatively more important in BK2 than in BK1 in the F and C fractions.

Table 2: Average Black Carbon / Organic Carbon ratios (BC/OC) for UF, F and C fractions of Bamako and Dakar samples.

	BK1	**BK2**	**DK**
UF	0.17	0.18	**0.49**
F	0.09	**0.35**	**0.54**
C	0.11	**0.34**	**0.36**
Bulk	0.10	0.31	**0.45**

Table 3: Mean elemental concentrations (ng.m^{-3}) in Ultrafine (UF), Fine (F) and Coarse (C) for Bamako and Dakar samples. In bold major trace elements.

Sites	BK1			BK2			DK		
Elements	UF	F	C	UF	F	C	UF	F	C
Ca	**3.8**	**107.5**	**1935.7**	**17.7**	**116.7**	**964.2**	**8.8**	**72.3**	**1397.0**
Na	**8.9**	**69.9**	**735.0**	**9.1**	**35.9**	**155.6**	**48.4**	**104.9**	**1950.0**
K	**190.7**	**543.1**	**1627.9**	**178.8**	**391.2**	**381.0**	**95.8**	**151.2**	**264.7**
Mg	**1.8**	**80.9**	**873.6**	**5.8**	**42.7**	**233.5**	**1.4**	**19.1**	**390.2**
Al	388.6	553.1	6374.0	88.1	521.3	1865.4	267.3	76.9	858.0
Fe	17.1	272.3	3859.4	31.3	193.9	1750.8	11.4	59.4	806.7
Si	792.8	1128.3	13002.9	179.6	1063.4	3805.5	545.4	156.8	1750.3
Ti	8.5	28.9	279.2	4.5	22.6	105.9	4.6	7.1	60.1
Zn	4.0	9.7	23.6	2.8	7.8	15.8	8.7	14.5	19.0
Ni	2.2	2.0	9.3	0.5	1.2	2.3	2.1	7.8	2.5
P	1.1	7.5	98.0	1.7	12.5	71.7	62.5	26.8	90.9
Pb	1.3	4.4	7.6	1.2	3.4	5.2	1.6	2.8	4.6
B	14.1	18.0	46.2	12.1	27.6	27.6	6.8	8.7	11.3
Mn	0.9	6.9	54.7	0.7	4.0	21.7	7.3	5.8	12.8
Sn	0.0	0.0	1.0	0.3	0.6	2.0	16.0	2.6	2.1
Cu	0.3	1.0	7.4	0.3	1.0	3.4	0.8	5.0	12.7
V	0.0	0.8	8.3	0.1	0.5	3.3	5.1	20.1	5.2

Table 4: Relative quantity of water soluble organic carbon (WSOC) and light adsorption of black carbon (BC) in ultraviolets and infrared (UV BC/IR BC) in Bamako and Dakar PM samples.

	Bamako	**Dakar**
WSOC/OC	0.8	0.25
UV BC/IR BC	1	0.75

The DK sample was dominated by carbonaceous aerosol (BC and POM, which accounted for 66% (***Figure 2***). The most abundant component was POM (51% in the total mass) but it was in the UF and F fractions that POM had the highest contribution (62% and 65%, respectively). BC content was higher in the UF/F modes than in Bamako, as shown by BC/OC ratio, which was higher than in Bamako (***Table 2***). Note that this feature should be due to the relative importance of diesel vehicles in Dakar, while Bamako was dominated by more incomplete combustion sources. Such BC/OC ratio (0.45 in Dakar), was close to values of the order of 0.43, given for urban European sites **[17, 18, 19, 20]**. Dakar contained more

ions than Bamako but less dust that only represented 3% in UF/F modes. To summarize DK and BK2 samples showed a carbonaceous aerosol signature characterizing the combustion sources, while BK1 was more influenced by mineral dust probably from Sahel desert and unpaved roads as underlined by high amounts of Si, Al and Fe shown in the ***Table 3*** concerning trace element concentrations. The averaged mass concentration of dust tracers (Al, Fe and Si) showed a decreasing gradient from BK1, BK2 and DK samples. However, the concentrations of Cu were highest in DK: this could be explained by industrial sources, which were not negligible because the site was located only 10 km from an industrial area.

Due to the relative importance of the organic fraction, other measurements were performed, with a more simple approach as already mentioned (bulk measurements only). They confirm the importance of source emissions on PM concentration:

- First, measurements of 10 PAH were obtained for BK1, BK2 and DK (***Figure 2***). Total amounts of PAH were quite different over the different sites with DK having the highest concentration (280.5 $ng.m^{-3}$). At the BK site, the amount was different according to the sampling period and was particularly low for the BK1 sample (17.4 $ng.m^{-3}$) characterized by a dust event and higher for BK2 (85.5 $ng.m^{-3}$). Among these PAH, BaP African levels were much higher (factor of 7 for BK to 20 for DK) than those obtained in urban European sites such as Paris, Marseille or Grenoble **[21]**, N. Marchand (Personal communication). In addition to these quantitative differences in mass, the relative distribution of the 10 PAH highly varied between Bamako and Dakar situations: DK was dominated by 3 PAH (IncdP: indeno[1,2,3-cd]pyrene, BghiP: benzo[ghi]perylene, BbF: benzo[b]fluoranthene) representing more than 2/3 of the total mass and BaP (benzoapyrene) with 14%. 85% of total PAH were heavy PAH (5-6 cycles). This distribution profile and especially the relative abundance of BghiP were typical of diesel exhaust sources **[22]**. BK samples exhibited a more equally distributed pattern between the different PAH. Again, 4 PAH dominated the distribution (CHR: chrysene, BbF, BkF, BaP) each representing more than 12% and notably, BaP contributed to 29% of total PAH in BK2. The contribution of heavy PAH decreased to 61% for BK2 and 48% for BK1, compared to DK. Moreover, the relative importance of FLUA (fluoranthene), PHE (phenanthrene), PYR (pyrene) and CHR in BK samples, may be an indicator of the relative importance of incomplete combustion source e.g. biomass combustion **[23, 24]** and oil and gasoline motorcycle **[25]**.

- Second, the samples also differed in the relative abundances of organic polar compounds (***Figure 3***). Levoglucosan was the predominant species among those measured in the three samples. Stearic acid was more important in BK than DK due to domestic combustion

(cooking) higher in BK than in DK. This assumption is also supported by a higher relative abundance of cholesterol in BK than in DK.

- Third, Water Soluble Organic Compounds (WSOC) presented higher values in BK than in Dakar as shown with WSOC/OC ratio higher in Bamako than in Dakar (***Table 4***) showing different solubility properties of components. This difference could be significant for the aerosol biological effect, as shown in Ramgolam et al. **[15]**.

- Finally UV BC/IR BC (Ultraviolet BC/Infrared BC) ratios. (***Table 4***) showed higher values in Bamako than in Dakar, which indicated a more important "light absorbing organic carbon" contribution in Bamako than in Dakar. Such a component which could be partly formed by humic-like substances that was recently found to be the major redox active constituent of the water-extractable organic fraction in PM **[26]**.

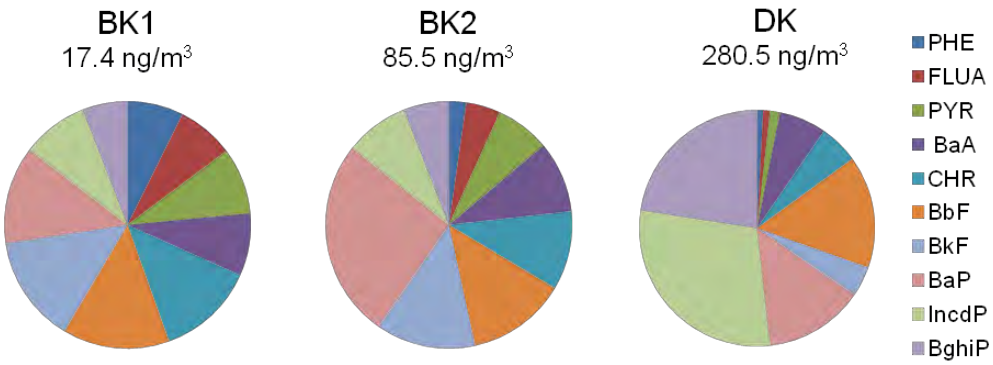

Figure 2: Relative mass distribution of polyaromatic hydrocarbons (PAH) for bulk aerosol of Bamako and Dakar samples. Results are expressed in percentage of the total PAH for each sample. The total quantity of PAH in the air is indicated in ng.m^{-3}.

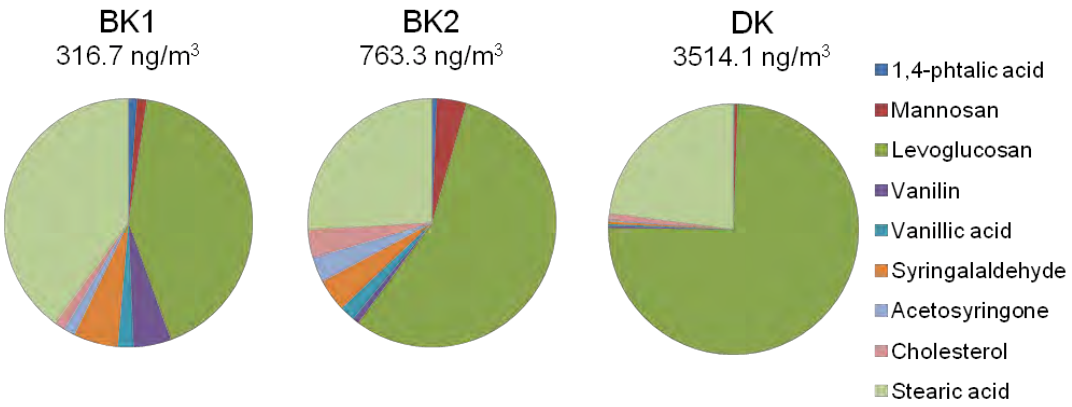

Figure 3: Relative mass distribution of polar organic compounds for bulk aerosol of Bamako and Dakar samples. The relative mass distribution of each sample was calculated for the bulk aerosol. The quantity of polar compounds in the air is indicated in ng.m^{-3}.

Site and size-dependence of the pro-inflammatory response

The pro-inflammatory effect of the size-segregated PM was investigated through the expression and release of two biomarkers (GM-CSF and IL-6) by 16HBE cells (***Figure 4A, B***). These pro-inflammatory cytokines have pleiotropic effects on the inflammatory process and act on inflammatory cell activation, recruitment, proliferation and survival **[27, 28]**. They were also induced in asthma and chronic obstructive pulmonary diseases (COPD) **[29, 30, 31]**, and after PM and nanoparticle exposure **[32, 16]**. Whatever the site, UF and F PM dose-dependent induced mRNA expression of the two biomarkers with generally a significant effect from 5 µg.cm^{-2} and for BK samples from 1 µg.cm^{-2} (***Figure 4A, B, right panel***). The BK2 sample distinguished itself by the high GM-CSF fold inductions (more than 10) for UF and F at 10 µg.cm^{-2}. By contrast, UF and F PM of BK1 and DK exhibited lower fold induction of GM-CSF mRNA. These data were consolidated with the measurement of the cytokine release especially for BK2 sample exhibiting again the highest GM-CSF release in a dose-dependent manner (***Figure 4A, left panel***). Nevertheless, C PM were not devoid of effects but their inductive potential towards GM-CSF expression mainly occurs with the BK2 sample.

For IL-6 cytokine (***Figure 4B***), mRNA inductions (i) were less important than for GM-CSF (2.5 fold), (ii) were less clearly associated to a dose response effect according to samples (iii) were significant whatever size fractions excepting C PM from DK and (iv) were similar between BK2 and the other samples, making this biomarker less discriminating than GM-CSF. Considering PM-induced IL-6 release (***Figure 4B, right panel***), a better dose response was observed but fold inductions never exceed 2 and statistically significant effects only concerned the highest concentrations for F and UF PM.

The growth factor amphiregulin (AREG) was also studied as this ligand of the epidermal growth factor receptor plays a pivotal role in the repair and maintenance of epithelial tissues **[34]**, but it is also overexpressed in asthmatic subjects during crisis **[35]**. Previous studies in the laboratory demonstrated that $PM_{2.5}$ of different sites induced AREG mRNA expression in 16HBE cells and primary human bronchial epithelial cells NHBE **[35, 16]** and was implicated in the persistence of GM-CSF pro-inflammatory response **[36, 37]**. Consequently, its overexpression was suspected of participating in airway epithelium remodeling. AREG expression was induced whatever the samples with the UF and F fractions mostly from 5 µg.cm^{-2}, C PM having a significant effect only for BK2 at 10 µg.cm^{-2} (figure 4C, left panel). As for GM-CSF, BK2 exhibited the highest fold induction (4 to 5) of AREG mRNA whatever the size fraction (***Figure 4C, left panel***) although it was not completely confirmed by the

protein release (***Figure 4C, right panel***) as the stronger effect was observed with DK UF and F PM.

Considering the 3 biomarkers, GM-CSF is the one exhibiting the most discriminating effect among the different sites. This induction was previously associated with organic compounds of particles and their ability to induce reactive oxygen species (ROS) overproduction **[38, 37]**, an effect also evaluated in this study.

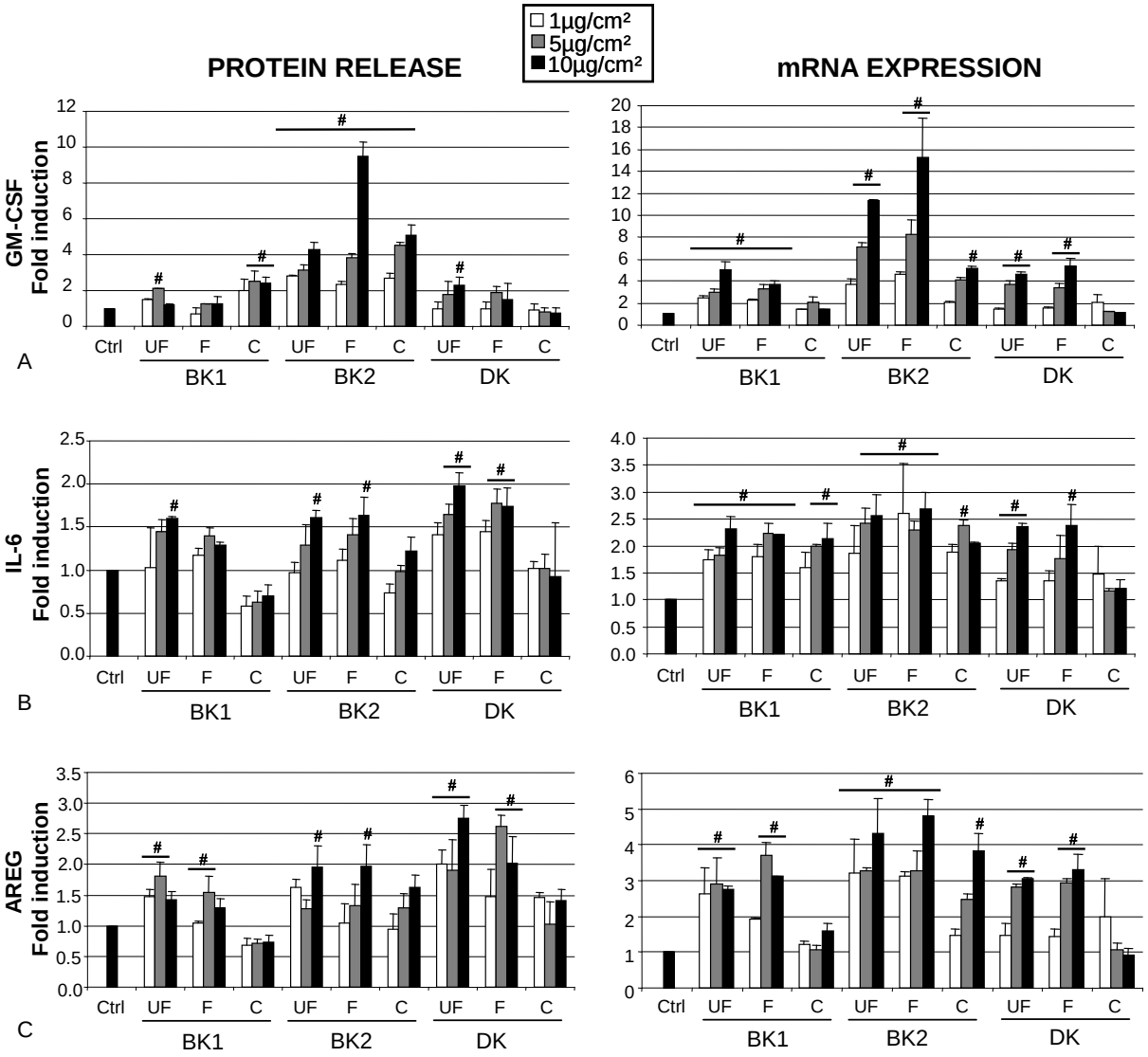

Figure 4: Effect of PM on the expression and release of GM-CSF, IL-6 and AREG biomarkers.

Ultrafine PM (UF [0.03 µm-0.17 µm]), fine PM (F [0.17 µm-1 µm]) and coarse PM (C [1 µm-10µm]) were used at 1 to 10 µg.cm^{-2} for 24 h exposures. The pro-inflammatory cytokines GM-CSF (A) and IL-6 (B) were studied as well as AREG growth factor (C). mRNA were evaluated by RT-qPCR and protein assessed in supernatants by ELISA assay. These data are expressed comparatively to the control (=1). mRNA and protein releases are mean of four replicates.

*** p<0.05 compared with the control fixed to 1.**

Induction of exposure biomarkers related to organic compounds metabolism and oxidative stress.

CYP1A1 is a xenobiotic metabolism enzyme (XME) known to be specifically induced by PAH and as such can be considered in our context as a biomarker of the PAH bioavailability **[40]**. Its activity produces electrophilic metabolites and reactive oxygen species contributing to the activation of NQO-1, another XME regulated by the antioxidant responsive element (ARE) **[39]** and HO-1, an antioxidant enzyme also containing ARE in its promoter **[41]**. Whatever the site, CYP1A1 was highly induced by UF and F PM (around 30 fold induction for 10 µg.cm^{-2} exposure) with significant effect from 1 µg.cm^{-2} and only to a lower extent by C PM only from BK2 (***Figure 5A***). CYP1A1 expression increased from 1 to 5 µg.cm^{-2} but did not further increase at 10 µg.cm^{-2}. Surprisingly, F BK2 PM exhibited an inverse dose dependent effect.

NQO-1 showed similar profiles but with lower mRNA fold inductions (max 3) and was induced in a dose dependent manner (***Figure 5B***). Again among C PM, only those of BK2 had a significant effect.

The increase in the antioxidant enzyme HO-1 expression was only observed in few samples (***Figure 5C***). It was also for the UF and F PM of BK2 that the most striking effects were observed from 5 µg.cm^{-2} (2.5 and 5 fold inductions for UF and F at 10 µg.cm^{-2} respectively). Otherwise UF PM of BK1 was the only other fraction inducing HO-1 at 10 µg.cm^{-2}.

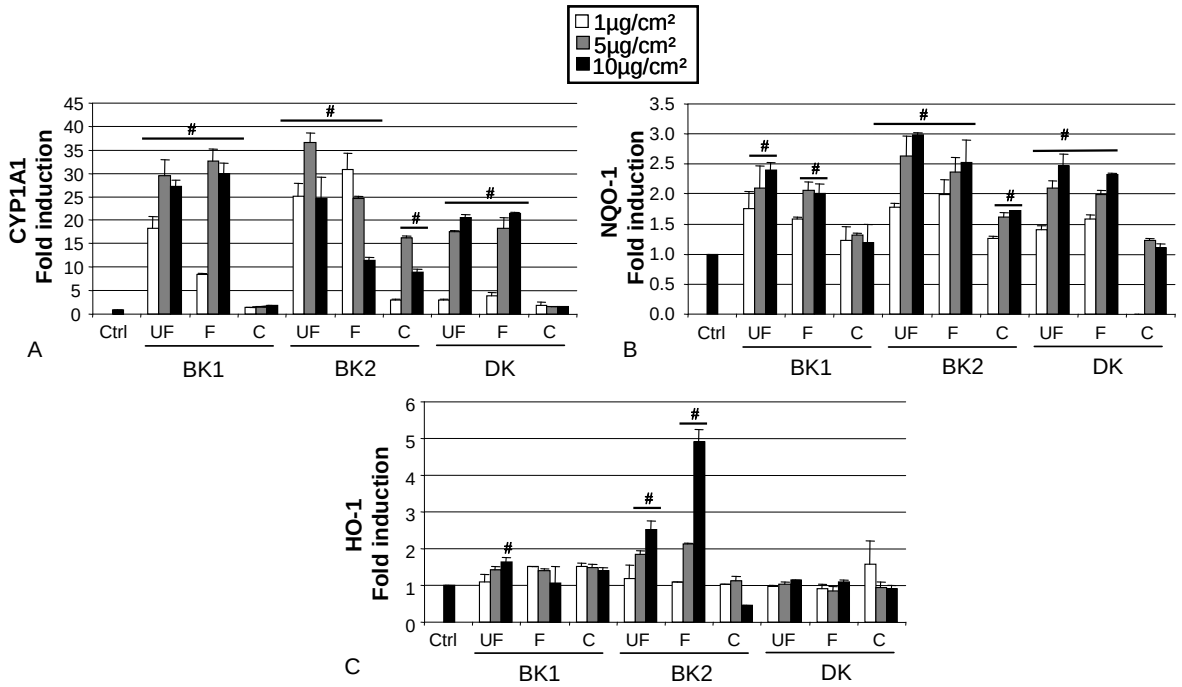

Figure 5: Effect of PM on the expression of CYP1A1, NQO-1 and HO-1 biomarkers.

Ultrafine PM (UF [0.03 µm-0.17 µm]), fine PM (F [0.17 µm-1 µm]) and coarse PM (C [1 µm-10µm]) were used at 1 to 10 µg/cm² for 24 h.mRNA of CYP1A1 (A), NQO-1 (B) and HO-1 (C) were assessed. CYP1A1 and NQO-1 are metabolizing enzymes and HO-1 is an antioxidant enzyme. These data are expressed comparatively to the control (=1). Results are mean of four replicates. * p<0.05 compared with the control fixed to 1.

Site dependent gene expression signature

In order to identify relationships between exposure biomarkers and effect biomarkers, correlation analyses were performed with the fold mRNA inductions shown in ***Figure 4*** and ***Figure 5***. For this purpose Pearson's correlation factors (r) and dendrogram hierarchical classifications were performed (***Table 5, Figure 6***).

BK1 and BK2 exhibited specific chemical closures leading to a lower biological reactivity of BK1 PM likely due to the dilution of the most toxic components by dusts. For BK1, cytokines/growth factor and CYP1A1 were highly correlated (***Table 5, Figure 6A***) underlying the importance of the combustion source in biological effects despite the high dust content. For BK2, closely related genes were GM-CSF and both HO-1 (0.97 for UF and 0.96 for F) and NQO-1 (0.9 for UF and 0.82 for F) which are two oxidative stress sensitive genes. Surprisingly GM-CSF induction was poorly correlated to CYP1A1 (0.08) due to a decrease in CYP1A1 induction with increasing PM concentrations (***Table 5, Figure 6B***). This result was confirmed in another human bronchial epithelial cell line, NCI-H292 (data not shown). Studies showed that several metals (cooper, mercury and arsenic) were able to inhibit CYP1A1 mRNA induction in response to dioxin inductor TCDD **[41, 42, 43]**. However the highest concentrations of cooper and arsenic were obtained in DK and not in BK2 (***Table 3***). Otherwise a specific metal speciation in BK2 sample and/or oxidative stress known to inhibit CYP1A1 **[44]** could explain the decrease of CYP1A1 mRNA for BK2 site at high PM concentrations which was related to HO-1 huge mRNA induction. Let us recall that BK presented more organic soluble fraction, and more "brown carbon" than DK, two organic indicators suspected for their oxidative properties **[16, 45, 26]**. The contribution of metals to oxidative stress is likely low. Indeed, the size fraction having the highest metal content was the coarse one (76 to 87 % of the total metal mass) and yet was not or less reactive on 16HBE cells suggesting that the metallic component had a low toxicological implication.

For DK site, all the genes excepting HO-1 were closely linked (***Figure 6C***) suggesting a strong association between exposure biomarkers (CYP1A1 and NQO-1) and effect biomarkers (GM-CSF, IL-6 and AREG). It was driven by UF and F PM of DK (***Table 5***), as observed with PM sampled in Paris near the traffic **[16]** (***Figure 6***). It could be explained by

the predominance of diesel fuel cars in these two cities, even if there are old diesel engines in Dakar. These results target the diesel exhaust source in the biological response.

In summary, whatever the samples, carbonaceous aerosols from combustion sources seem to contribute to biological responses.

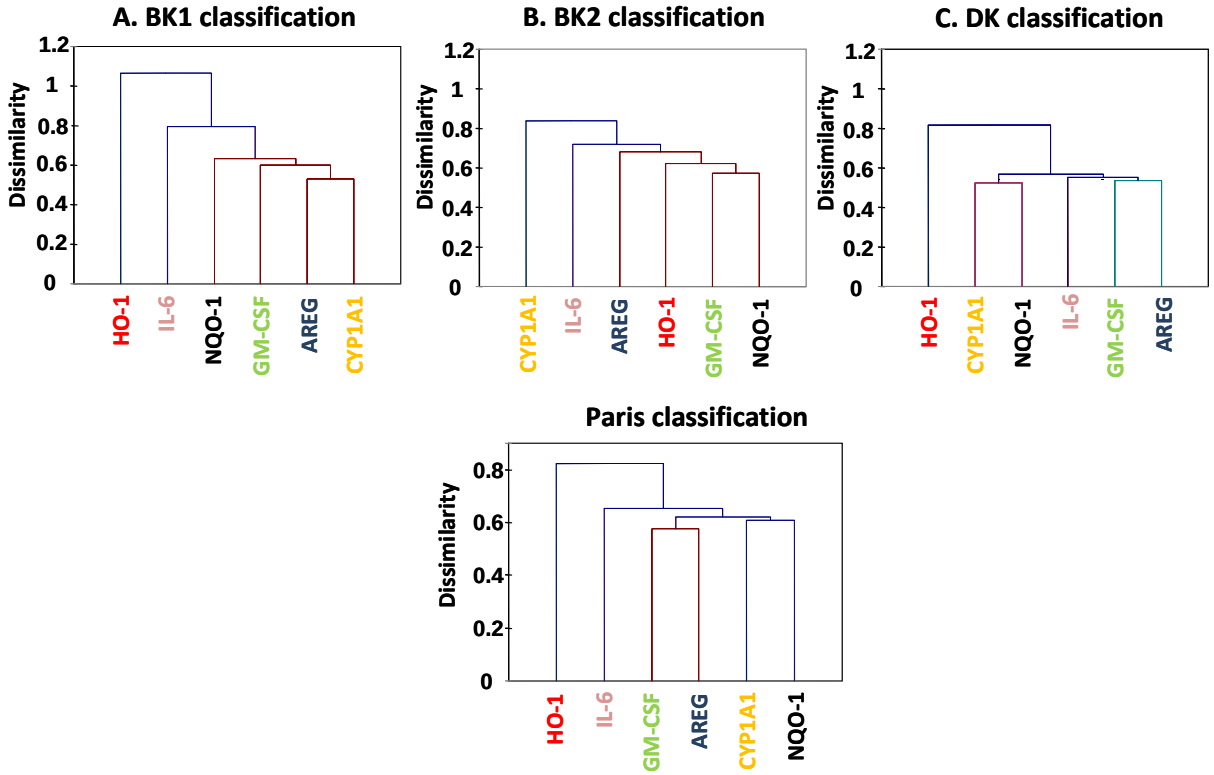

Figure 6: Dendrogram classifications of biological responses for Bamako and Dakar samples in comparison with Paris samples. Classifications were performed with Spearman's dissimilarity with the results presented in figure 4 and figure 5 for BK1 (A), BK2 (B) and DK (C). Dendrogram classification for Parisian PM was performed with the results of Val et al. [16] (D).

Role of the organic component in the biological response

In order to specify which component in each size fraction of PM could be responsible from biological responses, correlations between genes fold inductions and major compound content were calculated (***Table 6***). The effects of UF and F PM seemed to be driven by BC and POM components for all the biomarkers, especially for GM-CSF and HO-1, but not for CYP1A1 as already discussed (***Table 6A***). But BC showed slight slope of lines in correlation graphs, suggesting its low implication.

Considering each site (***Table 6B***), BK1 (dust event) showed a correlation between cytokines and dusts but also IL-6 with BC and POM. By contrast BK2 and DK showed high correlations with BC and POM for 4 biomarkers.

Globally whatever the samples and size (***Table 6, total***), POM was the sole parameter correlating statistically with most of the biomarkers suggesting that biological effects were mainly driven by carbonaceous aerosols.

Table 6: Correlation coefficients (Pearson) between biomarker responses studied after PM exposure of urban Parisian PM (adapted from the results of Val et al., 2011). Bold values significate a statistical correlation between biomarkers (p<0.05).

Paris UF	GM-CSF	IL-6	AREG	CYP1A1	NQO-1	HO-1
GM-CSF	**1**					
IL-6	**0.831**	**1**				
AR	0.463	0.497	**1**			
CYP1A1	**0.767**	0.553	0.326	**1**		
NQO-1	**0.770**	0.546	0.374	**0.895**	**1**	
HO-1	**0.893**	**0.749**	0.364	**0.823**	**0.785**	**1**

Paris F	GM-CSF	IL-6	AREG	CYP1A1	NQO-1	HO-1
GM-CSF	**1**					
IL-6	**0.893**	**1**				
AR	**0.894**	**0.819**	**1**			
CYP1A1	**0.804**	**0.754**	**0.843**	**1**		
NQO-1	**0.678**	**0.612**	**0.765**	**0.907**	**1**	
HO-1	**0.789**	**0.621**	**0.787**	**0.882**	**0.934**	**1**

Paris	GM-CSF	IL-6	AREG	CYP1A1	NQO-1	HO-1
GM-CSF	**1**					
IL-6	**0.848**	**1**				
AR	**0.788**	**0.710**	**1**			
CYP1A1	**0.830**	**0.709**	**0.722**	**1**		
NQO-1	**0.753**	**0.647**	**0.727**	**0.884**	**1**	
HO-1	**0.701**	**0.633**	**0.671**	**0.756**	**0.804**	**1**

Are African traffic aerosols more reactive than French ones?

The effects of the 3 samples according to their size were compared with aerosols from traffic in Paris that were tested in the same conditions **[16]** (***Figure 7***). Globally, it appears that whatever the size, higher effects were observed with BK2 whereas BK1, DK and Paris exhibited lower and similar effects. For BK2, UF PM had a lower effect than F PM whereas for the other sites both size fractions had the same effect. In all the cases, C PM had a lower effect on an equal mass basis strengthening our previous observations on occidental urban and rural aerosols **[15, 16]**.

Our experiments were performed exposing cells at isomass that does not take into account the ambient level of PM. The French urban site used for comparison had a concentration of 25 $\mu g.m^{-3}$, lower compared to African sites (BK1, BK2 and DK showed 206, 122 and 81 $\mu g.m^{-3}$,

respectively). It means that a longer exposure is necessary in Paris to be exposed at the same concentration in African cities that reinforces the strong toxicity of BK aerosol and to a lower extend of DK aerosol.

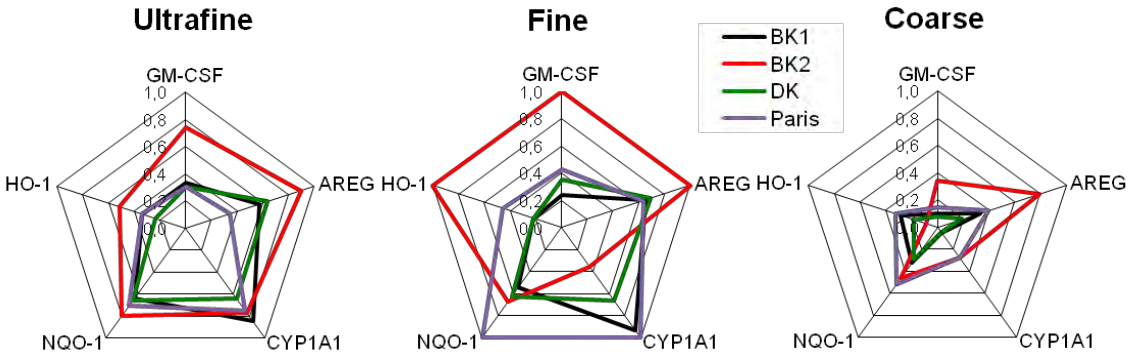

Figure 7: Synthesis of African and French PM effects on 16HBE cells. Data are represented in radar graphs in order to compare the effect of size fractions and the origin of the particles. For each biomarker and whatever PM size and origin, the most induced condition is fixed to 1, and the other results are related to this value.

Conclusions

This study shows that the finest PM (< 1µm) of African urban aerosols from three different conditions triggered adaptive responses of the airway epithelium whereas coarse PM had no or low effect. Discrimination among the different sites was highlighted with GM-CSF, a relevant pro-inflammatory cytokine for airway diseases. Bamako aerosol was characterized by an impressive biological reactivity associated with local sources as it was less reactive when diluted by external input such as dusts. PM-induced responses are related to carbonaceous aerosol content underlying the contribution of combustion sources. In line with the recent reclassification by IARC of diesel engine exhaust as carcinogenic to human **[45]**, our work underlines the negative effect of diesel particles. Regarding the prevailing sources in each site, aerosol biological impacts are higher for incomplete combustion sources (two-wheel vehicles, domestic fires) with higher relative OC content exhibiting hydrosolubility properties than for diesel vehicles (Dakar site) with higher relative BC content. This underlines the importance of emission mitigation (e.g. composition of the traffic fleet) and the imperative need to evaluate and regulate particulate pollution in Africa. Taking into consideration PM mass quantities in the air of BK and DK sites, the African population is highly exposed to toxic particulate pollution that could lead to strong adverse health effects especially in susceptible people such as children.

Methods

Sampling locations

Aerosol samples were collected in Africa during the frame of the POLCA campaigns at two sampling sites: Bamako (12°39'N, 8°04'W), located in a basin in southwestern Mali, is a dusty city with 2.2 million inhabitants (2009), and Dakar (14°40'N, 17°25'W), is a coastal city in west Senegal with a population of about 3 million people (25% of the national population). Period of sampling was January 20 to 22, 2009 and January 27 to 29, 2009 in Bamako for BK1 and BK2 samples respectively and December 5 to 7, 2009 in Dakar (called DK sample). Particles were collected downtown near intense traffic roads on a 3 meter high balcony.

PM sample collection

Aerosol collection was performed by three cascade impactors (two 13-stage electrical low pressure impactors Dekati/ELPI working at a flow rate of 30 $L.min^{-1}$ and one of 5-stage Sioutas impactor at a flow rate of 9 $L.min^{-1}$), running in parallel for 48-h. One of them, mounted with 25mm diameter polycarbonate Nuclepore filters (1 µm porosity), was devoted to gravimetric measurements including number and mass size distribution, and for biological analyzes. The other impactor, mounted with 25mm diameter quartz filters (QMA, Whatman), was dedicated to carbonaceous aerosol measurements (black carbon, BC and organic carbon, OC). An additional Sioutas impactor was mounted with 25mm diameter Teflon filter (Zefluor, Pall Corporation) at the four first stages and 37mm diameter at the last stage, for gravimetric measurements (mass) and water soluble ion and trace elements analysis. Aerodynamic particle diameters given by Dekati ELPI are ranged between 0.03 and 10µm while Sioutas cascade impactor collects particles in the following size range : >2.5µm, 1-2.5µm, 0.5-1µm, 0.25-0.50µm and <0.25µm.

In accordance with mass distribution of aerosols obtained for BK and DK samples (***Figure 8***), three particle size fractions were selected: ultrafine particle, UF [0.03-0.1 µm], fine, F [0.1-1 µm], and coarse, C [1-10 µm].

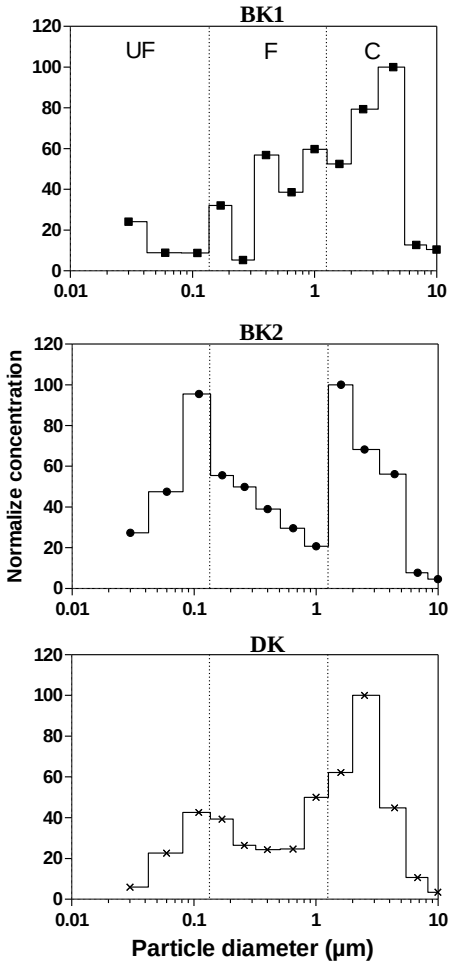

Figure 8: Aerosol size distribution in Bamako (BK1 and BK2) and Dakar (DK). PM mass was determined for each membrane of impactor. Normalized concentration (µg) is represented as a function of particle aerodynamic diameter (µm).

Chemical analyses

All Nuclepore and Teflon filters were weighed before and after sampling for mass determination, using a Mettler Microbalance MC21S with 1 µg sensitivity. One half sections of the filters were analyzed for major ion contents (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^-, Cl^-), using ion chromatographic (IC) analyzer. These measurements were conducted following the analytical protocol described in Adon et al. **[46]**. Inductively coupled plasma mass spectrometry (ICP-MS) was applied after microwave digestion in acids (HNO_3 and HF), to the others half sections of the filters, to determine the concentration of trace elements **[47]**. Black carbon (BC) and total carbon (TC) concentrations were measured on quartz filter with a thermal method developed by Cachier **[20]**. Prior to analyses, carbonates are removed under HCl fumes (due to carbonates interference with carbon measurements). Two similar aliquots

of the same filter were then separately analyzed. One portion was directly analyzed for its total carbon content (TC). The other portion was firstly submitted to a pre-combustion step (2 h at 340°C under pure oxygen) in order to eliminate OC, and then analyzed for its BC content. Organic carbon (OC) concentrations were calculated as the difference between TC and BC.

Aerosol chemical mass closure

PM mass closure was performed following Guinot **[48]** methodology in order to obtain estimates POM (Particulate Organic Matter), dust, and no determined (n.d.) mass, which is refer to the difference between the aerosols weighed mass and the reconstructed mass. In first instance, OC-to-POM conversion factor was arbitrary fixed to be 1.8 and then linear regression was performed between Ca^{2+} concentration (obtained by IC) and the missing mass, which is calculated by the difference between the reconstructed coarse mass (sum of BC, POM and ions mass concentrations) and the weighed coarse mass. The slope of this linear regression represents Ca^{2+}-to-dust conversion factor. However, OC-to-POM conversion factor is modulated in order to obtain a reconstructed mass as close as possible below the weighed mass **[49, 48]**. OC-to-POM conversion factor is generally taken in the range 1.2-1.6 for urban aerosols **[50, 51]** with higher values (1.6-2.1) for non urban aerosols **[52]**. In our case, OC/POM ratios are of the order of 1.63, 1.46 and 1.37 for BK1, BK2 and DK respectively.

Dust concentrations obtained by Guinot **[53]** methodology are confirmed with dust estimates obtained from trace element measurements **[54]** and calculation using the following equation:

$$Dust = 1.89 * Al + 1.21 * K + 1.95 * Ca + 1.66 * Mg + 1.7 * Ti + 2.14 * Si + 1.42 * Fe$$

Using these two methodologies, Guinot (Terzi) measured dust concentrations are 88.15 (64.18), 32.48 (24.64) and 15.09 (11.04) $\mu g.m^{-3}$ in BK1, BK2 and DK, respectively.

This aerosol chemical closure was performed for each ultrafine, fine and coarse fraction of BK1, BK2 and DK samples.

Other measurements

In parallel, aerosol particles were collected on A4 filter with high volume impactor and analyzed for 18 polar and non polar PAHs by external calibration performed with a gas chromatography coupled to a mass spectrometry following the method described in Besombes **[55]**. Another 5 stages high volume cascade impactor (Staplex® Model 235) was dedicated to WSOC measurements. WSOC were quantified using the protocol described by Favez **[56]**. Note that WSOC was also determined on Teflon filters of a Dekati impactor sampled in the same conditions (common source characteristics) but for different days than for BK2 and DK.

Finally, BC concentrations measurements were also performed for UV and IR wavelengths with aethalometers in Bamako and Dakar for all the sampling periods, UV BC/IR BC ratio indicating relative "brown" like carbon or "light absorbing organic matter"fraction **[57]**.

Reconstitution of particle suspensions for biological experiments

For toxicological studies, the three size-fractions presented before were reconstituted from Nuclepore membranes. Recovery of the particles was achieved as previously described by Ramgolam **[15]**. Briefly, polycarbonate membranes were sonicated (Ultrasonic Processor, Bioblock scientific) 3 x 5 sec at 60 Watt in presence of DMEM/F12 medium (Invitrogen®) supplemented with glutamax (1%), penicillin (100 U/ml), streptomycin (100 µg/ml) and fungizone (0.125 µg/ml). Particle suspensions were stored at -20°C until use and were again sonicated (3 x 10 sec) just before dilution in the culture medium for cell exposure.

Cell cultures

The human bronchial epithelial cell line 16HBE 14o- was kindly given by Dr D.C. Gruenert (San Francisco, California, USA). Cells were grown in DMEM/F12 culture medium (Invitrogen®) supplemented with Glutamax (1%) (Gibco) and UltroserG (2%) (Life Technologies). Cells were seeded on 75 cm² flasks or 12-wells plates (Costar®) coated by a solution containing collagen (Bovine collagen I, Vitrogen 2.9 $mg.ml^{-1}$, BD Laboratories; human fibronectin, 1 mg/ml, BD Laboratories; Bovine Serum Albumin 1 $mg.ml^{-1}$, Biosource; LHC medium, Biosource).

Cells were maintained in 95% humidified air with 5% CO_2 at 37°C until 70 to 80% confluency and deprived of ultroser G or growth factors 4 h before exposure to different PM-size fractions for 24 h. Particles were used from 1 $\mu g.cm^{-2}$ to 10 $\mu g.cm^{-2}$ that are non cytotoxic concentrations (data not shown), diluted in DMEM/F12 without growth factors and containing penicillin (100 $\mu g.ml^{-1}$), streptomycin (100 $\mu g.ml^{-1}$) and fungizone (1 $\mu g.ml^{-1}$) from Sigma-Aldrich.

4 h before treatment, cells were deprived from serum and then treated with particles at 1, 5 and 10 $\mu g.cm^{-2}$ for 24 h (corresponding respectively to 5.4, 27.1 and 54.3 $\mu g.ml^{-1}$).

Real-time quantitative polymerase chain reaction (qPCR)

Polymerase chain reaction (PCR) was performed to evaluate GM-CSF, IL-6, CYP1A1, NQO-1, HO-1 and AREG mRNA expression. The ribosomal protein (RPL19) gene was used as an internal control. After 24 h of treatment mRNA extraction and purification were performed

using a commercially available kit (SV Total RNA Isolation System, Promega) according to the manufacturer's recommendations. Reverse transcription was done by M-MLV (Moloney Murine Leukemia Virus) Reverse Transcriptase kit (Promega). Finally, Real-time quantitative PCR (qPCR) analysis was performed using MX3000p (Stratagene).

The following primer sequences were used:
RPL19: Sense: 5'-GGCTCGCCTCTAGTGTCCTC-3'
Antisense: 5'-CAAGGTGTTTTTCCGGCATC-3'
GM-CSF: Sense: 5'-AGCCGACCTGCCTACAGAC-3'
IL-6: Sens : 5'-ACAGCCACTCACCTCTTCAG-3'
Antisens: 5'-TGGAAGCATCCATCTTTTTC-3'
CYP1A1: Sense: 5'-GAGCCTCATGTATTTGGTGATG-3'
Antisense: 5'-TTGTGTCTCTTGTTGTGCTGTG-3'
NQO-1: Sense: 5'-AAGAAAGGATGGGAGGTGGT-3'
Antisense: 5'-GCTTCTTTTGTTCAGCCACA-3'
HO-1: Sense: 5'-CAGGCAGAGAATGCTGAGTTC-3'
Antisense: 5'-GCTCTTCTGGGAAGTAGACAGG-3'
AREG: Sense: 5'-TGGTGCTGTCGCTCTTGATA-3'
Antisense: 5'-CCCTGAAGACATCTCACTTC-3'
The relative quantification of the gene of interest was done according to the method described by Pfaffl **[58]**.

Cytokine release assay: Enzyme linked immunosorbent assay (ELISA)

After 24 h of PM treatment, the culture medium was removed, centrifuged at 10,000 *g* for 10 min at 4°C to eliminate particles, and stored at -20°C until use. GM-CSF, IL-6 and amphiregulin (AREG) amounts in supernatants were evaluated using an ELISA kit provided by R&D Systems. The optic density was measured at 450 nm with a microplate photometer MR5000 (Dynex technologies).

Statistical analysis

Data represented as mean ± SD were evaluated by analysis of variance (ANOVA) followed by Dunnet's t-test to examine the differences between the different treated groups with respect

to the control. Correlations were calculated using Pearson's correlation. Dendrograms were calculated using the Spearman's dissimilarity (XLstat software).

List of abbreviations

16HBE 16 human bronchial epithelial

ARE Antioxidant responsive element

AREG Amphiregulin

BaP Benzoapyrene

BC Black carbon

BbkF Benzo[k]fluoranthene

BghiP Benzo[ghi]perylene,

BK Bamako

C Coarse

CHR Chrysene

COPD Chronic obstructive pulmonary disease

CYP1A1 Cytochrome P450 1A1

DK Dakar

ELISA Enzyme linked immunosorbent assay

F Fine

FLUA Fluoranthene

GM-CSF Granulocyte macrophage-colony stimulating factor

HO-1 Heme oxygenase 1

IARC International agency for research on cancer

IL-6 Interleukin 6

IncdP Indeno[1,2,3-cd]pyrene

UV Ultraviolet

IR Infrared

NHBE Normal human bronchial epithelial

NQO-1 NADPH quinine oxydoreductase 1

OC Organic carbon

PCR Polymerase chain reaction

PHE Phenanthrene

PM Particulate matter

POLCA Pollution des capitales africaines

POM Particulate organic matter

PYR Pyrene
UF Ultrafine
RPL-19 Ribosomal protein L19
TC Total carbon
WSOC Water soluble organic carbon
XME Xenobiotic responsive element

Competing interests

The authors declare no conflict of interest.

Authors contribution

SV performed the biological analyses, interpreted the results and contributed to write the paper. CL designed the research and with EHTD performed field experiments, analyzed the data and drafted the paper. CGL designed the research and performed field experiments with EG. HC contributed to the interpretation of the data. EHTD, HC, NM, EG and AS performed the chemical analysis. AB provided advices for statistical analysis. ABS directed the joint project and contributed to write the paper. All authors read and approved the manuscript.

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References (A5)

1. Pope CA, Young B, Dockery DW. Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association. 2006;56(6):709-42.
2. Mazzoli-Rocha F, Fernandes S, Einicker-Lamas M, Zin WA. Roles of oxidative stress in signaling and inflammation induced by particulate matter. Cell Biology and Toxicology. 2010;26(5):481-98.
3. Ling S, Van Eeden S. Particulate matter air pollution exposure: role in the development and exacerbation of chronic obstructive pulmonary disease. Int J Chron Obstruct Pulmon Dis. 2009;4:233-43.
4. Happo MS, Hirvonen M-R, Halinen AI, Jalava PI, Pennanen AS, Sillanpaa M, et al. Chemical compositions responsible for inflammation and tissue damage in the mouse lung by coarse and fine particulate samples from contrasting air pollution in Europe. Inhal Toxicol. 2008;20(14):1215-31.
5. Seagrave J, McDonald JD, Bedrick E, Edgerton ES, Gigliotti AP, Jansen JJ, et al. Lung toxicity of ambient particulate matter from southeastern U.S. sites with different contributing sources: relationships between composition and effects. Environ. Health Perspect. 2006;114(9):1387-93.
6. Huang S-L, Hsu M-K, Chan C-C. Effects of Submicrometer Particle Compositions on Cytokine Production and Lipid Peroxidation of Human Bronchial Epithelial Cells. Environmental Health Perspectives. 2002;111(4):478-82.
7. Mitschik S, Schierl R, Nowak D, Jörres RA. Effects of Particulate Matter on Cytokine Production In Vitro: A Comparative Analysis of Published Studies. Inhalation Toxicology. 2008;20(4):399-414.
8. Dieme D, Cabral-Ndior M, Garçon G, Verdin A, Billet S, Cazier F, et al. Relationship between physicochemical characterization and toxicity of fine particulate matter (PM2.5) collected in Dakar city (Senegal). Environ. Res. 2012;113:1-13.
9. Kouassi, K.S., Billet, S., Garçon, G., Verdin, A., Diouf, A., Cazier, F., Djaman, J., Courcot, D., Shirali, P. Oxidative damage induced in A549 cells by physically and chemically characterized air particulate matter (PM2.5) collected in Abidjan, Côte d'Ivoire. Journal of Applied Toxicology. 2010;30: 310–320.
10. Norman M, Hansel A, Wisthaler A. O2+ as reagent ion in the PTR-MS instrument: Detection of gas-phase ammonia. International Journal of Mass Spectrometry. 2007;265(2–3):382-7.
11. Doumbia EHT, Liousse C, Galy-Lacaux C, Ndiaye SA, Diop B, Ouafo M, et al. Real time black carbon measurements in West and Central Africa urban sites. Atmospheric Environment. 2012a;54(0):529-37.
12. Liousse C, Guillaume B, Grégoire JM, Mallet M, Galy C, Pont V, et al. Western african aerosols modelling with updated biomass burning emission inventories in the frame of the AMMA-IDAF program. Atmospheric Chemistry and Physics Discussions. 2010;10(3):7347-82.
13. Dionisio KL, Arku RE, Hughes AF, Vallarino J, Carmichael H, Spengler JD, et al. Air pollution in Accra neighborhoods: spatial, socioeconomic, and temporal patterns. Environmental science & technology. 2010;44(7):2270-6.
14. Assamoi E-M, Liousse C. A new inventory for two-wheel vehicle emissions in West Africa for 2002. Atmospheric Environment. 2010;44(32):3985-96.
15. Ramgolam K, Favez O, Cachier H, Gaudichet A, Marano F, Martinon L, et al. Size-partitioning of an urban aerosol to identify particle determinants involved in the proinflammatory response induced in airway epithelial cells. Part Fibre Toxicol. 2009;6:10.
16. Val S, Martinon L, Cachier H, Yahyaoui A, Marfaing H, Baeza-Squiban A. Role of size and composition of traffic and agricultural aerosols in the molecular responses triggered in airway epithelial cells. Inhal Toxicol 2011; 23(11): 627-640.
17. Kendall, M., Hamilton, R.S., Watt, J. and Williams, I.D. Characterisation of selected speciated organic compounds associated with particulate matter in London, Atmos. Environ. 2001; 35:2483-2495.
18. Müller K. A 3 year study of the aerosol in northwest Saxony (Germany). Atmospheric Environment. 1999;33(11):1679-85.
19. Heintzenberg J, Müller K, Birmili W, Spindler G, Wiedensohler A. Mass-related aerosol properties over the Leipzig basin. J. Geophys. Res. 1998;103(D11):PP. 13,125-13,135.
20. Cachier H, Brémond MP, Buat-Ménard P. Determination of atmospheric soot carbon with a simple thermal method. Tellus Series B-Chemical and Physical Meteorology. 1989;41(B):379-90.
21. El Haddad I, Marchand N, Wortham H, Piot C, Besombes J-L, Cozic J, et al. Primary sources of PM2.5 organic aerosol in an industrial Mediterranean city, Marseille. Atmospheric Chemistry and Physics. 2011;11(5):2039-58.
22. Kuo C-Y, Cheng Y-W, Chen C-Y, Lee H. Correlation between the Amounts of Polycyclic Aromatic Hydrocarbons and Mutagenicity of Airborne Particulate Samples from Taichung City, Taiwan. Environmental Research. 1998;78(1):43-9.
23. Marchand N, Besombes JL, Chevron N, Masclet P, Aymoz G, Jaffrezo JL. Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two

French alpine valleys: sources and temporal patterns. Atmos. Chem. Phys. 2004;4(5):1167-81.
24. Masclet P, Hoyau V, Jaffrezo JL, Legrand M. Evidence for the presence of polycyclic aromatic hydrocarbons in the polar atmosphere and in the polar ice of Greenland. Analusis. 23(6):250-2.
25. Pistikopoulos P, Masclet P, Mouvier G. A receptor model adapted to reactive species: Polycyclic aromatic hydrocarbons; Evaluation of source contributions in an open urban site—I. Particle compounds. Atmospheric Environment. Part A. General Topics. 1990;24(5):1189-97.
26. Lin P, Yu JZ. Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols. Environ. Sci. Technol. 2011;45(24):10362-8.
27. Ritz SA, Cundall MJ, Gajewska BU, Alvarez D, Gutierrez-Ramos J-C, Coyle AJ, et al. Granulocyte macrophage colony-stimulating factor-driven respiratory mucosal sensitization induces The differentiation and function independently of interleukin-4. Am. J. Respir. Cell Mol. Biol. 2002;27(4):428-35.
28. Hodge DR, Hurt EM, Farrar WL. The role of IL-6 and STAT3 in inflammation and cancer. Eur. J. Cancer. 2005;41(16):2502-12.
29. Vlahos R, Bozinovski S, Hamilton JA, Anderson GP. Therapeutic potential of treating chronic obstructive pulmonary disease (COPD) by neutralising granulocyte macrophage-colony stimulating factor (GM-CSF). Pharmacology & Therapeutics. 2006;112(1):106-15.
30. Donaldson GC, Seemungal TAR, Patel IS, Bhowmik A, Wilkinson TMA, Hurst JR, et al. Airway and systemic inflammation and decline in lung function in patients with COPD. Chest. 2005;128(4):1995-2004.
31. Walston JD, Fallin MD, Cushman M, Lange L, Psaty B, Jenny N, et al. IL-6 gene variation is associated with IL-6 and C-reactive protein levels but not cardiovascular outcomes in the Cardiovascular Health Study. Hum. Genet. 2007;122(5):485-94.
32. Val S, Hussain S, Boland S, Hamel R, Baeza-Squiban A, Marano F. Carbon black and titanium dioxide nanoparticles induce pro-inflammatory responses in bronchial epithelial cells: need for multiparametric evaluation due to adsorption artifacts. Inhal Toxicol. 2009;21 Suppl 1:115-22.
33. Bonner JC. The epidermal growth factor receptor at the crossroads of airway remodeling. Am J Physiol Lung Cell Mol Physiol. 2002;283(3):L528-L530.
34. Enomoto Y, Orihara K, Takamasu T, Matsuda A, Gon Y, Saito H, et al. Tissue remodeling induced by hypersecreted epidermal growth factor and amphiregulin in the airway after an acute asthma attack. J. Allergy Clin. Immunol. 2009;124(5):913-920.
35. Blanchet S, Ramgolam K, Baulig A, Marano F, Baeza-Squiban A. Fine Particulate Matter Induces Amphiregulin Secretion by Bronchial Epithelial Cells. Am. J. Respir. Cell Mol. Biol. 2004;30(4):421-7.
36. Rumelhard M, Ramgolam K, Auger F, Dazy A-C, Blanchet S, Marano F, et al. Effects of PM2.5 components in the release of amphiregulin by human airway epithelial cells. Toxicol. Lett. 2007;168(2):155-64.
37. Ramgolam K, Hamel R, Rumelhard M, Marano F, Baeza-Squiban A. Autocrine effect of EGFR ligands on the pro-inflammatory response induced by PM(2.5) exposure in human bronchial epithelial cells. Archives of toxicology . 2012;86(10):1537-46.
38. Baulig A, Garlatti M, Bonvallot V, Marchand A, Barouki R, Marano F, et al. Involvement of reactive oxygen species in the metabolic pathways triggered by diesel exhaust particles in human airway epithelial cells. Am. J. Physiol. Lung Cell Mol. Physiol. 2003;285(3):L671-679.
39. Bonvallot V, Baeza-Squiban A, Baulig A, Brulant S, Boland S, Muzeau F, et al. Organic compounds from diesel exhaust particles elicit a proinflammatory response in human airway epithelial cells and induce cytochrome p450 1A1 expression. Am. J. Respir. Cell Mol. Biol. 2001;25(4):515-21.
40. Prestera T, Talalay P, Alam J, Ahn YI, Lee PJ, Choi AM. Parallel induction of heme oxygenase-1 and chemoprotective phase 2 enzymes by electrophiles and antioxidants: regulation by upstream antioxidant-responsive elements (ARE). Mol. Med. 1995;1(7):827-37.
41. Korashy HM, El-Kadi AOS. Regulatory mechanisms modulating the expression of cytochrome P450 1A1 gene by heavy metals. Toxicol. Sci. 2005 nov;88(1):39-51.
42. Amara IEA, Anwar-Mohamed A, El-Kadi AOS. Mercury modulates the CYP1A1 at transcriptional and posttranslational levels in human hepatoma HepG2 cells. Toxicology Letters. 2010;199(3):225-33.
43. Anwar-Mohamed A, El-Kadi AOS. Arsenite down-regulates cytochrome P450 1A1 at the transcriptional and posttranslational levels in human HepG2 cells. Free Radical Biology and Medicine. 2010;48(10):1399-409.
44. Barouki R, Morel Y. Repression of cytochrome P450 1A1 gene expression by oxidative stress: mechanisms and biological implications. Biochemical Pharmacology. 2001;61(5):511-6.
45. Yang M., Howell S. G., Zhuang J., Huebert B. J. Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China – interpretations of atmospheric measurements

during EAST-AIRE. Atmos. Chem. Phys. 2009, 9:2035–2050.
46. Adon M, Galy-Lacaux C, Yoboué V, Delon C, Lacaux JP, Castera P, et al. Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers. Atmospheric Chemistry and Physics. 2010;10(15):7467-87.
47. Celo V, Dabek-Zlotorzynska E, Mathieu D, Okonskaia I. Validation of simple microwave-assisted acid digestion method using microvessels for analysis of trace elements in atmospheric PM2.5 in monitoring and fingerprinting studies. The Open Chemical & Biomedical Methods Journal. 2010;3:141-50.
48. Guinot B, Cachier H, Oikonomou K, others. Geochemical perspectives from a new aerosol chemical mass closure. Atmospheric Chemistry and Physics. 2007;7(6):1670.
49. Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H. Chemical characterisation of PM2.5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment. 2005;39(4):637-51.
50. Putaud J-P, Van Dingenen R, Mangoni M, Virkkula A, Raes F, Maring H, et al. Chemical mass closure and assessment of the origin of the submicron aerosol in the marine boundary layer and the free troposphere at Tenerife during ACE-2. Tellus B. 2000;52(2):141-68.
51. Gelencsér A. Carbonaceous Aerosol. Atmospheric and Oceanographic Sciences Library. Springer Netherlands; 2004.
52. Turpin BJ, Lim H-J. Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. Aerosol Science and Technology. 2001;35(1):602-10.
53. Guinot B, Cachier H, Sciare J, Tong Y, Xin W, Jianhua Y. Beijing aerosol: Atmospheric interactions and new trends. J. Geophys. Res. 2007;112(D14):D14314.
54. Terzi E, Argyropoulos G, Bougatioti A, Mihalopoulos N, Nikolaou K, Samara C. Chemical composition and mass closure of ambient PM10 at urban sites. Atmospheric Environment. 2010;44(18):2231-9.
55. Besombes J-L, Maître A, Patissier O, Marchand N, Chevron N, Stoklov M, et al. Particulate PAHs observed in the surrounding of a municipal incinerator. Atmospheric Environment. 2001;35(35):6093-104.
56. Favez O, El Haddad I, Piot C, Boréave A, Abidi E, Marchand N, et al. Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France). Atmospheric Chemistry & Physics. 2010;10:5295-314.
57. Andreae MO, Gelencsér A. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics Discussions. 2006;6(3):3419-63.
58. Pfaffl MW. A new mathematical model for relative quantification in real-time RT–PCR. Nucleic Acids Res. 2001;29(9):e45.

CONCLUSION GENERALE

Face aux risques sanitaires engendrés par la pollution atmosphérique particulaire, l'étude de la qualité de l'air est devenue un enjeu majeur dans les grandes villes du monde. Les travaux de thèse développés dans ce manuscrit s'inscrivent dans cette problématique appliquée à l'Afrique de l'Ouest. C'est en quelque sorte un travail pionnier à plusieurs titres. D'une part, très peu d'études systématiques ont été effectuées sur la pollution urbaine en Afrique, en Afrique de l'Ouest notamment, comparativement aux autres continents. D'autre part, le développement d'études coordonnées en épidémiologie et en toxicologie en Afrique de l'Ouest, relativement aux maladies respiratoires et cardio-vasculaires, abordé dans cette étude, est encore à étendre très largement. Enfin, troisième point, le couplage entre études de pollution urbaine en Afrique de l'Ouest et analyses toxicologiques, développé dans cette thèse, constitue largement une première approche et une voie dans laquelle il convient de s'engager plus profondément. Notre but est tout d'abord de procéder à une caractérisation physico-chimique et en tailles des particules atmosphériques, avant de passer au lien avec la santé des populations, ici pour deux villes d'Afrique de l'Ouest (Bamako et Dakar) où les niveaux de concentrations, les variations spatio-temporelles, la composition chimique, la distribution granulométrique, la caractérisation des sources n'ont jamais été étudiés de manière exhaustive. Ce travail a également permis de créer une première base de données, certes non assez exhaustive pour aider dès à présent à la mise en place de stratégies de lutte contre la pollution urbaine en Afrique de l'Ouest.

L'analyse bibliographique effectuée en première partie de thèse a permis de rendre compte des quelques études existantes sur la pollution particulaire urbaine en Afrique de l'Ouest. Alors qu'un séjour dans ces villes suffit pour réaliser que la pollution y constitue un très sérieux problème, les premières mesures à moyen terme du programme POLCA sur des sites à proximité du trafic ont permis de dresser un premier bilan de la pollution liée au black carbon (BC). Les variations temporelles montrent des pics de concentrations aux heures de pointes, le matin entre 6h et 8h et le soir entre 18h et 20h, quel que soit le site. Cette pollution apparait comme liée aux activités humaines, notamment le transport avec de fortes variations d'une ville à une autre, mais également dans une même ville. L'évolution mensuelle présente une variation saisonnière marquée avec des maxima de concentrations en saison sèche coïncidant avec la période des feux au nord du Sénégal par exemple. Les niveaux de BC mesurés à Bamako et Dakar sont du même ordre de grandeur que ceux obtenus dans la plupart des mégacités mondiales et les grandes villes industrialisées, confirmant la situation alarmante à laquelle sont confrontées les villes d'Afrique de l'Ouest. Finalement, la concentration

moyenne annuelle de $PM_{2.5}$ à Dakar estimée à partir du BC est 4 fois la norme de 10 µg/m^3 fixée par l'OMS.

La troisième partie de ce travail porte sur l'analyse et l'exploitation des échantillons collectés par types d'impacteurs, permettant une étude granulométrique et par filtration lors de campagnes intensives de terrain, respectivement en Janvier et Décembre 2009 à Bamako et à Dakar. Cette étape était tout particulièrement intéressante, puisqu'il s'agissait pour moi de tester et valider de nouveaux protocoles analytiques pour la détermination des métaux ainsi que pour la matière carbonée. L'ensemble des analyses effectuées a permis d'établir la composition chimique complète (matière carbonée, plus de 50 éléments traces, ions majeurs et HAPs) de l'aérosol à Bamako et à Dakar, pour différentes fractions granulométriques, mais également dans un suivi de l'évolution temporelle. Une étude préliminaire d'identification des sources de particules a été ensuite menée, basée sur les variations journalières, la distribution en classes de tailles et sur l'analyse des rapports et des corrélations entre différents éléments. Ce travail a conduit à l'identification d'éléments traceurs de sources à Bamako et à Dakar. Enfin, la spéciation chimique a révélé que l'aérosol est majoritairement constitué de poussières (crustales et resuspension) et d'aérosol carboné, à Bamako comme à Dakar.

Au chapitre IV, notre travail a montré que les modèle-récepteurs mettant notamment en œuvre l'Analyse en Composantes Principales (ACP) et la Factorisation en Matrice Positive (PMF) ont toutefois permis d'obtenir une quantification assez précise des différentes sources contribuant aux émissions de particules à nos deux sites. Le travail en amont du chapitre II était indispensable pour l'interprétation des sources. Les modèles ACP et PMF ont révélé 5 et 6 sources à Bamako et à Dakar respectivement. Les différentes sources identifiées à Bamako sont la source crustale (5-20%), la combustion de fuel (28-70%) (véhicules, deux-roues à 2-temps, fuels domestiques), les sels inorganiques (3-9%), l'usure des pneus et freins des véhicules (5-13%) et les particules en resuspension issues du trafic (8-29%). A Dakar, les poussières en resuspension contribuent pour 13 à 23%, la source liée au trafic 32-42%, la source marine 15-21%, la source associée à la production du ciment et au secteur du bâtiment constructions 13-18%, la source de combustion de fuels liée aux activités portuaires 5-13% et l'usure de freins des véhicules 5-13%. Sur les deux sites, la contribution des particules d'origine anthropiques est prédominante, représentant 67-81% à Bamako et 61-68% à Dakar.

Le chapitre V portant sur l'impact sanitaire des particules, constitue une étude novatrice. L'objectif était d'étudier le dépôt des particules dans le système respiratoire des populations Ouest Africaines à partir du modèle DEPCLUNG (DEPosition Clearance LUNG), adapté de celui de la CIPR (Commission Internationale pour la Protection

Radiologique). La difficulté de ce travail repose sur la détermination des paramètres physiologiques et respiratoires de populations ouest africaines pour lesquelles ces données sont quasi inexistantes, particulièrement chez les enfants. Après une bibliographie très poussée, les paramètres manquants ont été estimés à partir de méthodes allométriques de « scaling ». L'étude de la fraction déposée DF dans les divers compartiments de l'appareil respiratoire chez les adultes ouest africains montre qu'entre 31 ± 9% et 36 ± 12% des particules se déposent dans la région extrathoracique, 3 ± 1% dans les bronches, 6 ± 5% dans les bronchioles et 24 ± 15% dans la région alvéolaire. Ce dernier pourcentage est à peu prés deux fois supérieur chez les enfants. L'application aux différents types d'aérosols réellement mesurés sur nos sites en entrée du modèle DEPCLUNG nous a permis de montrer que les aérosols carbonés (BC et POM), dominant dans les fines particules, se retrouvent majoritairement dans les régions thoracique et alvéolaire, tandis que les grosses particules composées largement de poussières se déposent dans la partie supérieure de l'appareil respiratoire. Les poussières fines descendent également jusque dans les alvéoles.

Le dernier chapitre sur l'étude d'impact sanitaire de l'aérosol, a consisté en des analyses *in vitro* en laboratoire afin de déterminer le degré de toxicité de différents types de particules à Bamako (BK1 lors d'un épisode de poussière et BK2 après le passage de cet événement) et à Dakar (DK), en les confrontant à des cellules épithéliales bronchiques humaines (lignée 16HBE). Les réponses proinflammatoires de 6 biomarqueurs (GM-CSF, IL-6, CYP1A1, NQO-1, HO-1 et AREG) pour trois classes de tailles de particules (ultrafines, fines et grosses) ont été étudiées. Les faits majeurs sont les suivants :

a) généralement, les effets sont plus importants pour les particules ultrafines et fines, sauf pendant BK2, où les particules grossières ont également un impact. Ceci pourrait être lié à des quantités importantes de carbone organique sur les particules de dust naturellement présentes à Bamako ;
b) la sécrétion de cytokines est maximale à BK2 par rapport à BK1 et DK, peut être en liaison avec le caractère plus soluble des particules de BK2 par rapport à BK1 et DK ;
c) l'expression des CYP1A1 est moindre à Dakar qu'à Bamako alors que, connus pour induire les CYP1A1, les HAPs sont plus élevées à Dakar. Des questions se posent alors, quand à la biodisponibilité des HAPs à Dakar. Par ailleurs, est-ce la présence d'éléments dans les HAPs à Dakar qui contribuerait à inhiber la sécrétion des CYP1A1 ? la présence de toxines dont l'induction des CYP1A1 est avérée, liée aux feux de décharges à Bamako ?

d) les meilleures corrélations sont obtenues entre GM-CSF et concentrations de carbone suie et organique, et c'est encore pendant BK2 que ces effets sont les plus marquants.

Ce travail a permis la caractérisation de la pollution particulaire à deux sites de trafic en Afrique de l'Ouest mais également d'étudier ses effets potentiels sur la santé respiratoire des populations. La conclusion est que les hauts niveaux de concentrations en particules et le degré de mélange entre sources font que l'aérosol Ouest Africain constitue un véritable risque avéré pour la santé des populations. Les résultats développés ici seront utiles pour d'autres études du même type à venir et à généraliser. Ils doivent également permettre aux autorités compétentes de réaliser l'urgence qu'il y'a pour prendre des décisions en vue de lutter contre cette pollution.

Les perspectives issues de ce travail sont nombreuses et de divers ordres, notamment :

- il s'agit de la première base de données complète sur la spéciation physico-chimique et en tailles de l'aérosol urbain de trafic en Afrique de l'Ouest, lesquelles s'inscrivent comme faisant partie des plus polluées au monde, avec des programmes de recherche sur la pollution très rares. Ainsi, ces résultats devraient servir à mieux spécifier les futurs projets d'étude de pollution particulaire à développer : 1) l'identification de nouvelles sources ; 2) une étude satellitale de pollution à l'échelle urbaine et régionale ;

- évaluer les risques sanitaires cardio-respiratoires liés à la pollution atmosphérique sur ces mêmes populations par une approche épidémiologique et toxicologique. Cette double approche consistera à croiser les résultats expérimentaux avec les données cliniques recueillies dans ces villes (enquêtes épidémiologiques, suivi de cohortes, analyses toxicologiques).

Enfin, de procéder au développement plus poussé du modèle DEPCLUNG (intégration de l'hygroscopicité et de la solubilité des particules dans le calcul du dépôt). Plus généralement, ces travaux sont une contribution au développement de la chaîne intégrée combinant approches expérimentale in situ de terrain sur les sources urbaines d'émission de polluants de combustion (particules, gaz), niveaux résultant d'exposition des populations, modélisation (in silico) des doses inhalées réparties dans les différents compartiments du système respiratoire, établissement de fonctions doses-réponses et détermination des réponses toxicologiques et épidémiologiques.

Ces projections s'inscrivent ainsi dans une approche pluridisciplinaire et surtout innovante pour une région, l'Afrique de l'Ouest, où les différentes composantes de cette

chaîne intégrée sont très peu documentées comparativement aux autres continents et où les besoins sur ces diverses composantes sont extrêmement forts, compte tenu d'une démographie galopante et d'une urbanisation encore largement incontrôlée.

REFERENCES BIBLIOGRAPHIQUES

Adejumo, J.A., Obioh, I.B., Ogunsola, O.J., Akeredolu, F.A., Olaniyi, H.B., Asubiojo, O.I., Oluwole, A.F., Akanle, O.A., Spyrou, N.M., 1994. The atmospheric deposition of major, minor and trace elements within and around three cement factories. Journal of Radioanalytical and Nuclear Chemistry Articles 179, 195 – 204.

Adepetu, J.A., Asubiojo, O.I., Iskander, F.Y., Bauer, T.L., 1988. Elemental composition of Nigerian harmattan dust. Journal of radioanalytical and nuclear chemistry 121, 141–147.

Adon, M., Galy-Lacaux, C., Yoboué, V., Delon, C., Lacaux, J.P., Castera, P., Gardrat, E., Pienaar, J., Al Ourabi, H., Laouali, D., others, 2010. Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers. Atmos. Chem. Phys 10, 7467–7487.

Afeti, G.M., Resch, F.J., 2000. Physical characteristics of Saharan dust near the Gulf of Guinea. Atmospheric Environment 34, 1273–1279.

Akanle, O., Akintanmide, A., Durosinmi, M., Oluwole, A., Spyrou, N., 1999. Elemental analysis of blood of nigerian hypertensive subjects. Biological Trace Element Research 71-72, 611–616.

Akeredolu, F., 1989. Atmospheric environment problems in Nigeria—An overview. Atmospheric Environment (1967) 23, 783–792.

Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., Romero, P.-M., Exposito, F., García, O., Pedro Diaz, J., Dingenen, R.V., Putaud, J.P., 2005. Characterisation of TSP and $PM_{2.5}$ at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan Dust Episode (July 2002). Atmospheric Environment 39, 4715–4728.

Alleman, L.Y., Lamaison, L., Perdrix, E., Robache, A., Galloo, J.-C., 2010. PM_{10} metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. Atmospheric Research 96, 612–625.

Allen, J.O., Mayo, P.R., Hughes, L.S., Salmon, L.G., Cass, G.R., 2001. Emissions of size-segregated aerosols from on-road vehicles in the Caldecott tunnel. Environ. Sci. Technol. 35, 4189–4197.

Almeida, S.M., Pio, C.A., Freitas, M.C., Reis, M.A., Trancoso, M.A., 2005. Source apportionment of fine and coarse particulate matter in a sub-urban area at the Western European Coast. Atmospheric Environment 39, 3127–3138.

Amara, I.E.A., Anwar-Mohamed, A., El-Kadi, A.O.S., 2010. Mercury modulates the CYP1A1 at transcriptional and posttranslational levels in human hepatoma HepG2 cells. Toxicology Letters 199, 225–233.

Ancellet, G., Orlandi, E., Real, E., Law, K.S., Schlager, H., Fierli, F., Nielsen, J.K., Thouret, V., Mari, C., 2011. Tropospheric ozone production related to West African city emissions during the 2006 wet season AMMA campaign. Atmos. Chem. Phys. 11, 6349–6366.

Andreae, M.O., 1983. Soot Carbon and Excess Fine Potassium: Long-Range Transport of Combustion-Derived Aerosols. Science 220, 1148–1151.

Andreae, M.O., Browell, E.V., Garstang, M., Gregory, G.L., Harriss, R.C., Hill, G.F., Jacob, D.J., Pereira, M.C., Sachse, G.W., Setzer, A.W., Dias, P.L.S., Talbot, R.W., Torres, A.L., Wofsy, S.C., 1988. Biomass-burning emissions and associated haze layers over Amazonia. J. Geophys. Res. 93, 1509–1527.

Andreae, M.O., Gelencsér, A., 2006. Black carbon or brown carbon ? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics Discussions 6, 3419–3463.

Andriejauskienė, J., 2008. Black carbon aerosol at the background site in the coastal zone of the Baltic Sea. Lithuanian Journal of Physics 48, 183–194.

Anwar-Mohamed, A., El-Kadi, A.O.S., 2010. Arsenite down-regulates cytochrome P450 1A1 at the transcriptional and posttranslational levels in human HepG2 cells. Free Radical Biology and Medicine 48, 1399–1409.

Arku, R.E., Vallarino, J., Dionisio, K.L., Willis, R., Choi, H., Wilson, J.G., Hemphill, C., Agyei-Mensah, S., Spengler, J.D., Ezzati, M., 2008. Characterizing air pollution in two low-income neighborhoods in Accra, Ghana. Science of The Total Environment 402, 217–231.

Asgharian, B., Ménache, M.G., Miller, F.J., 2004. Modeling age-related particle deposition in humans. J. Aerosol Med. 17, 213–224.

Assamoi, E.-M., Liousse, C., 2010. A new inventory for two-wheel vehicle emissions in West Africa for 2002. Atmospheric Environment 44, 3985–3996.

Asubiojo, O.I., Obioh, I.B., Oluyemi, E.A., Oluwole, A.F., Spyrou, N.M., Farooqi, A.S., Arshed, W., Akanle, O.A., 1993. Elemental characterization of airborne particulates at two Nigerian locations during the Harmattan season. Journal of Radioanalytical and Nuclear Chemistry Articles 167, 283 – 293.

Ayi Fanou, L., Mobio, T.A., Creppy, E.E., Fayomi, B., Fustoni, S., Møller, P., Kyrtopoulos, S., Georgiades, P., Loft, S., Sanni, A., Skov, H., Øvrebø, S., Autrup, H., 2006. Survey of air pollution in Cotonou, Benin—air monitoring and biomarkers. Science of The Total Environment 358, 85–96.

Bair, W.J., 1995. The ICRP Human Respiratory Tract Model for Radiological Protection. Radiat Prot Dosimetry 60, 307–310.

Bair, W.J., al., 1994. Human Respiratory Tract Model for Radiological Protection. volume 24 of Annals of the ICRP: ICRP Publication 66, Pergamon Oxford.

Barouki, R., Morel, Y., 2001. Repression of cytochrome P450 1A1 gene expression by oxidative stress: mechanisms and biological implications. Biochemical Pharmacology 61, 511–516.

Bartley, D.L., Vincent, J.H., 2011. Sampling Conventions for Estimating Ultrafine and Fine Aerosol Particle Deposition in the Human Respiratory Tract. Annals of Occupational Hygiene 55, 696–709.

Baulig, A., Garlatti, M., Bonvallot, V., Marchand, A., Barouki, R., Marano, F., Baeza-Squiban, A., 2003. Involvement of reactive oxygen species in the metabolic pathways triggered by diesel exhaust particles in human airway epithelial cells. Am. J. Physiol. Lung Cell Mol. Physiol. 285, L671–679.

Baumbach, G., Vogt, U., Hein, K.R.G., Oluwole, A.F., Ogunsola, O.J., Olaniyi, H.B., Akeredolu, F.A., 1995. Air pollution in a large tropical city with a high traffic density -- results of measurements in Lagos, Nigeria. The Science of the Total Environment 169, 25–31.

Beavington, F., Cawse, P.A., Wakenshaw, A., 2004. Comparative studies of atmospheric trace elements: improvements in air quality near a copper smelter. Sci. Total Environ. 332, 39–49.

Bertrand, J., Baudet, J., Drochon, A., 1974. Importance des aérosols naturels en Afrique de l'Ouest. Journal de Recherhce Atmosphérique 8, 845–860.

Bhanuprasad, S.G., Venkataraman, C., Bhushan, M., 2008. Positive matrix factorization and trajectory modelling for source identification: A new look at Indian Ocean Experiment ship observations. Atmospheric Environment 42, 4836–4852.

Blake, N.J., Blake, D.R., Sive, B.C., Chen, T.-Y., Rowland, F.S., Jr, J.E.C., Sachse, G.W., Anderson, B.E., 1996. Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region. J. Geophys. Res. 101, 24151–24,164.

Blanchet, S., Ramgolam, K., Baulig, A., Marano, F., Baeza-Squiban, A., 2004. Fine Particulate Matter Induces Amphiregulin Secretion by Bronchial Epithelial Cells. Am. J. Respir. Cell Mol. Biol. 30, 421–427.

Bolch, W.E., Farfán, E.B., Huh, C., Huston, T.E., Bolch, W.E., 2001. Influences of parameter uncertainties within the ICRP 66 respiratory tract model. Health Physics 81, 378–394.

Bousquet, J., Ndiaye, M., Aït-Khaled, N., Annesi-Maesano, I., Vignola, A.-M., 2003. Management of chronic respiratory and allergic diseases in developing countries. Focus on sub-Saharan Africa. Allergy 58, 265–283.

Bowen, H.J.M., 1966. Trace elements in biochemistry. Academic Press.

Brook, R.D., 2008. Cardiovascular effects of air pollution. Clin. Sci. 115, 175–187.

Brown, J.S., Zeman, K.L., Bennett, W.D., 2002. Ultrafine Particle Deposition and Clearance in the Healthy and Obstructed Lung. Am. J. Respir. Crit. Care Med. 166, 1240–1247.

Brugge, D., Durant, J.L., Rioux, C., 2007. Near-highway pollutants in motor vehicle exhaust: A review of epidemiologic evidence of cardiac and pulmonary health risks. Environmental Health 6, 23.

Brunekreef, B., 2010. Air Pollution and Human Health: From Local to Global Issues. Procedia - Social and Behavioral Sciences 2, 6661–6669.

Bryant, F., Yamold, P.R., 1995. Principal-components analysis and confirmatory factor analysis, American Psychological Association. ed, Reading and understanding multivariate statistics. In L. G. Grimm & P. R. Yarnold (Eds.), Washington, DC.

Cachier, H., Brémond, M.P., Buat-Ménard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. Tellus Series B-Chemical and Physical Meteorology 41(B), 379–390.

Callén, M.S., de la Cruz, M.T., López, J.M., Navarro, M.V., Mastral, A.M., 2009. Comparison of receptor models for source apportionment of the PM_{10} in Zaragoza (Spain). Chemosphere 76, 1120–1129.

Callot, Y., Marticorena, B., Bergametti, G., 2000. Geomorphologic approach for modelling the surface features of arid environments in a model of dust emissions: application to the Sahara desert. Geodinamica Acta 13, 245–270.

Camail, M., Mahamane, M., Pucci, B., Rigaud, J.P., 1987. Analyses chimiques des eaux du fleuve Niger à Niamey: Premiers résultats d'une campagne annuelle de mesures. Hydrol. continent 2, 87–99.

Celo, V., Dabek-Zlotorzynska, E., Mathieu, D., Okonskaia, I., 2010. Validation of simple microwave-assisted acid digestion method using microvessels for analysis of trace elements in atmospheric $PM_{2.5}$ in monitoring and fingerprinting studies. The Open Chemical & Biomedical Methods Journal 3, 141–150.

Chan, Y., Hawas, O., Hawker, D., Vowles, P., Cohen, D.D., Stelcer, E., Simpson, R., Golding, G., Christensen, E., 2011. Using multiple type composition data and wind data in PMF analysis to apportion and locate sources of air pollutants. Atmospheric Environment 45, 439–449.

Cheng, Y., Zheng, M., He, K., Chen, Y., Yan, B., Russell, A.G., Shi, W., Jiao, Z., Sheng, G., Fu, J., Edgerton, E.S., 2011. Comparison of two thermal-optical methods for the determination of organic carbon and elemental carbon: Results from the southeastern United States. Atmospheric Environment 45, 1913–1918.

Cheng, Y.S., 2003. Aerosol Deposition in the Extrathoracic Region. Aerosol Science and Technology 37, 659–671.

Cho, S.-H., Tong, H., McGee, J., Baldauf, R., Krantz, Q., Gilmour, M., 2009. Comparative Toxicity of Size-Fractionated Airborne Particulate Matter Collected at Different Distances from an Urban Highway. Environmental Health Perspectives.

Chow, J.C., Watson, J.G., 2002. Review of $PM_{2.5}$ and PM_{10} Apportionment for Fossil Fuel Combustion and Other Sources by the Chemical Mass Balance Receptor Model. Energy Fuels 16, 222–260.

Chow, J.C., Watson, J.G., Chen, L.-W.A., Chang, M.-C.O., Miranda, G.P., 2005. Comparison of the DRI/OGC and Model 2001 Thermal/Optical Carbon Analyzers.

Chow, J.C., Watson, J.G., Fujita, E.M., Lu, Z., Lawson, D.R., Ashbaugh, L.L., 1994. Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the southern California air quality study. Atmos. Environ. 28, 2061–2080.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The dri thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies. Atmospheric Environment. Part A. General Topics 27, 1185–1201.

Chueinta, W., Hopke, P.K., Paatero, P., 2000. Investigation of sources of atmospheric aerosol at urban and suburban residential areas in Thailand by positive matrix factorization. Atmospheric Environment 34, 3319–3329.

Clean Air Initiative, 2003. Banque mondiale: Initiative sur la qualité de l'air dans les villes d'Afrique sub-saharienne. Rapport d'avancement 1998-2002 (Document de travail No. 11). Banque mondiale.

D'Almeida, G.A., Koepke, P., Shettle, E.P., 1991. Atmospheric Aerosols: Global Climatology and Radiative Characteristics. A. Deepak, Hampton, Va. 561.

De Longueville, F., Hountondji, Y.-C., Henry, S., Ozer, P., 2010. What do we know about effects of desert dust on air quality and human health in West Africa compared to other regions? Science of The Total Environment 409, 1–8.

Deboudt, K., Flament, P., Choël, M., Gloter, A., Sobanska, S., Colliex, C., 2010. Mixing state of aerosols and direct observation of carbonaceous and marine coatings on African dust by individual particle analysis. J. Geophys. Res. 115, D24207.

Delfino, R.J., Chang, J., Wu, J., Ren, C., Tjoa, T., Nickerson, B., Cooper, D., Gillen, D.L., 2009. Repeated hospital encounters for asthma in children and exposure to traffic-related air pollution near the home. Ann. Allergy Asthma Immunol. 102, 138–144.

Delmas, R.A., Druilhet, A., Cros, B., Durand, P., Delon, C., Lacaux, J.P., Brustet, J.M., Serça, D., Affre, C., Guenther, A., Greenberg, J., Baugh, W., Harley, P., Klinger, L., Ginoux, P., Brasseur, G., Zimmerman, P.R., Grégoire, J.M., Janodet, E., Tournier, A., Perros, P., Marion, T., Gaudichet, A., Cachier, H., Ruellan, S., Masclet, P., Cautenet, S., Poulet, D., Biona, C.B., Nganga, D., Tathy, J.P., Minga, A., Loemba-Ndembi, J., Ceccato, P., 1999. Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO): An overview. J. Geophys. Res. 104, 30609–30,624.

Derimian, Y., Léon, J.-F., Dubovik, O., Chiapello, I., Tanré, D., Sinyuk, A., Auriol, F., Podvin, T., Brogniez, G., Holben, B.N., 2008. Radiative properties of aerosol mixture observed during the dry season 2006 over M'Bour, Senegal (African Monsoon Multidisciplinary Analysis campaign). J. Geophys. Res. 113, D00C09.

DHS, 2006. DHS (Demography Health Survey) Final Reports [WWW Document]. URL http://. www.measuredhs.com/pubs/browse_region.cfm.

Díaz, J., Tobías, A., Linares, C., 2012. Saharan dust and association between particulate matter and case-specific mortality: a case-crossover analysis in Madrid (Spain). Environmental Health 11, 11.

Dieme, D., Cabral-Ndior, M., Garçon, G., Verdin, A., Billet, S., Cazier, F., Courcot, D., Diouf, A., Shirali, P., 2012. Relationship between physicochemical characterization and toxicity of fine particulate matter ($PM_{2.5}$) collected in Dakar city (Senegal). Environ. Res. 113, 1–13.

Dionisio, K.L., Arku, R.E., Hughes, A.F., Vallarino, J., Carmichael, H., Spengler, J.D., Agyei-Mensah, S., Ezzati, M., 2010. Air pollution in Accra neighborhoods: spatial, socioeconomic, and temporal patterns. Environmental science & technology 44, 2270–2276.

Dionisio, K.L., Rooney, M.S., Arku, R.E., Friedman, A.B., Hughes, A.F., Vallarino, J., Agyei-Mensah, S., Spengler, J.D., Ezzati, M., 2010. Within-Neighborhood Patterns and Sources of Particle Pollution: Mobile Monitoring and Geographic Information System Analysis in Four Communities in Accra, Ghana. Environmental Health Perspectives 118, 607–613.

Dockery, D.W., Pope, C.A., 1994. Acute Respiratory Effects of Particulate Air Pollution. Annual Review of Public Health 15, 107–132.

Dockery, D.W., Pope, C.A., 3rd, Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Jr, Speizer, F.E., 1993. An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med. 329, 1753–1759.

Donaldson, G.C., Seemungal, T.A.R., Patel, I.S., Bhowmik, A., Wilkinson, T.M.A., Hurst, J.R., Maccallum, P.K., Wedzicha, J.A., 2005. Airway and systemic inflammation and decline in lung function in patients with COPD. Chest 128, 1995–2004.

Dongarrà, G., Manno, E., Varrica, D., Vultaggio, M., 2007. Mass levels, crustal component and trace elements in PM_{10} in Palermo, Italy. Atmospheric Environment 41, 7977–7986.

Doumbia, E.H.T., Liousse, C., Galy-Lacaux, C., Ndiaye, S.A., Diop, B., Gardrat, E., Zouiten, C., Candaudap, F., Rosset, R., 2012b. Urban West Africa aerosols concentration levels and differentiated PM characteristics at Bamako (Mali) and Dakar (Senegal). In submission progress.

Doumbia, E.H.T., Liousse, C., Galy-Lacaux, C., Ndiaye, S.A., Diop, B., Ouafo, M., Assamoi, E.M., Gardrat, E., Castera, P., Rosset, R., Akpo, A., Sigha, L., 2012a. Real time black carbon measurements in West and Central Africa urban sites. Atmospheric Environment 54, 529–537.

Dufetel, P., Pigearias, B., Lonsdorfer, J., Derossi, G., Diaine, C., Faltot, P.J., 1989. Spirometric Reference Values in Senegalese Black Adults. Eur. Respir. J. 2, 352–358.

Dufetel, P., Sambiani, K., Togbey, K., Kolani, M., 1990. Characteristics of lung volume and expiratory flow seen in black Africans adults. Rev. Mal. Respir. 7, 215–222.

Durosinmi, M.A., Ojo, J.O., Oluwole, A.F., Akanle, O.A., Arshed, W., Spyrou, N.M., 1993. Trace elements in sickle cell disease. Journal of Radioanalytical and Nuclear Chemistry Articles 168, 233 – 242.

Eliasson, I., Jonsson, P., Holmer, B., 2009. Diurnal and intra-urban particle concentrations in relation to windspeed and stability during the dry season in three African cities. Environmental Monitoring and Assessment 154, 309–324.

Eltayeb, M.A.H., Injuk, J., Maenhaut, W., Van Grieken, R.E., 2001. Elemental composition of mineral aerosol generated from Sudan Sahara sand. Journal of atmospheric chemistry 40, 247–273.

EPA PMF 3.0 User Guide, 2008. EPA PMF 3 0 User Guide v16 092208 final pdf free ebook download. Washington DC.

Esteve, A.R., Estellés, V., Utrillas, M.P., Martínez-Lozano, J.A., 2012. In-situ integrating nephelometer measurements of the scattering properties of atmospheric aerosols at an urban coastal site in western Mediterranean. Atmospheric Environment 47, 43–50.

Ezzati, M., Bailis, R., Kammen, D.M., Holloway, T., Price, L., Cifuentes, L.A., Barnes, B., Chaurey, A., Dhanapala, K.N., 2004. Energy Management and Global Health. Annual Review of Environment and Resources 29, 383–419.

Fall, M., Bion, A., Keravec, V., Ciss, M., Diouf, A., Dionnet, F., Morin, J.-P., 2008. Réponse toxicologique d'une culture organotypique de tissu pulmonaire exposée à des gaz

d'échappement issus d'un moteur à combustion. Environnement, Risques & Santé 7, 123–129.

Favez, O., Cachier, H., Sciare, J., Alfaro, S.C., El-Araby, T.M., Harhash, M.A., Abdelwahab, M.M., 2008. Seasonality of major aerosol species and their transformations in Cairo megacity. Atmospheric Environment 42, 1503–1516.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., D'Anna, B., 2010. Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France). Atmospheric Chemistry & Physics 10, 5295–5314.

Flament, P., Deboudt, K., Cachier, H., Châtenet, B., Mériaux, X., 2011. Mineral dust and carbonaceous aerosols in West Africa: Source assessment and characterization. Atmospheric Environment 45, 3742–3749.

Fritsch, P., 2006. Uncertainties in aerosol deposition within the respiratory tract using the ICRP 66 model: A study in workers. Health Physics 90, 114–126.

Galy-Lacaux, C., Carmichael, G.R., Song, C.H., Lacaux, J.P., Al Ourabi, H., Modi, A.I., 2001. Heterogeneous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations. Journal of Geophysical Research 106, 12559–12578.

Gehring, U., Wijga, A.H., Brauer, M., Fischer, P., Jongste, J.C. de, Kerkhof, M., Oldenwening, M., Smit, H.A., Brunekreef, B., 2010. Traffic-related Air Pollution and the Development of Asthma and Allergies during the First 8 Years of Life. Am. J. Respir. Crit. Care Med. 181, 596–603.

Gelencsér, A., 2004. Carbonaceous Aerosol, Atmospheric and Oceanographic Sciences Library. ed. Springer Netherlands.

Gianini, M.F.D., Gehrig, R., Fischer, A., Ulrich, A., Wichser, A., Hueglin, C., 2012. Chemical composition of PM10 in Switzerland: An analysis for 2008/2009 and changes since 1998/1999. Atmospheric Environment 54, 97–106.

Goldberg, E.D., 1963. H.M. Hill (Ed.), Composition of sea Water, Comparative Oceanography, Vol.2 of the seaWiley. New York.

Gordon, G.E., 1988. Receptor models. Environ. Sci. Technol. 22, 1132–1142.

Graedel, T.E., Keene, W.C., 1995. Tropospheric budget of reactive chlorine. Global Biogeochemical Cycles 9, 47–77.

Gu, Y., Liou, K.N., Jiang, J.H., Su, H., Liu, X., 2012. Dust aerosol impact on North Africa climate: a GCM investigation of aerosol-cloud-radiation interactions using A-Train satellite data. Atmos. Chem. Phys. 12, 1667–1679.

Guinot, B., Cachier, H., Oikonomou, K., 2007. Geochemical perspectives from a new aerosol chemical mass closure. Atmospheric Chemistry and Physics 7, 1670.

Guinot, B., Cachier, H., Sciare, J., Tong, Y., Xin, W., Jianhua, Y., 2007. Beijing aerosol: Atmospheric interactions and new trends. J. Geophys. Res. 112, D14314.

Gupta, I., Salunkhe, A., Kumar, R., 2012. Source Apportionment of PM_{10} by Positive Matrix Factorization in Urban Area of Mumbai, India. Scientific World Journal 2012.

Halonen, J.I., Lanki, T., Yli-Tuomi, T., Kulmala, M., Tiittanen, P., Pekkanen, J., 2008. Urban air pollution, and asthma and COPD hospital emergency room visits. Thorax 63, 635–641.

Han, X., Naeher, L.P., 2006. A review of traffic-related air pollution exposure assessment studies in the developing world. Environment International 32, 106–120.

Happo, M.S., Hirvonen, M.-R., Halinen, A.I., Jalava, P.I., Pennanen, A.S., Sillanpaa, M., Hillamo, R., Salonen, R.O., 2008. Chemical compositions responsible for inflammation and tissue damage in the mouse lung by coarse and fine particulate samples from contrasting air pollution in Europe. Inhal. Toxicol. 20, 1215–1231.

Harvey, R.P., Hamby, D.M., 2002. Age-specific Uncertainty in Particulate Deposition for 1 µm AMAD Particles Using the ICRP-66 Lung Model. Health Physics 82, 807–816.

Hays, M.D., Cho, S.-H., Baldauf, R., Schauer, J.J., Shafer, M., 2011. Particle size distributions of metal and non-metal elements in an urban near-highway environment. Atmospheric Environment 45, 925–934.

Heiko Paeth, J.F., 2012. Greenhouse-gas versus aerosol forcing and African climate response. Climate Dynamics 26, 35–54.

Heintzenberg, J., Müller, K., Birmili, W., Spindler, G., Wiedensohler, A., 1998. Mass-related aerosol properties over the Leipzig basin. J. Geophys. Res. 103, PP. 13,125–13,135.

Henry, R.C., 1997. History and fundamentals of multivariate air quality receptor models. Chemometrics and intelligent laboratory systems 37, 37–42.

Herner, J.D., Ying, Q., Aw, J., Gao, O., Chang, D.P.Y., Kleeman, M.J., 2006. Dominant Mechanisms that Shape the Airborne Particle Size and Composition Distribution in Central California. Aerosol Science and Technology 40, 827–844.

Heyder, J., 2004. Deposition of Inhaled Particles in the Human Respiratory Tract and Consequences for Regional Targeting in Respiratory Drug Delivery. Proc. Am. Thorac. Soc. 1, 315–320.

Hinds, W.C., 1982. Aerosol technology: properties, behavior, and measurement of airborne particles.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L., Puxbaum, H., 2006. Intercomparison of Thermal and Optical Measurement Methods for Elemental Carbon and Black Carbon at an Urban Location. Environ. Sci. Technol. 40, 6377–6383.

Hodge, D.R., Hurt, E.M., Farrar, W.L., 2005. The role of IL-6 and STAT3 in inflammation and cancer. Eur. J. Cancer 41, 2502–2512.

Hong, Y.C., Leem, J.H., Ha, E.H., Christiani, D.C., 1999. PM_{10} exposure, gaseous pollutants, and daily mortality in Inchon, South Korea. Environ. Health Perspect. 107, 873–878.

Hopke, P.K., 1991. An introduction to receptor modeling. Chemometrics and Intelligent Laboratory Systems 10, 21–43.

Huang, S.-L., Hsu, M.-K., Chan, C.-C., 2002. Effects of Submicrometer Particle Compositions on Cytokine Production and Lipid Peroxidation of Human Bronchial Epithelial Cells. Environmental Health Perspectives 111, 478–482.

Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C., Vonmont, H., 2005. Chemical characterisation of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment 39, 637–651.

ICRP, 1994. Human Respiratory Tract Model for Radiological Protection, Annal of the international Commission on Radiological Protection (ICRP). Pergamon Press, Oxford, UK.

Iskander, F., 1985. Neutron activation analysis of an Egyptian cigarette and its ash. Journal of Radioanalytical and Nuclear Chemistry 89, 511–518.

James, A.C., Stahlhofen, W., Rudolf, G., Egan, M.J., Nixon, W., Gehr, P., Briant, J.K., 1991. The Respiratory Tract Deposition Model Proposed by the ICRP Task Group. Radiat. Prot. Dosimetry 38, 159–165.

Jaques, P.A., Kim, C.S., 2000. Measurement of total lung deposition of inhaled ultrafine particles in healthy men and women. Inhal. Toxicol. 12, 715–731.

Karanasiou, A., Moreno, N., Moreno, T., Viana, M., de Leeuw, F., Querol, X., 2012. Health effects from Sahara dust episodes in Europe: Literature review and research gaps. Environ. Int. 47, 107–114.

Karanasiou, A.A., Sitaras, I.E., Siskos, P.A., Eleftheriadis, K., 2007. Size distribution and sources of trace metals and n-alkanes in the Athens urban aerosol during summer. Atmospheric Environment 41, 2368–2381.

Katsouyanni, K., Touloumi, G., Spix, C., Schwartz, J., Balducci, F., Medina, S., Rossi, G., Wojtyniak, B., Sunyer, J., Bacharova, L., Schouten, J.P., Ponka, A., Anderson, H.R., 1997. Short term effects of ambient sulphur dioxide and particulate matter on mortality in 12 European cities: results from time series data from the APHEA project. BMJ 314, 1658–1658.

Kendall, M., Hamilton, R.S., Watt, J., Williams, I.D., 2001. Characterisation of selected speciated organic compounds associated with particulate matter in London. Atmospheric Environment 35, 2483–2495.

Kim, C.S., Hu, S.-C., 2006. Total respiratory tract deposition of fine micrometer-sized particles in healthy adults: empirical equations for sex and breathing pattern. J. Appl. Physiol. 101, 401–412.

Kim, E., Hopke, P.K., 2004. Source apportionment of fine particles in Washington, DC, utilizing temperature-resolved carbon fractions. J. Air Waste Manag. Assoc. 54, 773–785.

Knaapen, A.M., Shi, T., Borm, P.J.A., Schins, R.P.F., 2002. Soluble metals as well as the insoluble particle fraction are involved in cellular DNA damage induced by particulate matter. Molecular and Cellular Biochemistry 234-235, 317–326.

Korashy, H.M., El-Kadi, A.O.S., 2005. Regulatory mechanisms modulating the expression of cytochrome P450 1A1 gene by heavy metals. Toxicol. Sci. 88, 39–51.

Kouassi, K.S., Billet, S., Garçon, G., Verdin, A., Diouf, A., Cazier, F., Djaman, J., Courcot, D., Shirali, P., 2009. Oxidative damage induced in A549 cells by physically and chemically characterized air particulate matter ($PM_{2.5}$) collected in Abidjan, cote d'Ivoire. Journal of Applied Toxicology 30, 310-320.

Kuloglu, E., Tuncel, G., 2005. Size Distribution of Trace Elements and Major Ions in the Eastern Mediterranean Atmosphere. Water Air and Soil Pollution 167, 221–241.

Kuo, C.-Y., Cheng, Y.-W., Chen, C.-Y., Lee, H., 1998. Correlation between the Amounts of Polycyclic Aromatic Hydrocarbons and Mutagenicity of Airborne Particulate Samples from Taichung City, Taiwan. Environmental Research 78, 43–49.

Lacaux, J.., Cachier, H., Delmas, R., 1993. Biomass burning in Africa: An overview of its impact on the atmospheric chemistry. In: Fire in the Environment: Its Ecological, Atmospheric, and Climatic Importance. N. W. 159–191.

Lapp, N.L., Amandus, H.E., Hall, R., Morgan, W.K.C., 1974. Lung volumes and flow rates in black and white subjects. Thorax 29, 185–188.

Larsen, R.K., Baker, J.E., 2003. Source Apportionment of Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere: A Comparison of Three Methods. Environ. Sci. Technol. 37, 1873–1881.

Laupsa, H., Denby, B., Larssen, S., Schaug, J., 2009. Source apportionment of particulate matter ($PM_{2.5}$) in an urban area using dispersion, receptor and inverse modelling. Atmospheric Environment 43, 4733–4744.

Law, K.S., Fierli, F., Cairo, F., Schlager, H., Borrmann, S., Streibel, M., Real, E., Kunkel, D., Schiller, C., Ravegnani, F., Ulanovsky, A., D'Amato, F., Viciani, S., Volk, C.M., 2010. Corrigendum to "Air mass origins influencing TTL chemical composition over West Africa during 2006 summer monsoon" published in Atmos. Chem. Phys., 10, 10753–10770, 2010. Atmos. Chem. Phys. 10, 10939–10940.

Li, N., Xia, T., Nel, A.E., 2008. The role of oxidative stress in ambient particulate matter-induced lung diseases and its implications in the toxicity of engineered nanoparticles. Free Radical Biology and Medicine 44, 1689–1699.

Li, X., Wang, L., Wang, Y., Wen, T., Yang, Y., Zhao, Y., Wang, Y., 2012. Chemical composition and size distribution of airborne particulate matters in Beijing during the 2008 Olympics. Atmospheric Environment 50, 278–286.

Lin, P., Yu, J.Z., 2011. Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols. Environ. Sci. Technol. 45, 10362–10368.

Lindén, J., Boman, J., Holmer, B., Thorsson, S., Eliasson, I., 2012. Intra-urban air pollution in a rapidly growing Sahelian city. Environ. Int. 40, 51–62.

Lindén, J., Thorsson, S., Eliasson, I., 2008. Carbon Monoxide in Ouagadougou, Burkina Faso – A Comparison between Urban Background, Roadside and In-traffic Measurements. Water Air & Soil Pollution 188, 345–353.

Ling, S., Van Eeden, S., 2009. Particulate matter air pollution exposure: role in the development and exacerbation of chronic obstructive pulmonary disease. Int. J. Chron. Obstruct. Pulmon. Dis., 4, 233–243.

Liousse, C., Galy-Lacaux, C., 2010. Urban pollution in West Africa. La Météorologie.

Liousse, C., Guillaume, B., Grégoire, J.M., Mallet, M., Galy, C., Pont, V., Akpo, A., Bedou, M., Castéra, P., Dungall, L., Gardrat, E., Granier, C., Konaré, A., Malavelle, F., Mariscal, A., Mieville, A., Rosset, R., Serça, D., Solmon, F., Tummon, F., Assamoi, E., Yoboué, V., Van Velthoven, P., 2010. Western african aerosols modelling with updated biomass burning emission inventories in the frame of the AMMA-IDAF program. Atmospheric Chemistry and Physics Discussions, 10, 7347–7382.

Liousse, C., Penner, J.E., Chuang, C., Walton, J.J., Eddleman, H., Cachier, H., 1996. A global three-dimensional model study of carbonaceous aerosols. J. Geophys. Res. 101, 19411–19,432.

Lokken, R.P., Wellenius, G.A., Coull, B.A., Burger, M.R., Schlaug, G., Suh, H.H., Mittleman, M.A., 2009. Air pollution and risk of stroke: underestimation of effect due to misclassification of time of event onset. Epidemiology 20, 137–142.

Löndahl, J., Massling, A., Pagels, J., Swietlicki, E., Vaclavik, E., Loft, S., 2007. Size-Resolved Respiratory-Tract Deposition of Fine and Ultrafine Hydrophobic and Hygroscopic Aerosol Particles During Rest and Exercise. Inhalation Toxicology 19, 109–116.

Lukács, H., Gelencsér, A., Hammer, S., Puxbaum, H., Pio, C., Legrand, M., Kasper-Giebl, A., Handler, M., Limbeck, A., Simpson, D., Preunkert, S., 2007. Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe. J. Geophys. Res. 112, D23S18.

Lyamani, H., Olmo, F.J., Alados-Arboledas, L., 2008. Light scattering and absorption properties of aerosol particles in the urban environment of Granada, Spain. Atmospheric Environment 42, 2630–2642.

Makkonen, U., Hellén, H., Anttila, P., Ferm, M., 2010. Size distribution and chemical composition of airborne particles in south-eastern Finland during different seasons and wildfire episodes in 2006. Science of The Total Environment 408, 644–651.

Marchand, N., Besombes, J.L., Chevron, N., Masclet, P., Aymoz, G., Jaffrezo, J.L., 2004. Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: sources and temporal patterns. Atmos. Chem. Phys. 4, 1167–1181.

Masclet, P., Hoyau, V., Jaffrezo, J.L., Legrand, M., n.d. Evidence for the presence of polycyclic aromatic hydrocarbons in the polar atmosphere and in the polar ice of Greenland. Analusis 23, 250–252.

Matassoni, L., Pratesi, G., Centioli, D., Cadoni, F., Malesani, P., Caricchia, A.M., di Bucchianico, A.D.M., 2009. Saharan dust episodes in Italy: influence on PM_{10} daily limit value (DLV) exceedances and the related synoptic. Journal of Environmental Monitoring 11, 1586.

Mauderly, J.L., Chow, J.C., 2008. Health Effects of Organic Aerosols. Inhalation Toxicology 20, 257–288.

Mazzoli-Rocha, F., Fernandes, S., Einicker-Lamas, M., Zin, W.A., 2010. Roles of oxidative stress in signaling and inflammation induced by particulate matter. Cell Biology and Toxicology 26, 481–498.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem. Geophys. Geosyst. 2, 1021–24.

McTainsh, G.H., Nickling, W.G., Lynch, A.W., 1997. Dust deposition and particle size in Mali, West Africa. CATENA 29, 307–322.

Messan, F., Lawani, M.M., Marqueste, T., Lounana, J., Aimihoue, D., Metodakou, A., Decherchi, P., Grélot, L., 2011. Assessment of MEF(25) in 156 children displayed to automobile pollution in Cotonou municipality. Mali Med 26, 16–21.

Miller, G.J., Saunders, M.J., Gilson, R.J.C., Ashcroft, M.T., 1977. Lung function of healthy boys and girls in Jamaica in relation to ethnic composition, test exercise performance, and habitual physical activity. Thorax 32, 486–496.

Miller, S.L., Anderson, M.J., Daly, E.P., Milford, J.B., 2002. Source apportionment of exposures to volatile organic compounds. I. Evaluation of receptor models using simulated exposure data. Atmospheric Environment 36, 3629–3641.

Millero, F.J., Feistel, R., Wright, D.G., McDougall, T.J., 2008. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. Deep Sea Research Part I: Oceanographic Research Papers 55, 50–72.

MO, T., 2000. Air pollution and respiratory health in Africa: a review. East Africa Medecin Journal 77, 71–5.

Morawska, L., Hofmann, W., Hitchins-Loveday, J., Swanson, C., Mengersen, K., 2005. Experimental study of the deposition of combustion aerosols in the human respiratory tract. Journal of Aerosol Science 36, 939–957.

Müller, K., 1999. A 3 year study of the aerosol in northwest Saxony (Germany). Atmospheric Environment 33, 1679–1685.

Norman, M., Hansel, A., Wisthaler, A., 2007. O2+ as reagent ion in the PTR-MS instrument: Detection of gas-phase ammonia. International Journal of Mass Spectrometry 265, 382–387.

Nweke, O.C., Sanders III, W.H., 2009. Modern Environmental Health Hazards: A Public Health Issue of Increasing Significance in Africa. Environ. Health Perspect. 117, 863–870.

Nyanganyura, D., Maenhaut, W., Mathuthu, M., Makarau, A., Meixner, F.X., 2007. The chemical composition of tropospheric aerosols and their contributing sources to a continental background site in northern Zimbabwe from 1994 to 2000. Atmospheric Environment 41, 2644–2659.

Oluyemi, E.A., Asubiojo, O.I., Oluwole, A.F., Toussaint, C.J.N., 1994. Elemental concentrations and source identification of air particulate matter at a Nigerian site: A preliminary study. Journal of Radioanalytical and Nuclear Chemistry Articles 179, 187 – 194.

Onyedum, C.C., Chukwuka, J.C., Onwubere, B.J.C., Ulasi, I.I., Onwuekwe, I.O., 2010. Respiratory symptoms and ventilatory function tests in Nigerians with HIV infection. African health sciences 10.

Ostro, B., Feng, W.-Y., Broadwin, R., Green, S., Lipsett, M., 2007. The effects of components of fine particulate air pollution on mortality in California: results from CALFINE. Environ. Health Perspect. 115, 13–19.

Ozer, P., 2005. Estimation de la pollution particulaire naturelle de l'air en 2003 à Niamey (Niger) à partir de données de visibilité horizontale. Environnement, Risques & Santé 4, 43–49.

Ozer, P., Laghdaf, M.B.O.M., Lemine, S.O.M., Gassani, J., 2006. Estimation of air quality degradation due to Saharan dust at Nouakchott, Mauritania, from horizontal visibility data. Water Air and Soil Pollution 178, 79–87.

Paatero, P., Hopke, P.K., Song, X.-H., Ramadan, Z., 2002. Understanding and controlling rotations in factor analytic models. Chemometrics and Intelligent Laboratory Systems 60, 253–264.

Paatero, P., Tapper, U., 1993. Analysis of different modes of factor analysis as least squares fit problems. Chemometrics and Intelligent Laboratory Systems 18, 183–194.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111–126.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Reviews 9, 269–298.

Pakkanen, T.A., Kerminen, V.-M., Korhonen, C.H., Hillamo, R.E., Aarnio, P., Koskentalo, T., Maenhaut, W., 2001. Urban and rural ultrafine ($PM_{0.1}$) particles in the Helsinki area. Atmospheric Environment 35, 4593–4607.

Pandey, K.D., Bolt, K., Deichmann, U., Hamilton, K., Ostro, B., Wheeler, D., 2002. Comparative Pollution Across Cities. Presented at the Urban Research Symposium, Washington DC.

Patel, R.B., Burke, T.F., 2009. Urbanization--an emerging humanitarian disaster. N. Engl. J. Med. 361, 741–743.

Paur, H.-R., Cassee, F.R., Teeguarden, J., Fissan, H., Diabate, S., Aufderheide, M., Kreyling, W.G., Hänninen, O., Kasper, G., Riediker, M., Rothen-Rutishauser, B., Schmid, O., 2011. In-vitro cell exposure studies for the assessment of nanoparticle toxicity in the lung-A dialog between aerosol science and biology. Journal of Aerosol Science 42, 668–692.

Pekney, N.J., Davidson, C.I., Robinson, A., Zhou, L., Hopke, P., Eatough, D., Rogge, W.F., 2006. Major Source Categories for $PM_{2.5}$ in Pittsburgh using PMF and UNMIX. Aerosol Science and Technology 40, 910–924.

Petaloti, C., Triantafyllou, A., Kouimtzis, T., Samara, C., 2006. Trace elements in atmospheric particulate matter over a coal burning power production area of western Macedonia, Greece. Chemosphere 65, 2233–2243.

Pichelin, M., Caillibotte, G., Katz, I., Martonen, T., 2012. Categorization of Lung Morphology Based on FRC and Height: Computer Simulations of Aerosol Deposition. Aerosol Science and Technology 46, 70–81.

Picouet, C., 1999. Géodynamique d'un hydrosystème tropical peu anthropisé : le bassin supérieur du Niger et son delta intérieur. (Thése sciences).

Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B., Matos, M., 2011. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmospheric Environment 45, 6121–6132.

Polissar, A.V., Hopke, P.K., Paatero, P., Malm, W.C., Sisler, J.F., 1998. Atmospheric aerosol over Alaska: 2. Elemental composition and sources. J. Geophys. Res. 103, 19045–19057.

Polissar, A.V., Hopke, P.K., Poirot, R.L., 2001. Atmospheric Aerosol over Vermont: Chemical Composition and Sources. Environ. Sci. Technol. 35, 4604–4621.

Pope, C.A., 3rd, Burnett, R.T., Krewski, D., Jerrett, M., Shi, Y., Calle, E.E., Thun, M.J., 2009. Cardiovascular mortality and exposure to airborne fine particulate matter and cigarette smoke: shape of the exposure-response relationship. Circulation 120, 941–948.

Pope, C.A., 3rd, Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. JAMA 287, 1132–1141.

Pope, C.A., Young, B., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association 56, 709–742.

Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H. ten, Tørseth, K., Wiedensohler, A., 2004. A European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment 38, 2579–2595.

Putaud, J.-P., Van Dingenen, R., Mangoni, M., Virkkula, A., Raes, F., Maring, H., Prospero, J.M., Swietlicki, E., Berg, O.H., Hillamo, R., Makela, T., 2000. Chemical mass closure and assessment of the origin of the submicron aerosol in the marine boundary layer and the free troposphere at Tenerife during ACE-2. Tellus B 52, 141–168.

Querol, X., Alastuey, A., Viana, M.M., Rodriguez, S., Artiñano, B., Salvador, P., Garcia do Santos, S., Fernandez Patier, R., Ruiz, C.R., de la Rosa, J., Sanchez de la Campa, A., Menendez, M., Gil, J.I., 2004. Speciation and origin of PM_{10} and $PM_{2.5}$ in Spain. Journal of Aerosol Science 35, 1151–1172.

Raabe, O.G., Howard, R.S., Cross, C.E., 1986. Aerosol considerations in asthma. Bronchial asthma. M. E. Gershwin. Orlando, FL, Brune & Stratton, Inc. 495–514.

Ramgolam, K., Favez, O., Cachier, H., Gaudichet, A., Marano, F., Martinon, L., Baeza-Squiban, A., 2009. Size-partitioning of an urban aerosol to identify particle determinants involved in the proinflammatory response induced in airway epithelial cells. Part. Fibre Toxicol. 6, 10.

Ramgolam, K., Hamel, R., Rumelhard, M., Marano, F., Baeza-Squiban, A., 2012. Autocrine effect of EGFR ligands on the pro-inflammatory response induced by $PM_{2.5}$ exposure in human bronchial epithelial cells. Archives of toxicology.

Rasmussen, R.A., Rasmussen, L.E., Khalil, M.A.K., Dalluge, R.W., 1980. Concentration Distribution of Methyl Chloride in the Atmosphere. Journal of Geophysical Research 85, 7350–7356.

Reff, A., Eberly, S.I., Bhave, P.V., 2007. Receptor modeling of ambient particulate matter data using positive matrix factorization: review of existing methods. J. Air Waste Manag. Assoc. 57, 146–154.

Risom, L., Møller, P., Loft, S., 2005. Oxidative stress-induced DNA damage by particulate air pollution. Mutat. Res. 592, 119–137.

Ritz, S.A., Cundall, M.J., Gajewska, B.U., Alvarez, D., Gutierrez-Ramos, J.-C., Coyle, A.J., McKenzie, A.N.J., Stämpfli, M.R., Jordana, M., 2002. Granulocyte macrophage colony-stimulating factor-driven respiratory mucosal sensitization induces Th2 differentiation and function independently of interleukin-4. Am. J. Respir. Cell Mol. Biol. 27, 428–435.

Rodríguez, S., Querol, X., Alastuey, A., Kallos, G., Kakaliagou, O., 2001. Saharan dust contributions to PM_{10} and TSP levels in Southern and Eastern Spain. Atmospheric Environment 35, 2433–2447.

Rodríguez, S., Querol, X., Alastuey, A., Viana, M.-M., Alarcón, M., Mantilla, E., Ruiz, C.., 2004. Comparative PM_{10}–$PM_{2.5}$ source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain. Science of The Total Environment 328, 95–113.

Roy, M., Becquemin, M.H., Bouchikhi, A., 1991. Ventilation rates and lung volumes for lung modelling purposes in ethnic groups. Radiation Protection Dosimetry, Nuclear Technology Publishing 38, 49–55.

Rumelhard, M., Ramgolam, K., Auger, F., Dazy, A.-C., Blanchet, S., Marano, F., Baeza-Squiban, A., 2007. Effects of $PM_{2.5}$ components in the release of amphiregulin by human airway epithelial cells. Toxicol. Lett. 168, 155–164.

Sandradewi, J., Prévôt, A.S.H., Weingartner, E., Schmidhauser, R., Gysel, M., Baltensperger, U., 2008. A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength Aethalometer. Atmospheric Environment 42, 101–112.

Sandroni, V., Smith, C.M.., 2002. Microwave digestion of sludge, soil and sediment samples for metal analysis by inductively coupled plasma–atomic emission spectrometry. Analytica Chimica Acta 468, 335–344.

Savadogo, P.W., Ouedraogo, Z.A., 2009. Etude de la gestion de la qualité de l'air à Ouagadougou. Presented at the Atelier sous-régional de l'Afrique de l'Ouest et du centre sur l'Amélioration de la Qualité de l'Air en zone Urbaine, Abidjan, cote d'Ivoire.

Schmid, H., Laskus, L., Jürgen Abraham, H., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H., 2001. Results of the "carbon conference" international aerosol carbon round robin test stage I. Atmospheric Environment 35, 2111–2121.

Seagrave, J., McDonald, J.D., Bedrick, E., Edgerton, E.S., Gigliotti, A.P., Jansen, J.J., Ke, L., Naeher, L.P., Seilkop, S.K., Zheng, M., Mauderly, J.L., 2006. Lung toxicity of ambient particulate matter from southeastern U.S. sites with different contributing sources: relationships between composition and effects. Environ. Health Perspect. 114, 1387–1393.

Seck, G., Kane, M., Fall, M., Faltot, P.J., 1990. Abaques de Références Anthropo-spirométriques chez les Sénégalais âgé de 3 à 23 ans, in: Symposium on Nouvelles Acquisitions Sur l'Asthme Bronchique. Ferrara, Italie.

Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric chemistry and physics: from air pollution to climate change, Wiley. New York.

Silverman, D.T., Samanic, C.M., Lubin, J.H., Blair, A.E., Stewart, P.A., Vermeulen, R., Coble, J.B., Rothman, N., Schleiff, P.L., Travis, W.D., Ziegler, R.G., Wacholder, S., Attfield, M.D., 2012. The Diesel Exhaust in Miners Study: A Nested Case-Control Study of Lung Cancer and Diesel Exhaust. JNCI Journal of the National Cancer Institute 104, 855–868.

Skonieczny, C., Bory, A., Bout-Roumazeilles, V., Abouchami, W., Galer, S.J.G., Crosta, X., Stuut, J.B., Meyer, I., Chiapello, I., Podvin, T., Chatenet, B., Diallo, A., Ndiaye, T., 2011. The 7-13 March 2006 major Saharan outbreak : multiproxy characterization of mineral dust deposited on the West African margin. Journal of Geophysical Research. Atmospheres 116.

Sloane, C.S., 1983. Optical properties of aerosols: Comparison of measurements with model calculations. Atmospheric Environment 17, 409–416.

Smith, K.R., Mehta, S., 2003. The burden of disease from indoor air pollution in developing countries: comparison of estimates. International Journal of Hygiene and Environmental Health 206, 279–289.

Smith, K.R., Samet, J.M., Romieu, I., Bruce, N., 2000. Indoor air pollution in developing countries and acute lower respiratory infections in children. Thorax 55, 518–532.

Song, Y., Xie, S., Zhang, Y., Zeng, L., Salmon, L.G., Zheng, M., 2006. Source apportionment of PM2.5 in Beijing using principal component analysis/absolute principal component scores and UNMIX. Science of The Total Environment 372, 278–286.

Sternbeck, J., Sjödin, Å., Andréasson, K., 2002. Metal emissions from road traffic and the influence of resuspension-results from two tunnel studies. Atmospheric Environment 36, 4735–4744.

Swami, K., Judd, C.D., Orsini, J., Yang, K.X., Husain, L., 2001. Microwave assisted digestion of atmospheric aerosol samples followed by inductively coupled plasma mass spectrometry determination of trace elements. Fresenius J. Anal. Chem. 369, 63–70.

Tabutin, D., Schoumaker, B., 2004. La démographie de l'Afrique au Sud du Sahara dès 1950 aux années 2000 ; Synthèse des changements et bilan statistique. Revue population 2004, INED, Paris.

Terzi, E., Argyropoulos, G., Bougatioti, A., Mihalopoulos, N., Nikolaou, K., Samara, C., 2010. Chemical composition and mass closure of ambient PM_{10} at urban sites. Atmospheric Environment 44, 2231–2239.

Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: a review. Sci. Total Environ. 400, 270–282.

Turpin, B.J., Lim, H.-J., 2001. Species Contributions to $PM_{2.5}$ Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. Aerosol Science and Technology 35, 602–610.

UN, 2006. World population prospects. The 2006 Revision.

US EPA, O., 2012. Why should you be concerned about air pollution? | Plain English Guide to The Clean Air Act [WWW Document]. URL http://www.epa.gov/air/peg/concern.html.

Val, S., Hussain, S., Boland, S., Hamel, R., Baeza-Squiban, A., Marano, F., 2009. Carbon black and titanium dioxide nanoparticles induce pro-inflammatory responses in bronchial epithelial cells: need for multiparametric evaluation due to adsorption artifacts. Inhal. Toxicol. 21 Suppl. 1, 115–122.

Val, S., Liousse, C., Doumbia, E.H.T., Galy-Lacaux, C., Cachier, H., Marchand, N., Badel, A., Gardrat, E., Baeza-Squiban, A., 2013. Physico chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells: description of a worrying situation. In review process on Particle and Fibre Toxicology.

Viau, C., Tardif, R., 2003. Toxicologie In. Environnement et santé publique: Fondements et pratiques.

Vinogradov, A.P., 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soft, Consultants Bureau. Inc., New york.

Vlahos, R., Bozinovski, S., Hamilton, J.A., Anderson, G.P., 2006. Therapeutic potential of treating chronic obstructive pulmonary disease (COPD) by neutralising granulocyte macrophage-colony stimulating factor (GM-CSF). Pharmacology & Therapeutics 112, 106–115.

Wade, C.S., Tremblay, R., Ndiaye, E.H.M., 2012. Etude de la complexité de la gestion des espaces publics à vocation de transport à Dakar (Sénégal). URL http://etudescaribeennes.revues.org/4445.

Walston, J.D., Fallin, M.D., Cushman, M., Lange, L., Psaty, B., Jenny, N., Browner, W., Tracy, R., Durda, P., Reiner, A., 2007. IL-6 gene variation is associated with IL-6 and C-reactive protein levels but not cardiovascular outcomes in the Cardiovascular Health Study. Hum. Genet. 122, 485–494.

Wang, M., Xu, B., Zhao, H., Cao, J., Joswiak, D., Wu, G., Lin, S., 2012. The Influence of Dust on Quantitative Measurements of Black Carbon in Ice and Snow when Using a Thermal Optical Method. Aerosol Science and Technology 46, 60–69.

Watson, J.., 2004. Desert Research Institute, Protocol for Applying and Validating the CMB Model for $PM_{2.5}$ and VOC. US Environmental Protection Agency, Air Quality Modeling Group.

Watson, J.G., Chow, J.C., 2001. Source characterization of major emission sources in the Imperial and Mexicali Valleys along the US/Mexico border. Science of The Total Environment 276, 33–47.

Watson, J.G., Chow, J.C., 2002. Particulate pattern recognition. In Introduction to Environmental Forensics, Murphy, B. L., Morrison, R., Eds. Academic Press: New York, NY 429–460.

Weinstein, J.P., Hedges, S.R., Kimbrough, S., 2010. Characterization and aerosol mass balance of $PM_{2.5}$ and PM_{10} collected in Conakry, Guinea during the 2004 Harmattan period. Chemosphere 78, 980–988.

WHO, 2000. World Health Organization. Air quality guidelines for Europe. URL (http://www.euro.who.int/document/e71922.pdf.

WHO, 2002a. Healthy environments for children: an alliance to shape the future of life.

WHO, 2002b. Addressing the Impact of Household Energy and Indoor Air Pollution on the Health of the Poor: Implications for policy action and intervention measures, paper prepared for the Commission on Macroeconomics and Health.

WHO, 2006. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Global update 2005. Summary of risk assessment. URL http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf.

WHO | Air quality and health, 2012.WHO. URL http://www.who.int/mediacentre/factsheets/fs313/en/index.html

Wilson, W.E., Mage, D.T., Grant, L.D., 2000. Estimating separately personal exposure to ambient and nonambient particulate matter for epidemiology and risk assessment: why and how. J. Air Waste Manag. Assoc. 50, 1167–1183.

World Bank, 2005. World Bank Transport Results Measurement: Africa Webpage. URL http://www.worldbank.org/transport/transportresults/regions/africa.html.

Xu, L., Chen, X., Chen, J., Zhang, F., He, C., Du, K., Wang, Y., 2012. Characterization of PM10 atmospheric aerosol at urban and urban background sites in Fuzhou city, China. Environmental Science and Pollution Research 19, 1443–1453.

Yaka, P., Sultan, B., Broutin, H., Janicot, S., Philippon, S., Fourquet, N., 2008. Relationships between climate and year-to-year variability in meningitis outbreaks: A case study in Burkina Faso and Niger. Int. J. Health Geogr. 7, 34.

Yamada, Y., Fukutsu, K., Kurihara, O., Momose, T., Miyabe, K., Akashi, M., 2007. Influences of Biometrical Parameters on Aerosol Deposition in the ICRP 66 Human Respiratory Tract Model: Japanese and Caucasians. Earozoru Kenkyu 22, 236–243.

Yang, F., He, K., Ye, B., Chen, X., Cha, L., Cadle, S.H., Chan, T., Mulawa, P.A., 2005. One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai. Atmos. Chem. Phys. 5, 1449–1457.

Yang, H., Yu, J.Z., Ho, S.S.H., Xu, J., Wu, W.-S., Wan, C.H., Wang, X., Wang, X., Wang, L., 2005. The chemical composition of inorganic and carbonaceous materials in $PM_{2.5}$ in Nanjing, China. Atmospheric Environment 39, 3735–3749.

Ye, S.-H., Zhou, W., Song, J., Peng, B.-C., Yuan, D., Lu, Y.-M., Qi, P.-P., 2000. Toxicity and health effects of vehicle emissions in Shanghai. Atmospheric Environment 34, 419–429.

Yu, J.Z., Tung, J.W.T., Wu, A.W.M., Lau, A.K.H., Louie, P.K.-K., Fung, J.C.H., 2004. Abundance and seasonal characteristics of elemental and organic carbon in Hong Kong PM10. Atmospheric Environment 38, 1511–1521.

Yuan, Z., Lau, A.K.H., Zhang, H., Yu, J.Z., Louie, P.K.K., Fung, J.C.H., 2006. Identification and spatiotemporal variations of dominant PM_{10} sources over Hong Kong. Atmospheric Environment 40, 1803–1815.

Zhang, R., Han, Z., Shen, Z., Cao, J., 2008. Continuous measurement of number concentrations and elemental composition of aerosol particles for a dust storm event in Beijing. Advances in Atmospheric Sciences 25, 89–95.

Zheng, M., Salmon, L.G., Schauer, J.J., Zeng, L., Kiang, C.S., Zhang, Y., Cass, G.R., 2005. Seasonal trends in $PM_{2.5}$ source contributions in Beijing, China. Atmospheric Environment 39, 3967–3976.