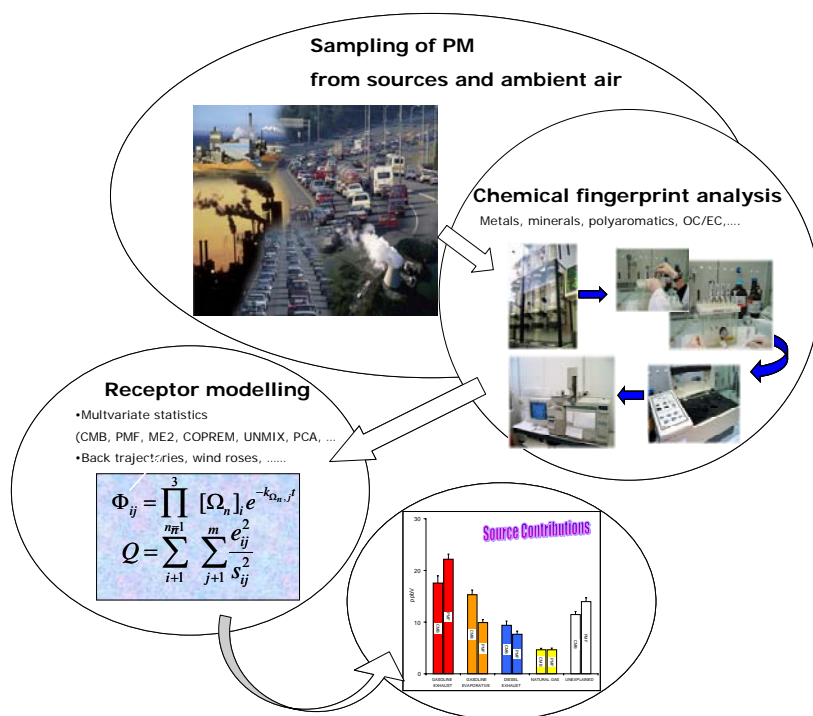# The Krakow receptor modelling inter-comparison exercise

Prepared by

**B. R. Larsen, H. Junninen, J. Mønster, M. Viana,
P. Tsakovski. R. M. Duvall. G. Norris. and X.Querol**

Sampling of PM from sources and ambient air

Chemical fingerprint analysis
Metals, minerals, polyaromatics, OC/EC,....

Receptor modelling
•Multvariate statistics
(CMB, PMF, ME2, COPREM, UNMIX, PCA, ...
•Back trajectories, wind roses, ...

$$\Phi_{ij} = \prod_{n=1}^{3} [\Omega_n]_i e^{-k_{\Omega_n,j} t}$$

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

Source Contributions

With contributions from:
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Foreword

Globally, coal is second to oil the biggest energy source. Coal combustion is utilized mainly for power generation, in industry and to a lesser extent also for home heating in small stoves and boilers. The latter is known to be a major burden for air quality. The present paper describes the results of a PM and PAH source apportionment case-study, carried out in Krakow (Poland), where coal is still widely used for residential heating. In the service and residential sectors Poland alone consumes much more coal than all the old EU member states together consume in these sectors. Krakow is Poland's second largest city and one of the most polluted cities with regards to particulate matter (PM) and associated compounds, such as benzo(a)pyrene (B(a)P). The present study was designed to apportion various coal combustion sources in comparison with other main sources for these pollutants, and the obtained results are expected to be useful for planning abatement strategies in all areas of the world, where coal combustion in small appliances is significant.

Outdoor and indoor PM_{10} collected in Krakow, during typical winter pollution events, was chemically analyzed together with PM emissions from 20 major sources and the obtained data was subjected to multivariate receptor modelling. 52 individual compounds were included comprising elementary and organic carbon (EC/OC), major anions and cations, trace elements, polyaromatic hydrocarbons and azaarenes.

The source apportionment was accomplished by seven different multivariate receptormodels: Chemical mass balance modelling (CMB), constrained positive matrix factorization (CMF), Edge analysis (UNMIX), positive matrix factorization (PMF), PCA coupled with multi-linear regression analysis (PCA-MLRA), Self organizing Maps (SOM), and cluster Analysis (CA).

The results of the source apportionment of PM_{10} and benzo(a)pyrene pollution from coal combustion in Krakow, Poland has been described elsewhere with focus on the pollution problem (Junninen et al., 2008). In the present report complete detailed information is given on the receptor modelling exercise, and all underpinning data. All material is available on an electronic form (bo.larsen@jrc.it).

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Acknowledgements:

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1. Introduction

In new EU member states, national circumstances may result in specific emission scenarios for air pollutants. Thus, sources of low to medium importance in the EU, like domestic heating with solid fuels, are of high relevance in certain new EU member states. For instance Poland alone consumes much more hard coal (10184 Gg in 2002) in the services and household sector than the entire EU-15 (3852 Gg in 2002; Eurostat, 2004). Moreover, the rapidly expanding transport sector in these countries poses additional environmental pressures to be tackled. In line with the EU strategies "Clean Air for Europe" (CAFE) and "Environment and Health for the Urban Environment", the problems of toxic emissions and their impacts on human health need to be addressed with an integrated approach. In order to offer policy makers an adequate support to the development of appropriate emission reduction strategies, the Joint Research Centre (JRC) of the European Commission in collaboration with relevant scientific partners has embarked on integrated studies in heavily polluted areas for the assessment of emission sources impact on air pollution, and human exposure/health.

PM is perhaps today's most significant air pollutant, affecting both human health (respiratory symptoms, morbidity and mortality; Pope et al., 2002) and natural processes (cloud formation, hydrological cycle; Seinfeld and Pandis, 1998; Segal et al., 2007). In many new EU member states electricity is mainly produced through combustion of coal and lignite. In the case of Poland more than 95% of the electricity used in the country derives from coal combustion and roughly half of the 8–9 million dwellings that have inefficient individual heating systems (small stoves) use coal as main fuel (Nilsson et al., 2006). Coal is a heavily polluting fuel in terms of black carbon (BC), SO_2 and other gaseous pollutants, as well as toxic and carcinogenic substances, especially when incompletely and inefficiently combusted (Madhavi and Badarinath, 2003; Pastuszka et al., 2003).

The city of Krakow is Poland's second largest city and one of the most polluted ones (Oudinet et al., 2006). The surroundings of Krakow comprise a confined area with typical emission sources suitable for a case study. There are a number of activities using coal as fuel - from residential heating to industry - typical for many areas in the new EU member states. Thus, information acquired in Krakow is not only

useful for the planning of future abatement strategies for this metropolitan area, but may also be useful as a case study and therefore valuable for the design of pollution control and policy strategies in similar metropolitan areas in Poland and other new EU member states. Coal is still widely utilized in Krakow for residential heating appliances. The results of a preliminary studies have indicated a high load of PM to ambient air with high concentrations of associated polycyclic aromatic hydrocarbons (PAHs) and dioxins (Christoph et al., 2006) and even in the surrounding mountain settlement, where no industry exists, high levels of PM and associated PAHs, dioxins, as well as SO_2 have been measured (Turzanski and Pauli-Wilga, 1999).

In 2004, JRC embarked on a major integrated project in Krakow in collaboration with the polish air quality authorities to support the design of appropriate air quality and emission reduction strategies in this area. The specific objectives of the project were *i*) to study emissions and their sources, air concentration levels and related health impacts of PM_{10} and associated pollutants, *ii*) to develop and test modelling tools for the estimation of the contribution of the various sources to ambient levels, human exposure and health impacts (compilation of detailed emission inventories, dispersion modelling, source apportionment) and *iii*) to evaluate air quality improvement and associated health impacts for synthetic scenarios of emission reductions focused on residential and transport sector. An overview of the preliminary findings of these integrated projects has been given by Jimenez and Niedzialek (2006) and the detailed scientific findings will be presented in separate scientific publications. The present paper presents the main results of the source apportionment exercise for PM_{10} and associated air pollutants. Supporting material on detailed emission profiles (chemical fingerprints) and detailed receptor modelling output cannot be presented here due to space limitations, and have thus been described elsewhere (Larsen et al., 2008).

A number of studies have tried to explain the severe smog episodes that happen in Polish and other eastern European cities, and to estimate the effects of coal combustion in total PM (Pastuszka, 1997; Löfstedt, 1998; Houthuijs et al., 2001; Kopcewicz and Kopcewicz, 2001; Bem et al., 2003). Stable meteorological conditions, with shallow inversion layers, occur frequently, and can cause concentrations of pollutants to reach extremely high values, especially in winter periods (Malek et al., 2006). None of these studies included extensive chemical analysis of the PM and therefore it has no been possible to make a distinction between

the various coal combustion sources from the domestic, industrial, and transport sectors. The source apportionment activities for the Krakow integrated project were planned to address this issue utilizing receptor modelling techniques. During two typical winter air pollution episodes, PM_{10} was collected from sampling sites representing remote urban, rural, urban background, industrial, and hot spot air quality conditions. In addition, PM emitted by combustion processes was sampled from 20 representative pollution sources. The collected samples were analyzed chemically for 52 individual source tracer compounds and the obtained chemical fingerprints subjected to multivariate statistical analysis utilizing an array of multivariate receptor models.

Receptor models rationalize the chemical concentrations in terms of a combination of source inputs to a given receptor site *i.e.* measurement station (Henry et al., 1984; Hopke, 1985). The fundamental principle of the source/receptor relationships is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere. Early attempts of source apportionment have used tracer compounds for specific sources. Today's approach for receptor modelling is to use multivariate statistical analysis on data sets containing a large number of chemical constituents and samples. For PM, a mass balance equation (Equation 1) can be written to account for all M chemical species in the n samples as contributions from N independent sources

$$x_{ij} = \sum_{n=1}^{N} g_{in} f_{nj} + e_{ij}$$

(Eq. 1)

Where x_{ij} is the measurement of jth chemical compounds in the ith PM_{10} sample for a data set of 1 to n (j) samples of 1 to M (i) species, and for 1 to N (n) sources, f_{nj} is the gravimetric concentration (μg/g) of the jth chemical species in PM from the nth source, and g_{in} is the airborne mass concentration (μg/m^3). A large number of multivariate statistical approaches (receptor models) have been proposed to address Eq. 1, and regardless of the utilized data de-convolution approach (e.g., conventional factorization, constrained factorization, mass balance or source 'marker' multiple linear regression), receptor modelling procedures typically require the incorporation of an error function, e_{ij}, within the basic receptor model expression and the extraction

of a 'minimum error' solution for the modeled data set. Often a number of mathematically equivalent solutions exist, thus, a certain amount of case knowledge is required to interpret the mathematical solutions, which add an element of subjectivity to the whole exercise. In the present source apportionment study we aimed at minimizing the subjectivity element by comparing the results obtained with the model that utilizes the maximum of knowledge of the sources in the Krakow area (CMB) with results from receptor models of the factorization type ("zero" case knowledge) and with a hybrid of these models.

2. The Krakow Study area characteristics

Krakow (50°04'N 19°56'E, Fig.1) with its more than 800,000 residents is Poland's second largest city. The city's area of 326.8 km^2 spreads on both banks of the Vistula (Wisla) river, about 219 meters above the sea level on the Malopolska Uplands at the foot of the Carpathian Mountains.

Zakopane (49°18′N 19°57′E) lies in a big valley between the Tatra Mountains and Gubałówka Hill some hundred kilometers south of Krakow. Zakopane was selected for comparison due and its predominant use of inefficient individual heating systems similar to Krakow and due to its remote geographical situation and its low number inhabitants of (28,000) which rule out road transport and industry as significant pollution sources. Preliminary data, obtained from the Polish authorities, confirmed Zakopane as suited 'home heating' receptor site due to its frequent episodes of temperature inversion during winter with corresponding high levels of PM$_{10}$ pollution.

Fig.1 – Location of the PM$_{10}$ sampling stations (white dots) and the characterized emission sources (black squares) in the Krakow metropolitan area.

Four receptor sites were selected in Krakow and one in Zakopane. The sites in Krakow (Fig. 1) included a rural/semi-rural sampling station placed in the N-W outskirts of the city (AGRI), an urban traffic station in the center of the city close to the main road (TRAFFI), an urban background station placed in a district of the city characterized by a high number of old apartments heated by coal combustion in small stoves (POLI) and an industrial site located between the Huta IM Sendzimia steel-works and the power station (INDU). The site in Zakopane was situated at the outskirts of the village and is best characterized as remote urban.

3. The Krakow Sources

Emission rates. The major sources for PM in Krakow as pointed out by the Malopolski Voivodship Inspectorate for Environment (MVIE) are indicated in Fig. 1. The emission rates for these sourecs, operated as close as possible to typical conditions, are summarized in Table 1 for PM and toxic air pollutants regulated by EU air quality directives (B(a)P, Pb, Ni, Cd, As, SO_2, CO, and NO_X). The emission rates for each individual source are listed in Appendix 1.

Table 1 - Emission rate measured during source characterization (average of 2-4 individual measurements).

		g/h	mg/h	g/h	g/h	mg/h	mg/h	kg/h	kg/h	kg/h
SOURCE TYPE	Source #	PM	B(a)P	Pb	Ni	Cd	As	SO$_2$	CO	NOx
Iron ore sinter plant	N11	11219	2207	163	14	4919	nd	nd	2721	72
Blast furnace (coke)	N13	7924	28	1	1	34	354	nd	54	4
Cement kiln (coal fired)	N19	4811	8	1	0.1	40	74	nd	13	32
Power plant coal combustion	N20, N21	2933	14	1	32	27	124	505	4	134
Steelworks power plant, coke-gas (and coal) combustion	N12	2592	83	1	5	99	78	188	nd	123
Fire proof material for steel production (natural gas)	N18	2226	3	15	0.1	466	31	nd	42	1
Steelworks power plant, coal (and coke-gas) combustion	N14	1275	7	1	13	22	66	83	nd	81
Basic oxygen furnace steel plant (coke)	N15	1015	27	1	9	346	7	nd	5	2
Low efficiency boilers (<5MW) coal combustion.	N3, N4, N7	309	10	2	0.1	20	171	3	3	1
Low efficiencyl boiler (<5MW) Heavy fuel oil	N8	159	2	0.01	0.22	6	5	4	nd	2
Residential coal combustion in small stoves and boilers	N1, N2, N10	27	13	0.003	0.001	0.1	0.01	nd	nd	nd
Residential wood combustion in small stoves and boilers	N5, N6, N9	13	5	0.0002	0.001	0.2	0.01	nd	nd	nd

The sources with the highest PM emission rates (1-11 kg/h) are situated in the north-eastern part of Krakow i.e. the Huta IM Sendzimia steel-works (the iron ore sinter plant, the blast furnace, the power plant with coke-gas and coal combustion, the production plant for fire proof material for steel production with natural gas combustion and the basic oxygen furnace steel plant with coke combustion), the Cementownia cement factory (coal fired cement kiln), and the EC-Krakow coal fired power plant (> 50 MW). The PM emission rates from coal combustion in small (< 5 MW) commercial boilers fitted with rudimentary PM removal systems such as e.g. a cyclone and the emission rates from small (< 5 MW) boilers fueled with heavy oil are, as expected, much lower (150-300 g/h). However, in Krakow there are numerous small coal fired commercial boilers distributed over the city, many of which are not fitted with any kind of abatement technology such as a cyclone (Jimenez and Niedzialek, 2006), which evidently makes this a major PM source in Krakow. The emission rate from coal and wood-fired small stoves are the lowest in Table 1 (27 and 13 g/h, respectively). Nonetheless, when the number of approximately 20.000 flats in Krakow heated with individual coal fired small stoves (NILU, Malpolska emission inventory; Jimenz and Niedzialek, 2008) is taken into consideration, also this type can be of major importance, especially at the POLI receptor site situated south of the old city center of Krakow, where flats with individual coal fired small stoves are prevailing. The overall estimation of the importance of this source type will come from source apportionment results at this receptor site in comparison with the results from Zakopane.

Chemical fingerprints of the sources. A total of 54 source samples were collected from the above mentioned sources and analyzed for 52 receptor compounds as described in detail in the Appendices 2 and 3. The basic assumption for source apportionment by receptor modelling, is that the contributing sources have chemical fingerprints different enough to be able to distinguish between the sources. As it appears in the following figures, this was actually the case in Krakow. On Fig. 1-6 the chemicals fingerprints for sources are compared to the average composition of PM_{10} at the receptor sites.
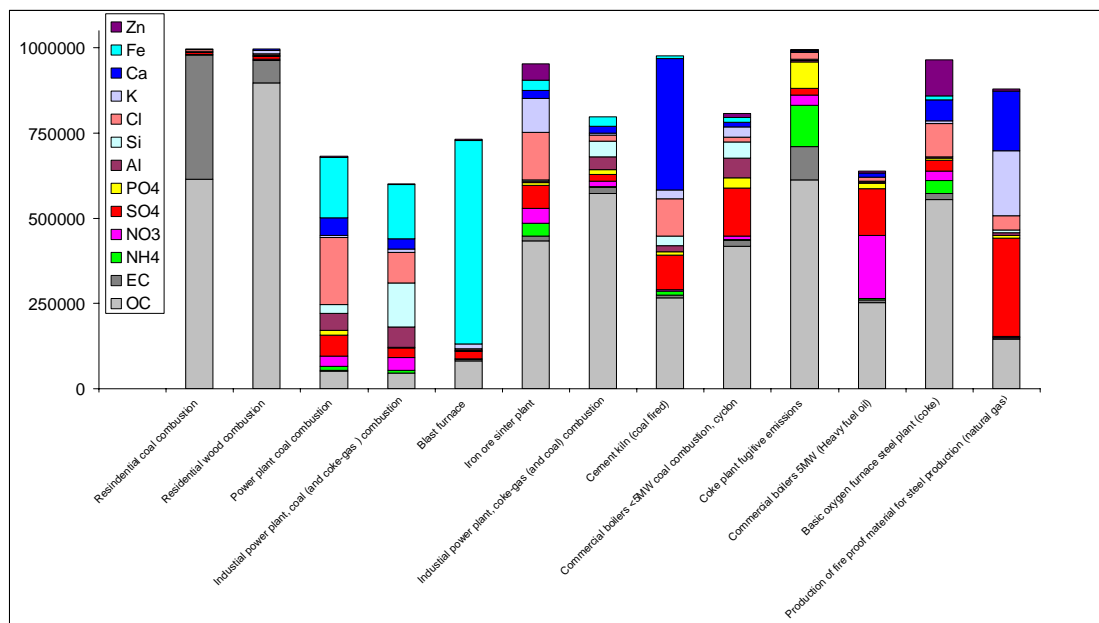
Figure 2a. Chemical fingerprints for Krakow sources. Bulk components.
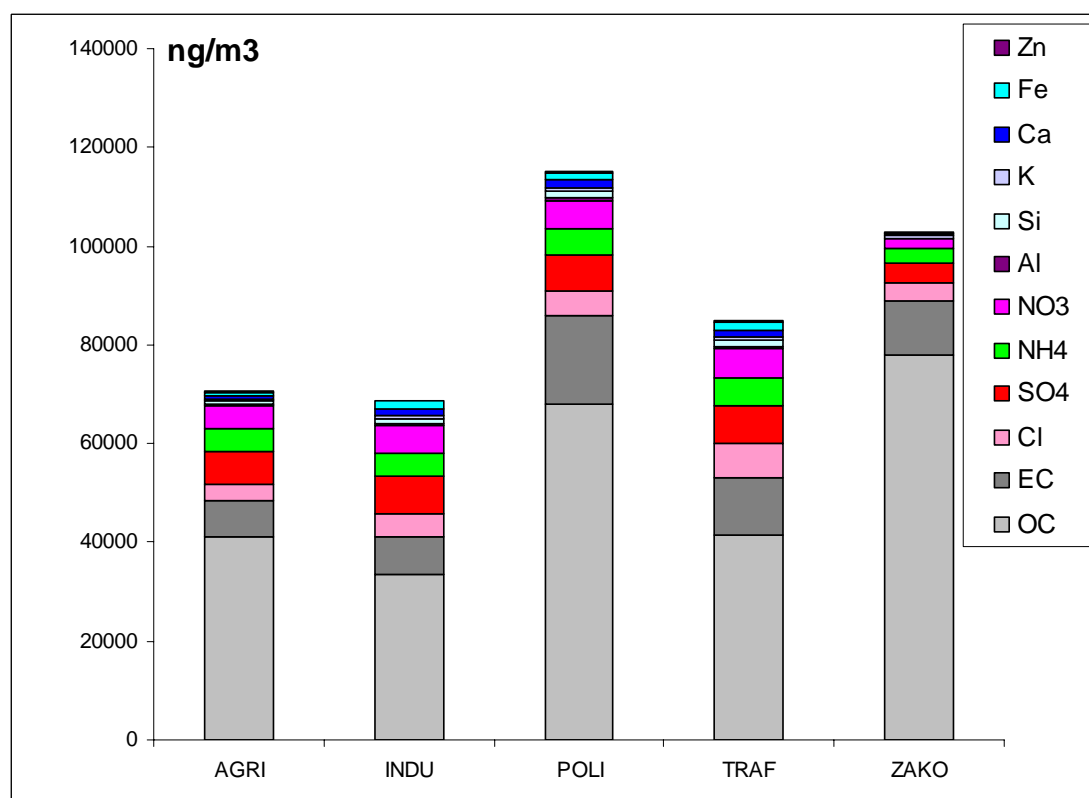
Figure 2b. Average composition of PM_{10} at the receptor sites. Bulk components.
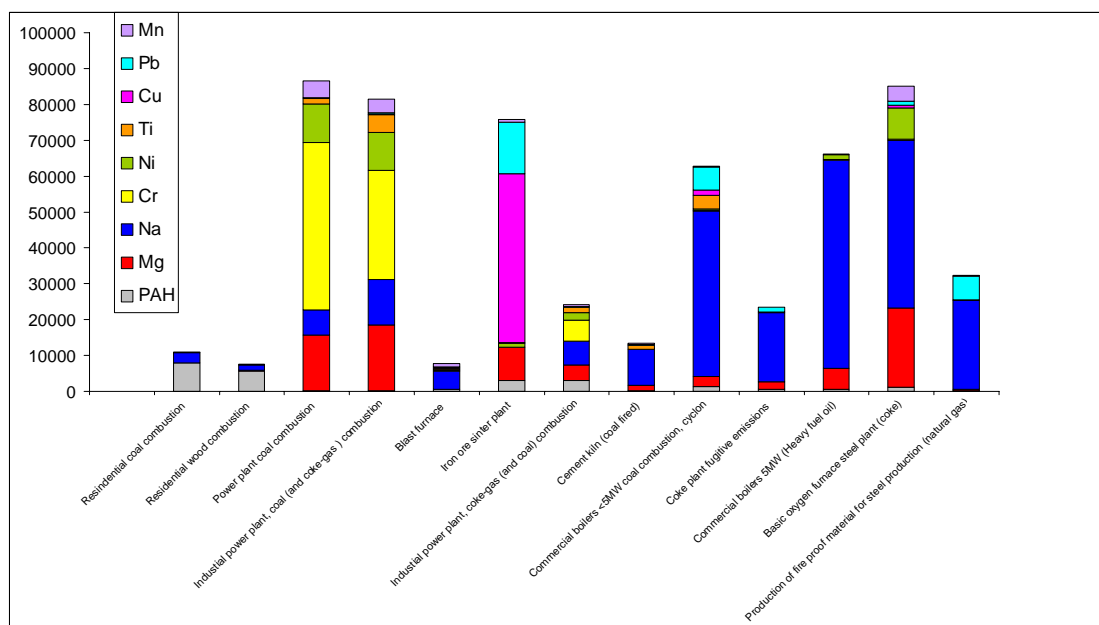
Figure 3a. Chemical fingerprints for Krakow sources. PAH and major tracers.
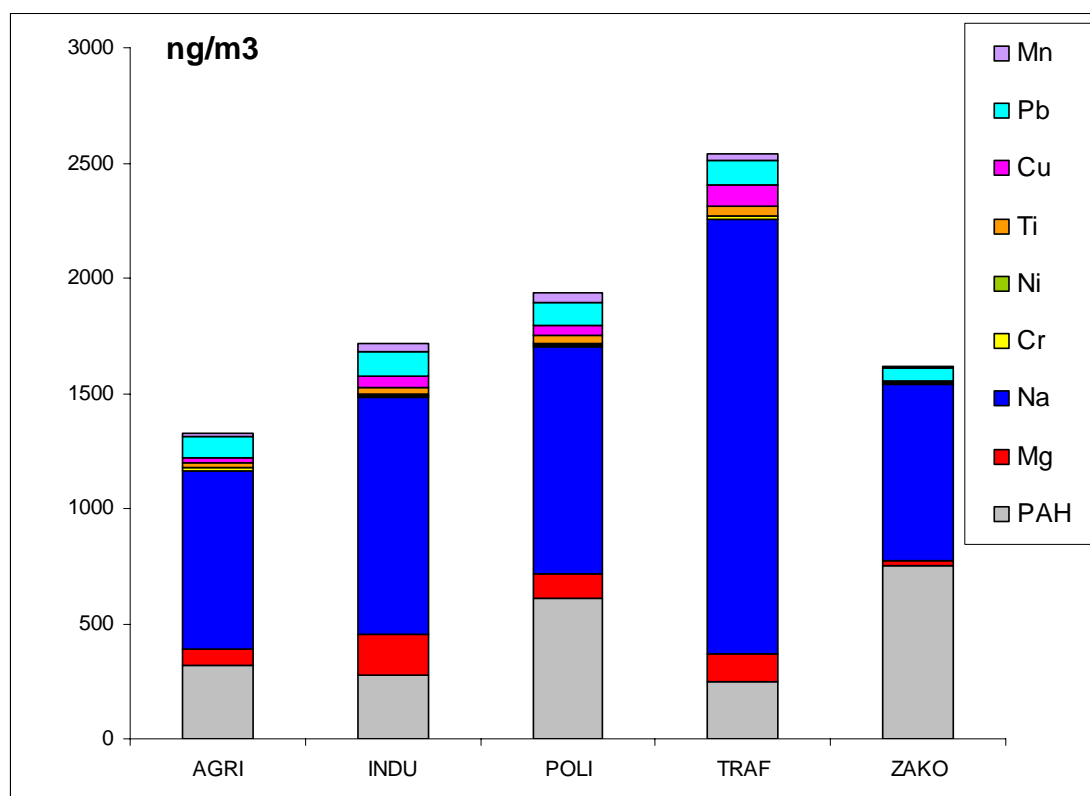
Figure 3b. Average composition of PM_{10} at the receptor sites. PAH and major tracers.
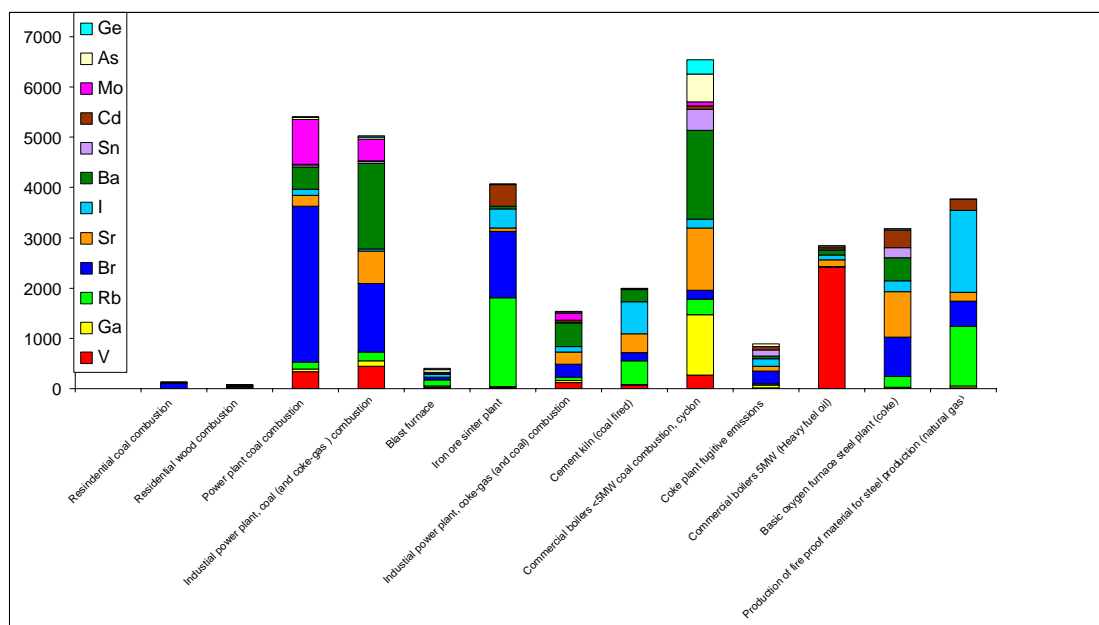
Figure 4a. Chemical fingerprints for Krakow sources. Minor tracers.
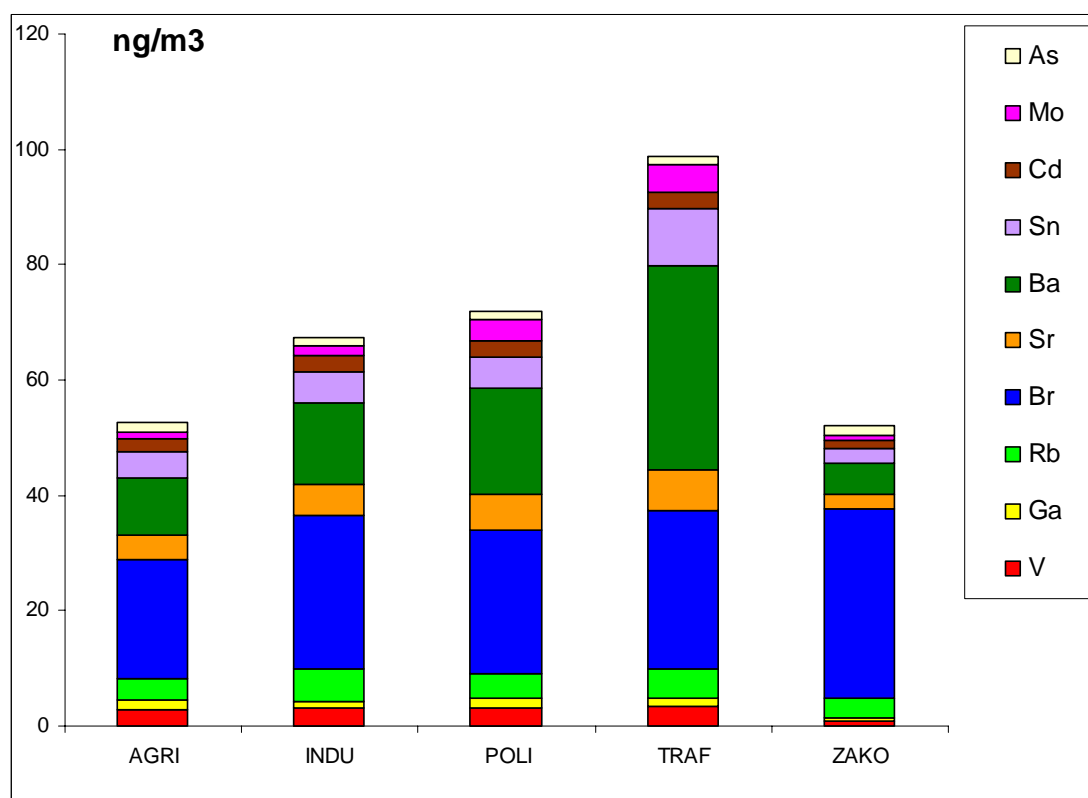
Figure 4b. Average composition of PM_{10} at the receptor sites. Minor tracers.
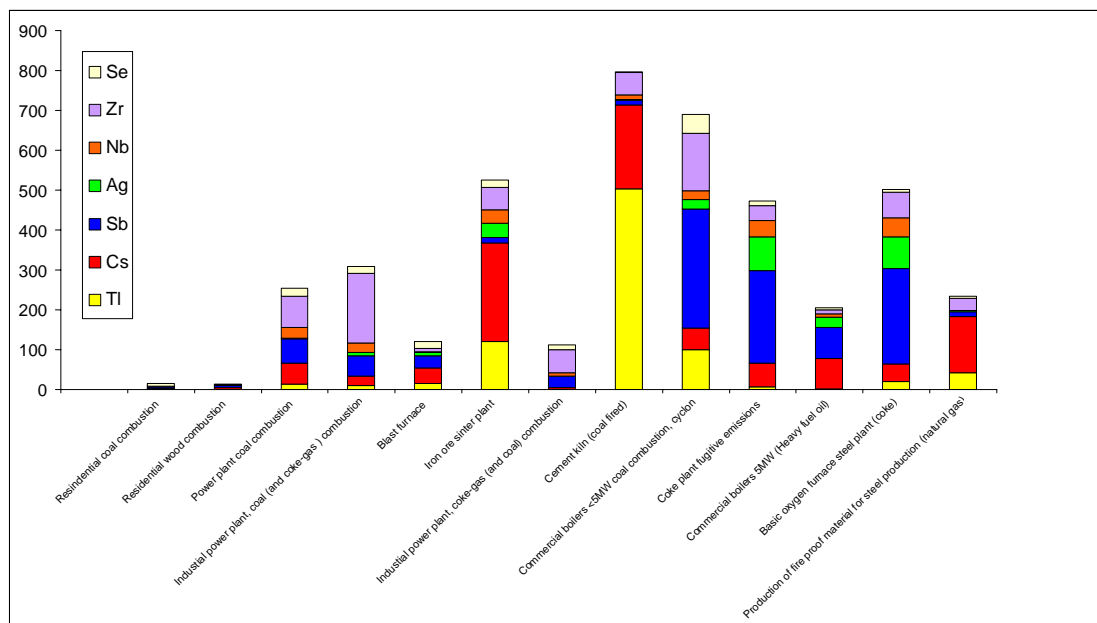
Figure 5a. Chemical fingerprints for Krakow sources. Ultra tracers.
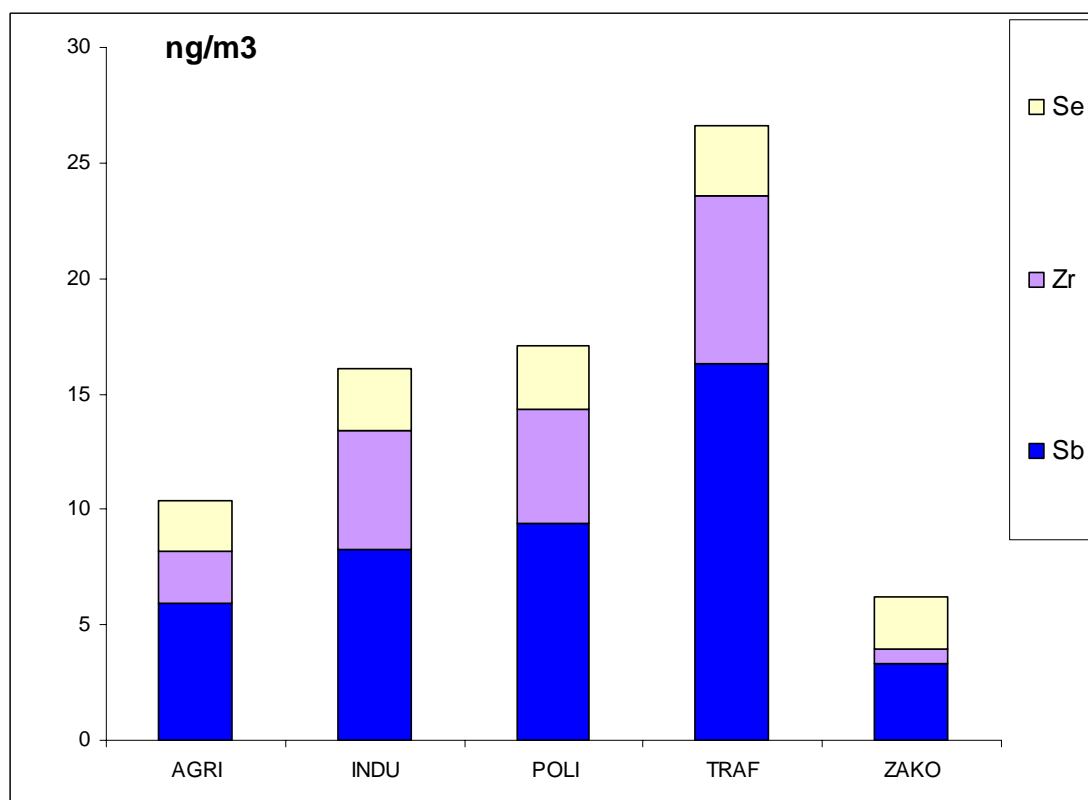
Figure 5b. Average composition of PM_{10} at the receptor sites. Ultra tracers.
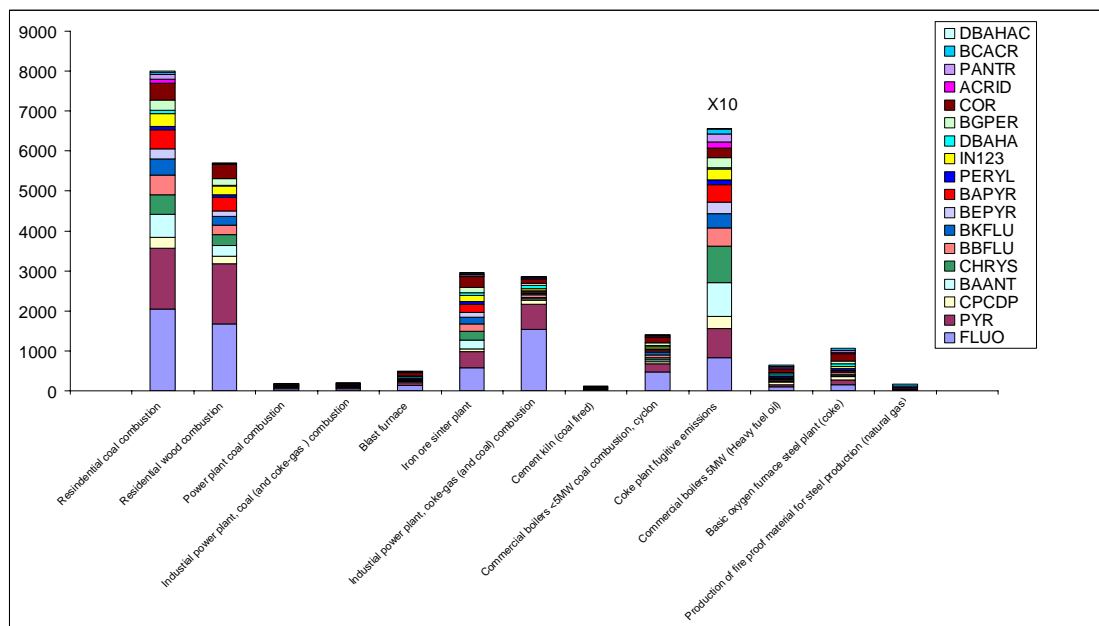
Figure 6a. Chemical fingerprints for Krakow sources. Individual PACs.
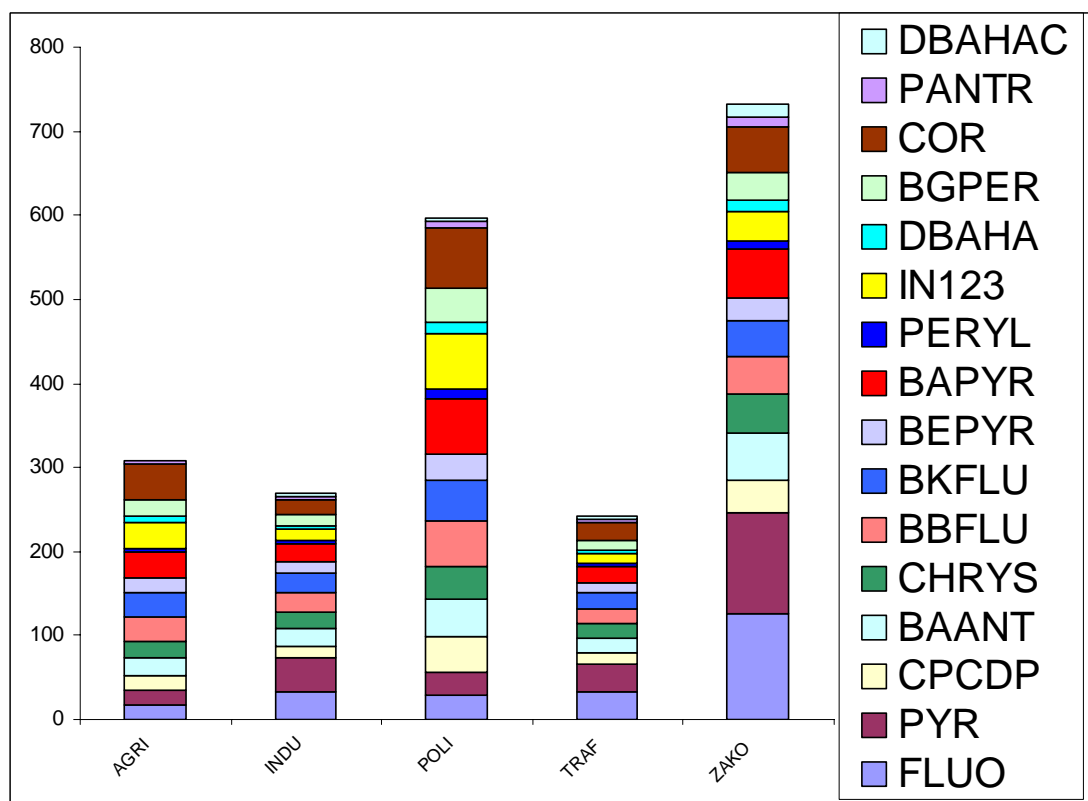
Figure 6b. Average composition of PM_{10} at the receptor sites. Individual PACs.

4. Receptor concentrations

The variation of PM_{10} (30 min average), wind speed and temperature for the period 14/1-2005 to 10/2-2005 is shown in Fig. 7. for the three sites where MVIE is running an air quality monitoring station (TRAFFI, INDU, and ZAKO). This figure represents the typical winter situation in Krakow, during which high to extremely high PM_{10} concentrations are connected with meteorological episodes of low wind-speed and temperature inversion. During three winter months (January-March) of 2005 the PM_{10} levels exceeded the 24 hr EU limit value of 50 $\mu g/m^3$ (EU Directive 1999/30/EC) for 31 days at the ZAKO site, for 46 days at the INDU site and for 70 days at the TRAFFI site with the highest value being close to 600 $\mu g/m^3$. For the calendar year 2005 exceeding concentrations were registered for 85 days per year at the ZAKO site, 161 days per year at the INDU site, and 230 days per year at the TRAFFI site (MVIE monitoring data).
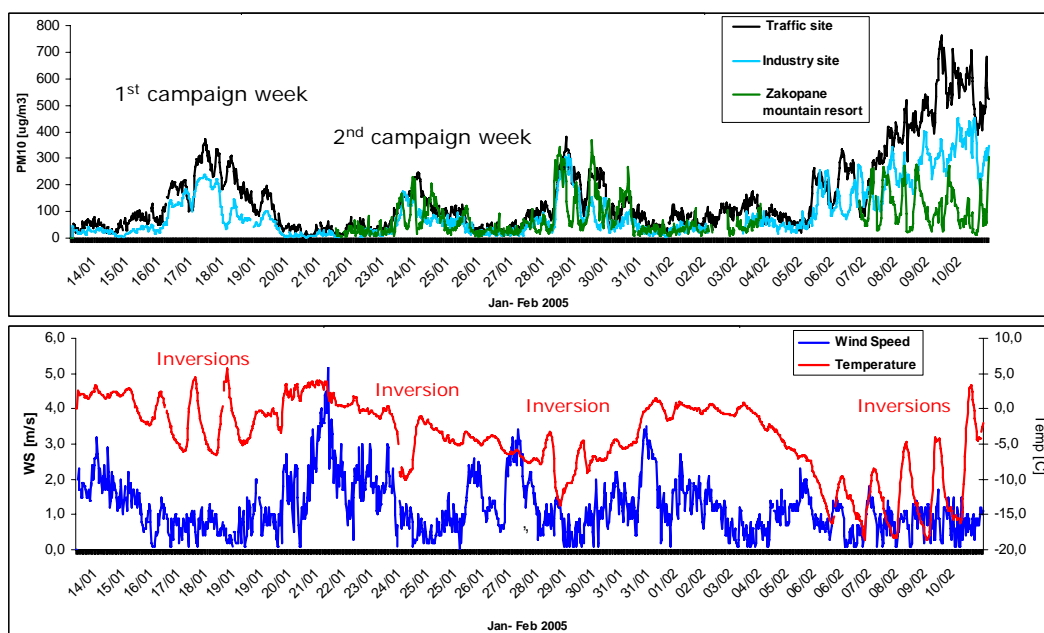
Fig. 7 – Variations of PM_{10} concentration (30 min average), wind speed and temperature in Krakow from 14/01/07 to 12/02/07.

The 24 hr mean concentrations of PM_{10} and associated priority pollutants during the measurement campaigns are shown in Fig. 8. In comparison, the EU limit value for lead in the PM_{10} fraction averaged over a calendar year is 500 ng/m³ (EU Directive 1999/30/EC) and the target concentrations averaged over a calendar year for Ni, As, Cd, and B(a)P are 20, 6, 5, and 1 ng/m³, respectively (EU Directive 2004/107/EC). These limit and target concentrations have been set to avoid, prevent or reduce harmful effects of these compounds on human health and the environment as a whole.
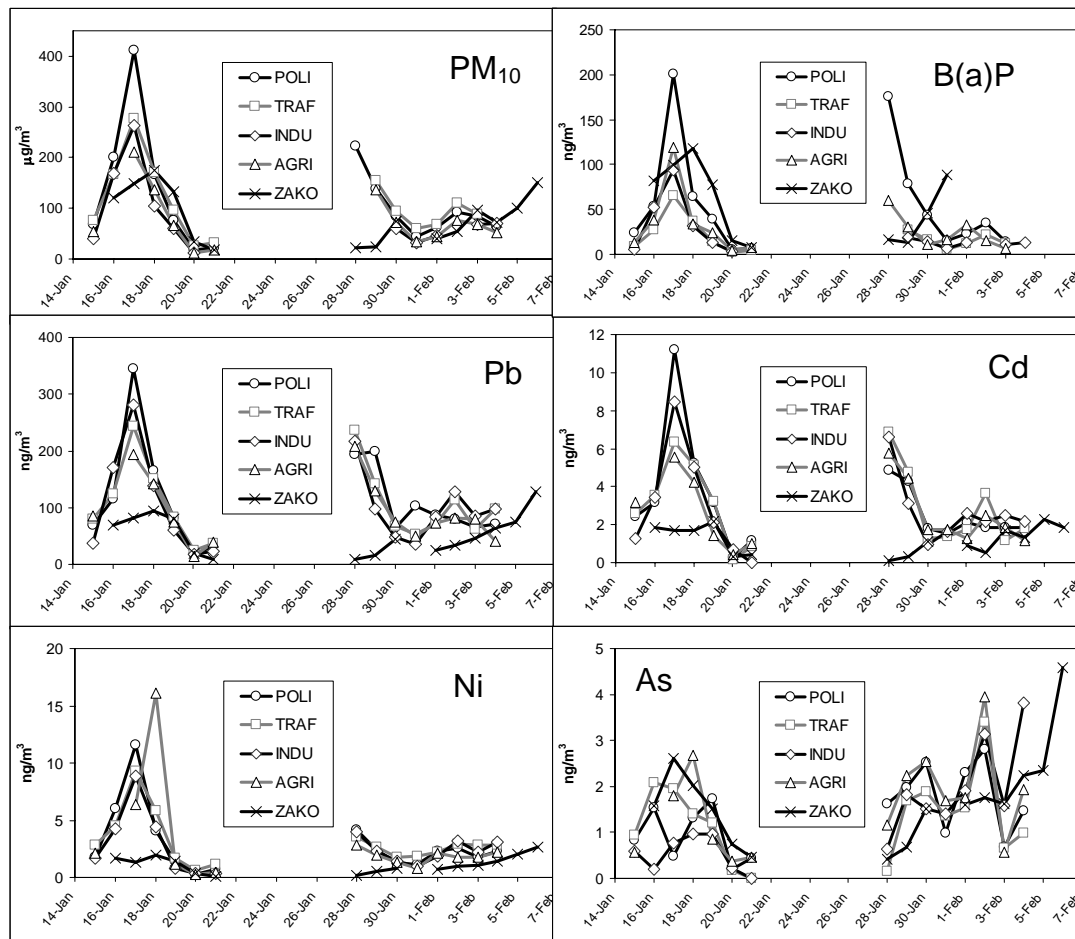
Fig. 8 – Concentration levels of PM_{10}, B(a)P, Pb, Cd, Ni, and As at the five measurement sites during the two campaign weeks.

The concentrations of B(a)P measured at all five stations were similar to concentrations we encountered in Krakow in a preliminary study, winter 2002, and are extremely high compared to the 1 ng/m^3 target value (mean value over the two measurement campaigns for the five sites POLI: 56 ng/m^3, TRAFFI: 20 ng/m^3, INDU 24 ng/m^3, AGRI: 29 ng/m^3, ZAKO: 56 ng/m^3. Maximum value = 200 ng/m^3). It is evident, that only a few pollution episodes per year similar to the ones encountered in the present study are enough to cause infringement of the 1 ng/m^3 target value averaged over a calendar year. The concentration levels of other PACs were also high, and followed the same time evolution as B(a)P.

The sum of all measured PAHs reached levels of up to 2000 ng/m^3 (400 ng/m^3 expressed as B(a)P toxicity equivalents) and the sum of the measured azaarenes in the five measurement sites on average for the two campaigns were: POLI 34 ng/m^3; TRAFFI 18 ng/m^3; INDU 24 ng/m^3; AGRI: 19 ng/m^3; ZAKO: 60 ng/m^3; Maximum value = 128 ng/m^3. These levels are one to two orders of magnitude higher than the highest levels previously reported for polluted areas in Europe and U.S.A (Sawicki et al., 1965; Dong et al., 1977; Nielsen et al., 1986; Chen and Preston, 1998; Warzecha, 1993). Although there are no air quality limits for azaarenes, the present findings may be a cause for concern. Like other PACs, some azaarenes are known as mutagens and/or carcinogens, some are active as tumor initiators on mouse skin, and some have broad reactivity in vivo, with threshold effects observed in membrane structure-function and respiratory process (Southworth, et al., 1978; Catallo et al., 1994).

The concentrations levels of heavy metals measured at all five stations (Fig. 8) are non-critical compared to the EU limit and target values for lead, arsenic, and nickel. On the peak days, cadmium slightly exceeded the yearly average target value of 5 ng/m^3. Considering that these measurements are taken during pollution episodes typical for the winter season. In the warm season with turbulent air and elevated mixed boundary layers PM concentrations are magnitudes lower than during winter, and it is thus expected that Cd over the whole calendar year does not breach the air quality directive.

The average concentration levels of polyaromatic compounds with four and more aromatic rings adsorbed on PM (μg PAC/g PM_{10}) during the two campaigns - the so-called PAC fingerprints - are shown for the five measurement sites in Fig. 9. The fingerprints are very similar for all sites indicating than one source type is dominating and the occurrence of azaarenes in the fingerprints points to coal

combustion (Chen and Preston, 1998). The contribution of azaarenes to the fingerprint was highest in Zakopane, in particular for dibenzo[a,h]acridine, which is to be expected if home-heating by inefficient combustion of coal is the main source in this area. The significantly lower PAC concentrations adsorbed on the particles from the TRAFFI site signify that other sources types with lower PAC emission factors than coal combustion are important at this site (e.g. PM emission from vehicles and re-suspension of road dust). In metropolitan areas receptor modelers are used to find the highest PAC concentrations on PM near main roads, and certain five-six ring PAH are even used in source apportionment studies as organic markers for gasoline fueled vehicle exhaust (Chow et al., 2006; Fujita et al., 2007). From the results of the present study in becomes evident, that in areas dominated by coal combustion such markers are not very useful.
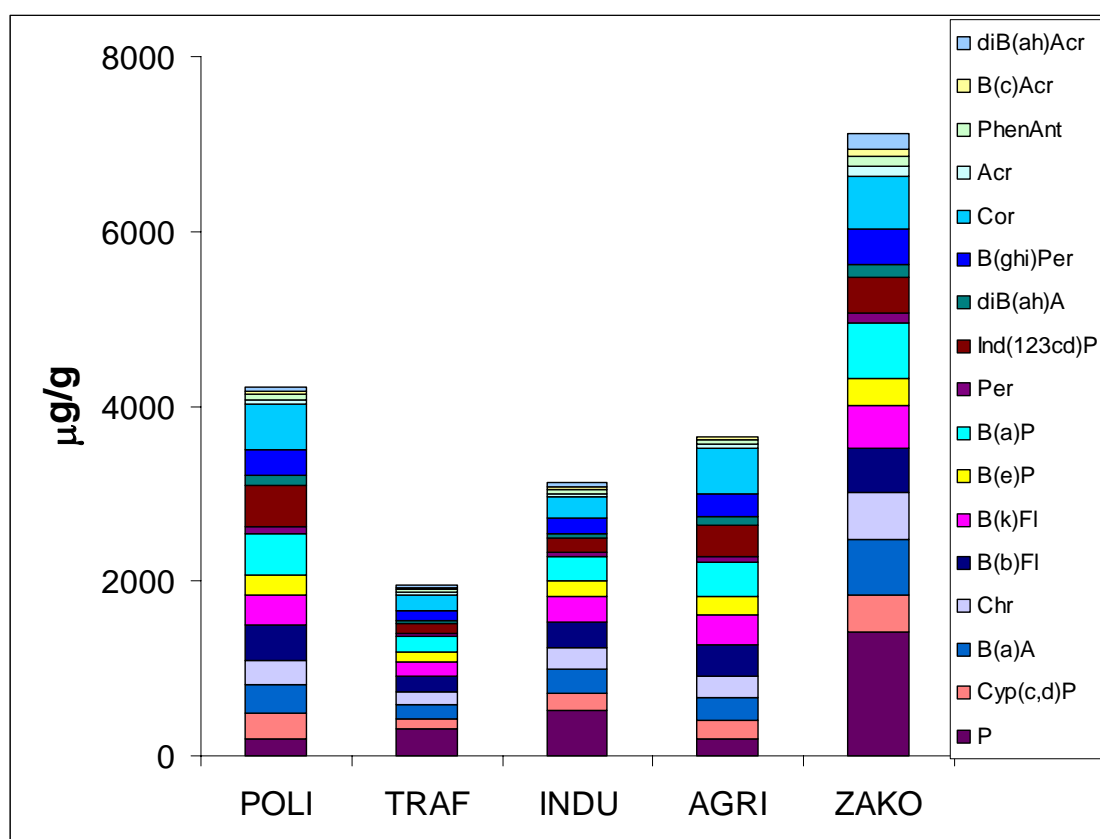
Fig. 9 – Concentration (μg PAC/g PM10) of polyaromatic compounds adsorbed on particles. Average per measurement site over the full period.

Very high concentrations of PACs were also found in the indoor air in the four investigated apartments. When comparing fingerprints it has to be considered that individual PACs are affected to different extends by the drastic change in temperature that occurs when particles enter the apartments from the cold winter air. Due to temperature driven partitioning the most volatile compounds are partially evaporated off the particles and only those with five or more aromatic rings are not significantly effected and remain in the particle phase. We observed very similar indoor and outdoor chemical fingerprints for the PAHs with five or more aromatic rings (Fig. 10a and 10b) and their indoor and out door concentrations (ng/m^3) were well correlated (Indoor = 0.55 * Outdoor; R^2 = 0.90; Fig 11).
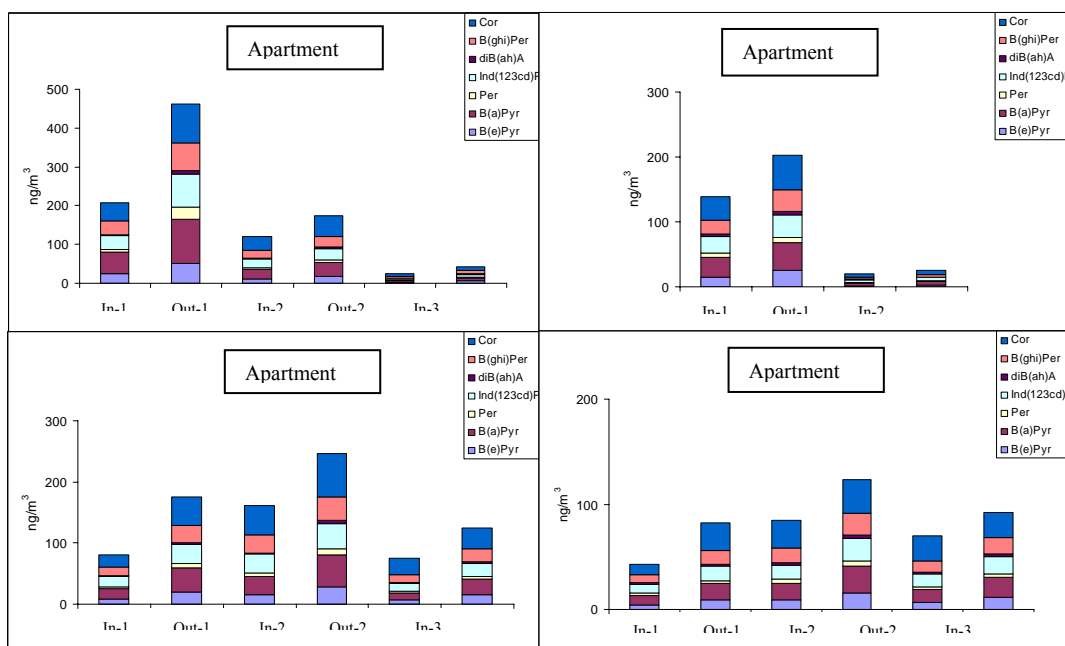
Fig. 10a – Concentrations of 5-6 ring PAHs in indoor (In) and outdoor (Out) air from four apartments.
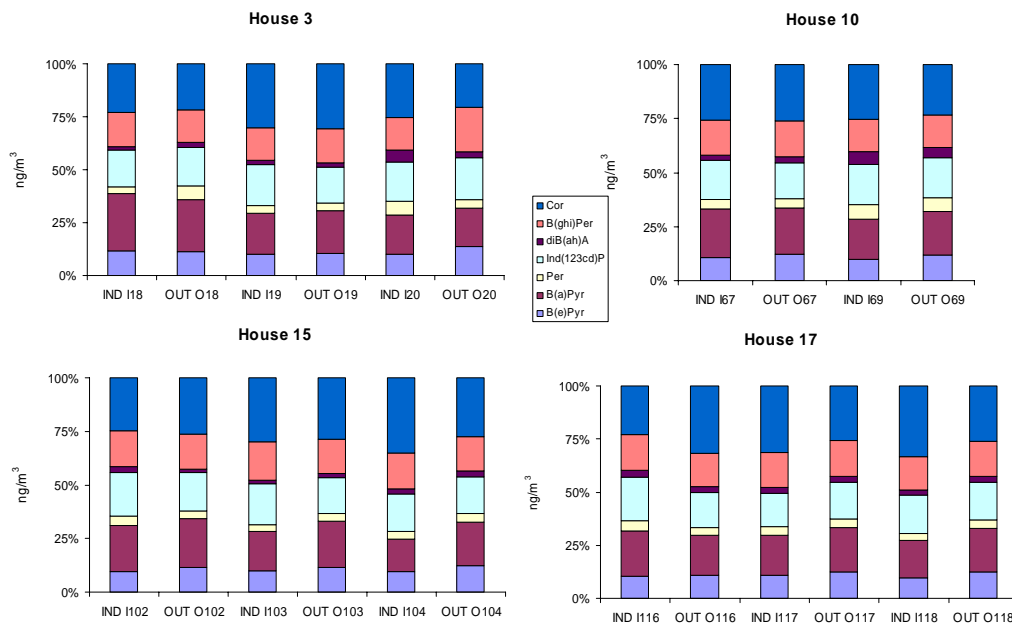
Fig. 10b – Chemical composition (5-6 ring PAHs) in indoor (In) and outdoor (Out) air from four apartments.
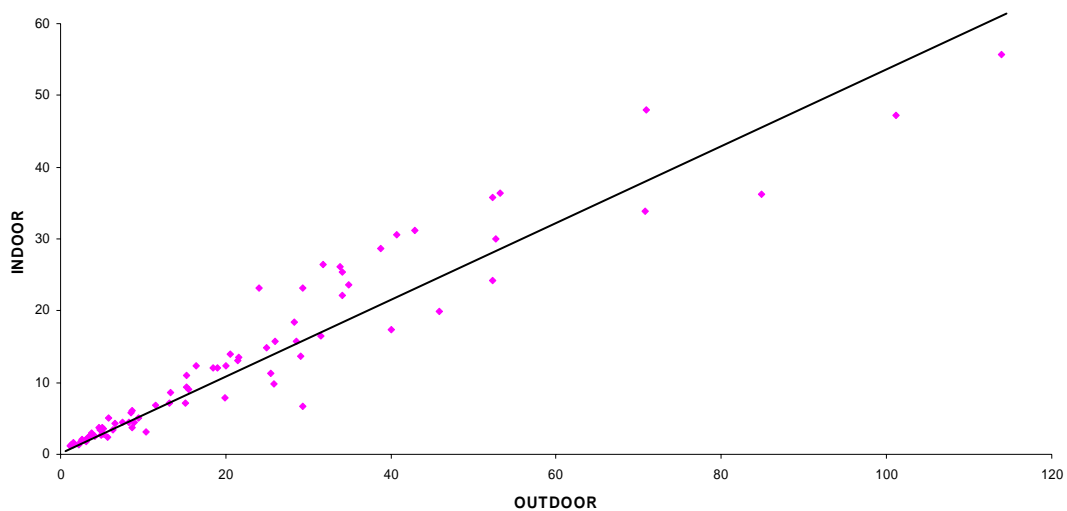
Fig. 11 – Correlations of 5-6 ring PAHs indoor and outdoor concentrations from four apartments.

In another work package of the integrated Krakow project investigation, a general correlations have also been established between indoor and outdoor concentrations of PM_{10} for 20 apartments (Jimenez and Niedzialek, 2006; Marelli et

al., 2008). These findings clearly demonstrate that during the winter period outdoor sources for PM_{10} and the associated PAC are so strong in coal combustion areas such as Krakow, that typical indoor sources such as e.g. cooking become insignificant for the indoor air quality. For health reasons, it is of particular concern that PAHs with five or more rings are transported with the PM from the outdoor air into the indoor environment, where they occur at very high concentrations, since these compounds are the most biologically active and have the highest toxicity equivalency factors of the group of PACs by orders of magnitude. The highest indoor concentration encountered for B(a)P alone was 60 ng/m^3, which speaks of the gravity of the pollution problem in this coal combustion area.

5. Receptor modelling

A total of 178 ambient air samples, 54 source samples and 22 indoor samples were collected and analyzed as described in detail in the Appendices 2 and 3. After a profound control of the data quality (Appendix 5) this produced a dataset of 52 PM components for the total of 75 receptor samples and 20 source samples, which was distributed to all the participating receptor modelers (Appendix 4). In total six multivariate receptor models were used in the inter-comparison: Self organizing Maps (SOM; Kohonen, 2001), and cluster Analysis (CA; Anderberg, 1973); PCA coupled with multi-linear regression analysis (PCA-MLRA; Thurston and Spengler, 1985), Edge analysis (UNMIX; Henry, 2003), positive matrix factorization (PMF; Paatero, 1997), Chemical mass balance (CMB; Friedlander, 1973); Constrained matrix factorization, which is a hybrid model of PMF and CMB based on ideas by Wåhlin (1993). The first two receptor models (SOM, CA) are more of a descriptive than a quantitative nature. UNMIX, PCA-MLRA, and PMF are pure factorization models that produce factors of co-varying elements as output, based on which source contribution estimates can be derived. The usefulness of these three models for the source apportionment depends on how well these factors resemble chemical fingerprints of the Krakow sources. CMB is a pure chemical mass balance model, which optimizes the solution to an over-determined set of linear equations involving the measured concentrations of the PM10 components in sources and receptors. Finally, CMF is a hybrid model that uses Krakow source fingerprints as input for known sources in a CMB-like approach and utilizes a factorization approach to search further factors of co-varying elements.

Tracer compounds. Before we start analyzing the results of the receptor models it is worthwhile spending a few words on another approach, which has been used for sources detection, namely analysis of tracer compound (indicator compounds). In the Krakow dataset a small number of the compounds are emitted mainly by one source category, and can therefore be used as tracers for this source category. One clear example is Cr, which is in the chemical fingerprint of coal combustion in power plants and in no other source (Fig. 3a). In the receptor samples, Cr is found in insignificant concentrations (Fig. 3b), which means that it can be inferred that coal

combustion in power plants can only have very low contribution to PM at the receptor sites. Another good example comes from B(a)P and PAHs in general, together with OC, EC, which are all found in significantly higher concentration at the POLI and ZAKO receptor sites (Fig. 2b, 6b). Amongst all sources these four compounds are highest in the source fingerprints from residential heating with small stoves and boilers (Fig. 2a, 6a). Thus, it may be inferred that this source category plays an important role at POLI and ZAKO, which is in good accordance with the predominance of residential heating with small stoves and boilers in these areas. Similarly, the data on the known traffic tracers Cu, Sn, Ba, Sb, Mo (Fig. 2a-5a and 2b-5b) indicates that road transport is a relatively small contributor to ambient PM_{10} in Krakow, even at the traffic site. Moreover, the data on Zr, OC, and EC (Fig. 2a and b; Fig 5a and b) points to LE boilers as significant contributors and finally, Ca (Fig. 2a and b) indicates that the cement plant is only a minor source in Krakow.

Ratios between tracer compounds have also been used as indicators for specific source categories. In Fig. 12 it is shown that based upon the ratios of the individual

	FLUO/FLUO+PYR	IN123/IN123+BGPER
AGRI	0,54 (± 0,03)	0,56 (± 0,09)
INDU	0,47 (± 0,04)	0,49 (± 0,02)
POLI	0,53 (± 0,03)	0,61 (± 0,04)
TRAF	0,51 (± 0,04)	0,49 (± 0,01)
ZAKO	0,51 (± 0,02)	0,49 (± 0,05)
HOUSE	0,53 (± 0,03)	0,53 (± 0,01)
Unburned Petroleum	<0,4	<0,2
Vehicle and Crude Oil	040-0,50	020-0,50
Coal and Wood Combustion	>0,50	>0,50
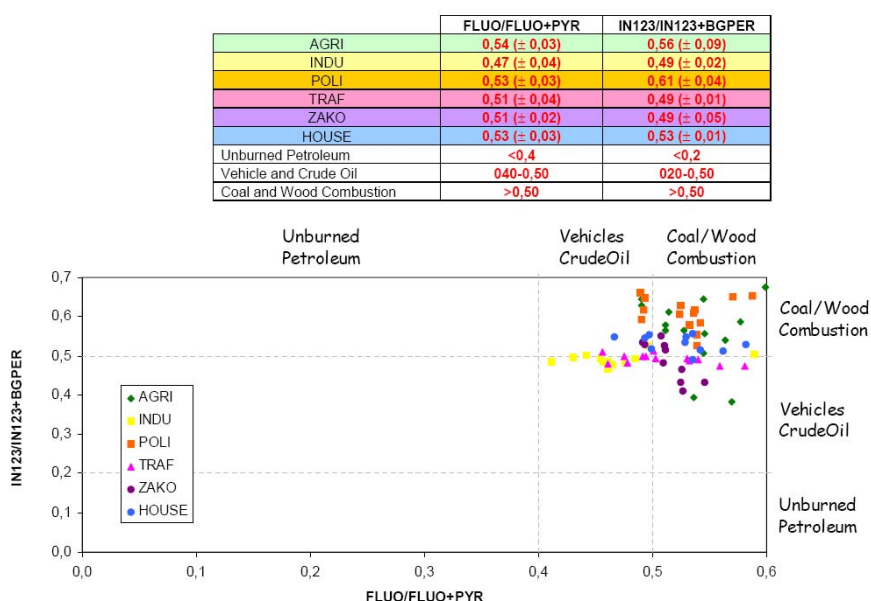
Fig. 12 – Ratios of individual PAHs as source indicators for coal combustion in Krakow and Zakopane.

PAHs fluoranthene, pyrene, indeno[1,2,3-cd]pyrene, and benzo(ghi)perylene it can be inferred that coal combustion/wood combustion is a major emission source in Krakow (including indoor air) and Zakopane as compared to unburned petroleum, vehicles, and crude oil (Robinson et al., 2006). As it appears in the following, the qualitative information obtained with tracer compounds and source indicators is in agreement with the output of the descriptive receptor models SOM and CA as well as with the source contribution estimates obtained by the quantitative receptor models PCA, PMF, CMB and CMF.

5.1. Cluster Analysis (CA)

The notion Cluster analysis (CA) or clustering incorporates a broad class of methods used to classify variables (usually chemical components) or objects (usually sampling sites) into groups. This exploratory approach is very useful for revealing and displaying of investigated data structure. In this aspect Cluster analysis is exploratory unsupervised pattern cognition technique which does not need *a priori* knowledge about investigated objects (Einax,et al, 1997).

Very often in environmental studies following questions have to be answered:
- What are the factors controlling the obtained data structure?
- Which is the proper set of variables for reliable environmental modelling?
- What is the optimal monitoring scheme?

The adequate modelling and source estimation need correct answers of abovementioned questions. This fact put exploratory data techniques like Cluster analysis, Principal component analysis, Self-organizing maps etc. as necessary preliminary step before modelling studies.

Two big families of clustering algorithms can be distinguished: hierarchical and nonhierarchical ones. The hierarchical clustering could be performed in an agglomerative and in a divisive way. At the start of agglomerative procedure each object is located in a separate cluster. In the agglomerative algorithms the aim is to join similar objects into cluster and to add objects to already formed "closest" cluster or to join similar clusters. The divisive algorithms start with one cluster including all objects and, step by step, the most "inhomogeneous" are stripped, forming "more

homogeneous" smaller clusters. The hierarchical clustering output is tree-like diagram called dendrogram.

The aim of classification by nonhierarchical clustering is to classify the objects under consideration into a certain number of preliminary intended clusters. The clusters are formed simultaneously by partitioning methods which allow the objects to re-arrange between the clusters. The main disadvantage of nonhierarchical clustering is the absence of graphical output.

The most common used procedures in environmental studies are clustering performed by hierarchical agglomerative procedures because of understandable graphical output and clear "hierarchical" relation between clusters (Simeonova et al., 2005; 2007)

In cluster analysis the *input data matrix* (raw data) is usually autoscaled and then a *similarity matrix* is calculated including all distances between the objects to be classified. There is a wide variability of hierarchical algorithms but the typical ones include the *single linkage*, the *complete linkage* and the *average linkage* methods. In the similarity matrix one seeks the two most similar objects p and q (with smallest distance D_{qp}) which are linked together, to start constructing the dendrogram. The process is repeated until all objects are linked in the hierarchical classification scheme. In principle, the most similar objects are considered to form a new object *p** out of these two. In this way the similarity matrix is reduced by one column and one row. In *average linkage*, the similarities between the new object and the rest are obtained by averaging the similarities of the two most similar objects with the others (e.g. $D_{ip*} = (D_{iq} + D_{ip})/2$). In *single linkage*, D_{ip*} is the distance between some object *i* and the nearest of the linked objects, i.e. equal to the smaller of the two distances D_{iq} and D_{ip}. In *complete linkage* the opposite rule is retained: D_{ip*} is the distance between object *i* and the most remote object *q* or *p*. Thus, in the different hierarchical clustering algorithms the only difference is the way to determine the linkage sequence. Generally, average linkage is a preferred procedure for larger datasets. However, the abovementioned algorithms are not recommendable, because they often form inversions mainly due to space revising. Special attention should be paid to *Ward's method* of clustering based on a heterogeneity criterion defined as the sum of the squared distances of each member of a cluster to the centroid of that cluster. The objects and clusters are joined on the bases of the criterion that the sum of

heterogeneities of all clusters (formed on the next step) should increase as little as possible. In general, Ward's method is space conserving and seems to give better results. If squared Euclidean distances are used as similarity measure, Ward's method tends also to optimize the data set variance (Vandeginste et al.1998, Simeonova et al. 2001, Massart, D.L., Kaufman, L, 1983)

Cluster analysis was applied to detect similarity groups between the PM components. The dataset was treated (after scaling by z-transformation) by the Ward's method of linkage with squared Euclidean distance as measure of similarity (see Fig. 13).
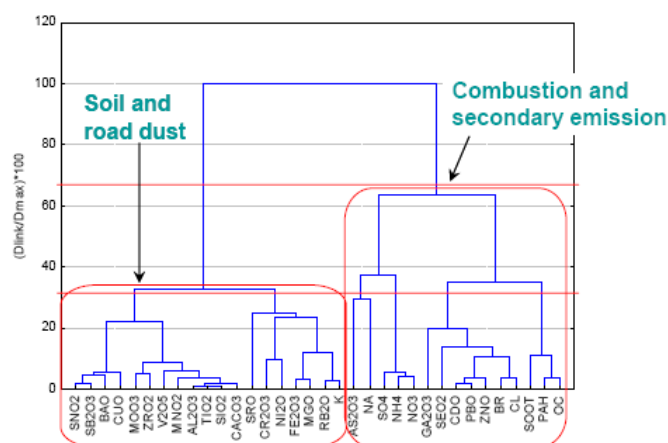
Figure 13 The CA classification of PM components.

The significance of the clusters obtained was tested by the Sneath's index of disjunction(Sneath, 1980). On the first level of significance (⅔ of D_{max}, where D_{max} is a maximum distance) two statistically significant clusters were formed: Cluster 1 includes metals with soil and transport origin and could be conditionally named "Soil and road dust", Cluster 2 consists of precursors of burning processes and secondary aerosol formation and could be identified as "Combustion and secondary emission". On the second level of similarity (⅓ of D_{max}) six clusters were formed. The "Soil and road dust" is divided in two smaller clusters where division on "soil" and "road" (brake) elements is not observed. The second level of similarity divides the "Combustion and secondary emission" cluster in four subclusters. The first one groups OC, SOOT and sum of PAH's and represents the combustion processes. The second one (Cl, Br, Zn, Pb, Cd, Se, Ga) includes tracers for metal smelters activity and industrial combustion processes. The third cluster (NO_3^-, NH_4^+, SO_4^{2-}) consists of species involved in secondary aerosol formation. The fourth subcluster (Na, As) has no logical explanation. Sodium has many emitters, unstable seasonal behavior and

often its modelling is unsuccessful. The position of As in classification scheme does not correspond to its major emitter - coal combustion.

5.1. Self-organized maps (SOM)

The SOM is an algorithm used to visualize and interpret large high-dimensional data sets (Kohonen, 2001). SOM is unsupervised pattern cognition method similarly to Cluster analysis. The main advantage of SOM is the simultaneous classification of variables (PM components) and objects (sampling sites). Typical applications are visualization of process states or financial results by representing the central dependencies within the data on the map. The map consists of a regular grid of processing units, "neurons". A model of some multidimensional observation, eventually a vector consisting of features, is associated with each unit. The map attempts to represent all available observations with optimal accuracy using a restricted set of models. At the same time the models become ordered on the grid so that similar models are close to each other and dissimilar models far from each other. Fitting of the model vectors is usually carried out by a sequential regression process, where $t = 1,2,...$ is the step index: For each sample $\mathbf{x}(t)$, first the winner index c (best match) is identified by the condition.

$$\forall i, ||\mathbf{x}(t) - \mathbf{m}_c(t)|| \leq ||\mathbf{x}(t) - \mathbf{m}_i(t)||.$$

After that, all model vectors or a subset of them that belong to nodes centered around node $c = c(\mathbf{x})$ are updated as

$$\mathbf{m}_i(t+1) = \mathbf{m}_i(t) + h_{c(\mathbf{x}),i}(\mathbf{x}(t) - \mathbf{m}_i(t)).$$

Here $h_{c(x),i}$ is the "neighborhood function", a decreasing function of the distance between the ith and cth nodes on the map grid. This regression is usually reiterated over the available samples.

The trained map could be graphically presented by 2D plane of U matrix representing the distances between map neurons and 2D planes for each PM components indicating the component values on the different map regions.

The ordering of 2D PM components planes on Figure 14 shows the variables structure similar to Cluster analysis. In the upper left corner the components belonging to "Soil and road dust" cluster are grouped. The PM components belonging to the second "big" cluster "Combustion and secondary emission" are not so well grouped. The

PAH's are located in lower part of the plane except DMPHE, DBAHAC and in some extent PYR and FLUO. Next to the PAH's group are OC, SOOT and Br. It is worth noting that PM mass, which was included as additional variable is located just between mentioned components of the two big clusters in the middle left part of the plane. The secondary emission species are not so well grouped in the middle right part of the plane. The unusual subsluster (Na, As) from CA does not exist and the position of both components is difficult to be explained.
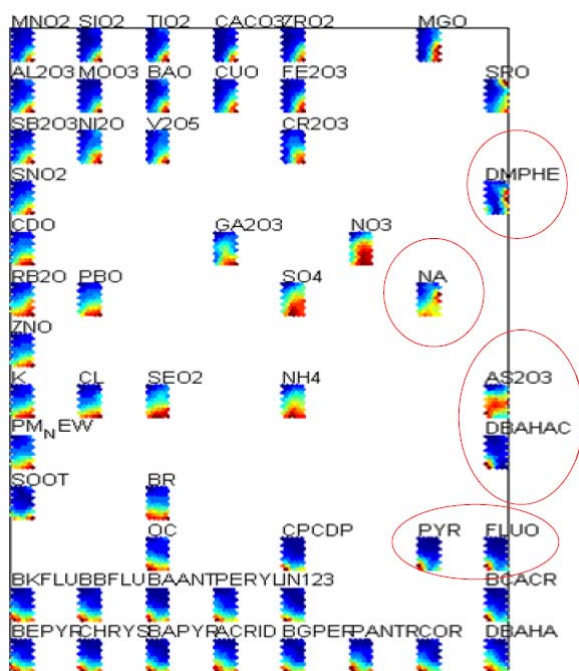
Figure. 14 The SOM classification of PM and PM components.

The obtained by trained map U matrix gives opportunity for reliable clustering of cases (measurements) from the sampling sites. Nonhierarchical K-nearest neighbor technique is used. Different values of k (predefined number of clusters) were tested and the sum of squares for each run was calculated. Finally, the best classification with the lowest Davies–Bouldwin index value (see Fig. 15) was chosen. It is seen that five clusters configuration has the lowest index.
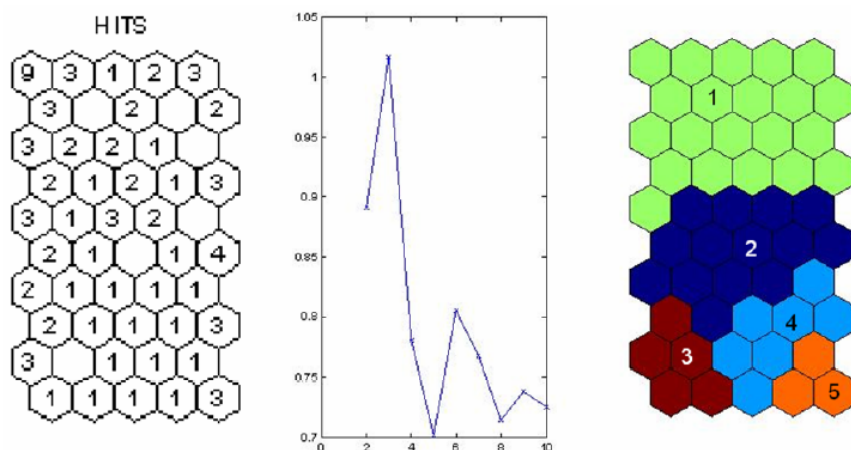
Figure 15 Classification of cases.

The Group 1 includes 44 cases from all sampling sites - almost all indoor cases (11 out of 12) and 33 out of all outdoor 74 measurements. There is a high level of similarity between indoor and outdoor cases. The lowest concentrations for all components are observed and the group could be conditionally named "Background" for the investigated sampling period and region.

The Group 2 includes 20 cases as 15 of them are in the period 29.01-04.02.06. The possible reason for group formation is the North Atlantic air transport leading to low PAH's and dust concentrations and increased (according to Group 1) secondary aerosol mass (see Fig. 16).
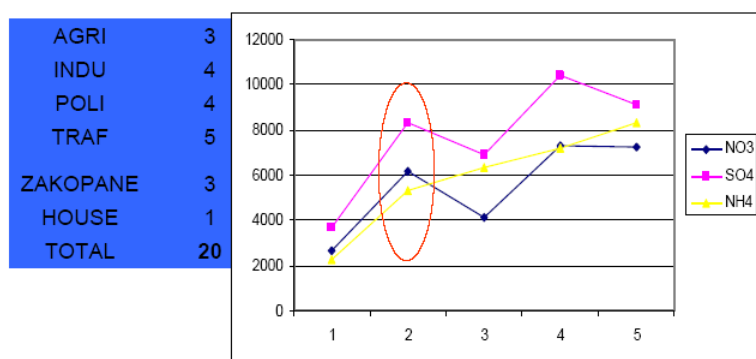
Figure 16 The content and statistics summary for Group 2.

The Group 3 is the small group dominated by Zakopane cases (5 out of 7). The cases includes two sampling periods (15-17.01.06 and 05-06.02.06) and are characterized by the highest concentrations of carboneous particles and some PAH's. The probable source for this elevated concentrations is residential combustion (see Fig 17). The

reason for including the other 2 cases of INDU and POLI (dated 28.01.06) are probably the regional events with common nature.

AGRI	0
INDU	1
POLI	1
TRAF	0
ZAKOPANE	5
HOUSE	0
TOTAL	7

Figure 17 The content and statistics summary for Group 3

Groups 4 and 5 are small groups form the period 16-17.01.06. The reason for grouping is the possible air-recirculation. The cases in Group 4 and Group 5 have the highest secondary aerosol and dust components, respectively (see Fig. 18).

AGRI	2
INDU	2
POLI	1
TRAF	4
ZAKOPANE	0
HOUSE	0
TOTAL	9

AGRI	1
INDU	1
POLI	2
TRAF	1
ZAKOPANE	0
HOUSE	0
TOTAL	5
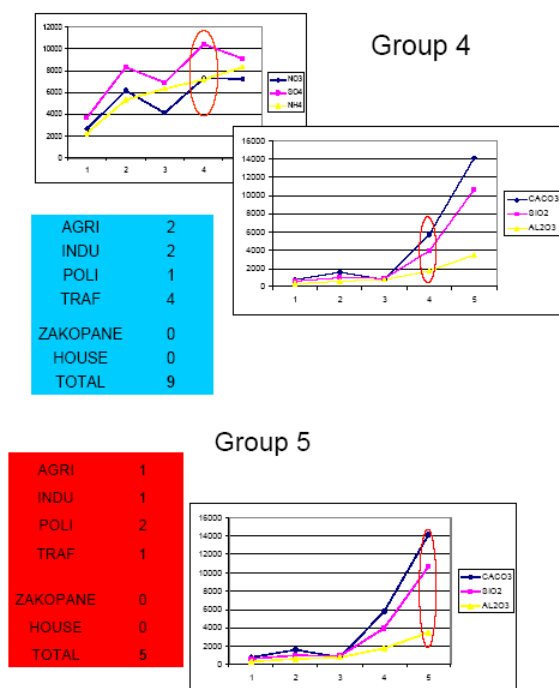
Figure 18 The contents and statistics summaries for Groups 4 and 5

PCA-MLRA

Like all bilinear models, the aim of Principal Component Analysis coupled with Multi-Linear Regression (PCA-MLRA) is to solve the factor analysis problem stated in Eq 1. in the introduction. This model was first described by Thurston & Spengler (1985), and it has been successfully applied in a large number of publications in the field of atmospheric pollution by particulate matter (Pratsinis et al., 1988; Salvador et al., 2004; Simeonov et al., 2004; Almeida et al., 2005; Park & Kim, 2005; Vallius et al., 2005). It is currently the most widely used receptor model in Europe, appearing in twice the number of publications than back-trajectory analysis or the Lenschow approach, and in three times more publications than PMF (Viana et al., 2006, results based on the review of 49 studies from 6 European countries).

The main advantage of PCA is that it provides unique solutions to the system, and the interpretation of the variance results is straightforward since factor scores and loadings are forced to be orthogonal (in order to explain the maximum variance). Therefore, pollution sources may be directly interpreted from the factor scores and loadings. However, the main drawback is that solutions may not always have a direct physical interpretation, as negative factor scores may be obtained. The fact that PCA searches for a linear combination of the sources to fulfil the orthogonality constraints implies that the solutions have good mathematical properties, but they may not always have a physical meaning. A number of solutions are generally applied in order to correct for negative scores, such as rotation of PCA factor matrices to simplify interpretation like in varimax orthogonal rotation, scores uncentering (to make them positive by introducing a "zero day") and regression to total sample mass (Thurston & Spengler, 1985).

The application of PCA-MLRA to the Krakow dataset was done both on the basis metals as their oxides and on the basis metals as pure elements. The relatively small number of receptor samples consisting of a complete data set (i.e. non-zero concentration values for all compounds) was a clear limitation for PCA-MLRA and the statistical variance in the data set restricted the number of source profiles. Thus, the outcome was basically profiles of mixed sources. Therefore, the interpretation of the source factors was not easy, and a number of different source attributions were obtained from the modelers in the "blind-fold" stage. However in a later stage, when

modelers were allowed to compare and discuss their source-profile interpretations, the elucidations tended to converge.

The output obtained by the two approaches very similar as can be seen in the background material presented in Appendix 6 and 7 and will be discussed in details in the following, only for the metals as pure elements. Four main factors were identified and interpreted as mixed sources of particulate matter. They explained 87% of the variance of the dataset. The best fit was obtained by rotating the principal components (varimax normalized). The chemical profiles of the factors as shown in Fig.19 were characterized by:

PCA-Factor 1. The main tracers of this source were Fe, Ca, Ti, Si, Mg, Ba, V, Al, Cu, Sr, Mn, Cr and Ni (Figure 1), among others. The presence of soil elements (Ca, Si, Al, Mg) in combination with tracers of oil/coke combustion (V, Ni) suggests that this source could represent a mixture of industrial emissions including fly ash (characterised by high Si, Ti and Al contents) from the local industrial power plants (burning coal, coke and gas) and possibly metal smelters (Fe, Cu, Mn, Cr) . This mixed source contributed with 25% of the PM_{10} mass (Table 2).
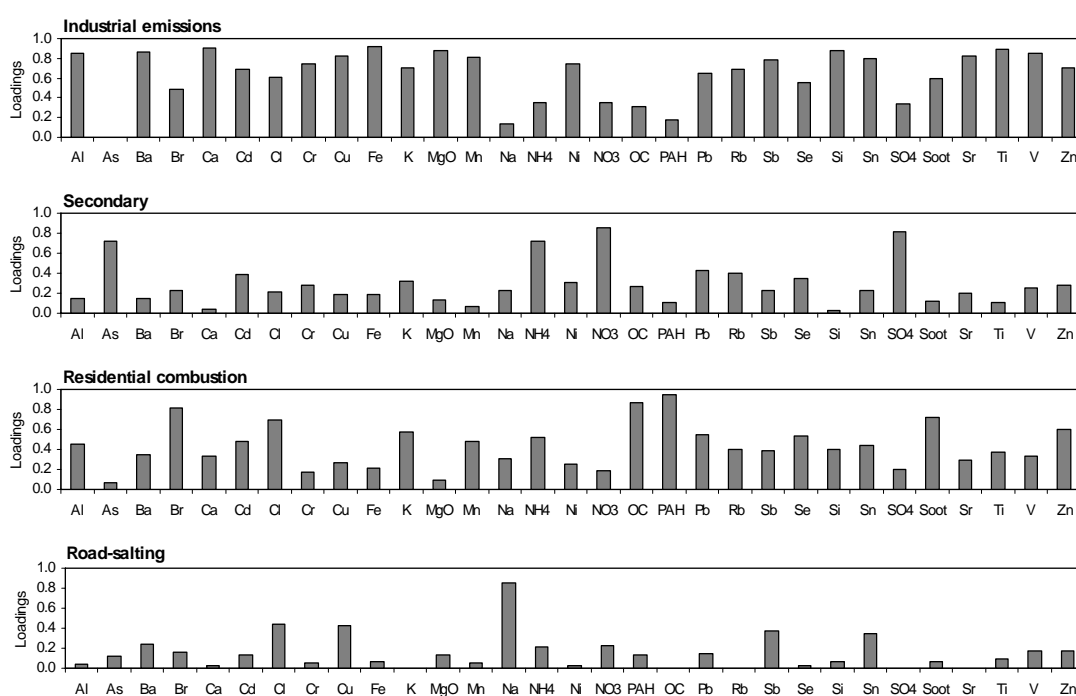
Fig. 19 - The chemical composition and loadings of the four PCA factors.

PCA-Factor 2. The main tracers for *PCA-factor 2:* were NO_3^-, NH_4^+, SO_4^{--}, indicating the presence of secondary aerosols, which is typically interpreted by

receptor modelers as being of regional origin deriving through long-range transport. However during the studied episodes in Krakow when the PM pollution build up during a number of consecutive days with very low wind-speeds (Fig. 7) significant contributions from long-range transport is excluded. This is also confirmed by back-trajectory calculations (Appendix 8). On the contrary, as already discussed for the CMB modelling, it is likely that local high efficiency coal combustion sources with their very high emissions of SO_2 and NO_X contribute significantly to secondary aerosol. Indeed this may explain the fact that arsenic had a high loading (0.7) into this factor and that a number of other components (Pb, Cd, Rb, Zn, Na, Cl, K, Br, Cr, OC, Sn, Sb, V) had intermediate loadings (0.57-0.31), into this factor. This mixed source profile contributed with 43% of the PM_{10} mass.

PCA-Factor 3: the main tracers of this source were PAH, OC, Br, Soot, Cl, Zn, K, Pb, Se and NH_4^+. PAH represents the sum of the organic species in the dataset, and it was used as a single variable. The chemical profile of this source strongly suggests combustion, and thus the most likely underlying source was estimated to be residential combustion (mainly coal and wood). Traffic emissions could also be included in this source in the form of gasoline. This mixed source contributed with 32% of the PM_{10} mass.

PCA-Factor 4: the main tracers of the last source were Na, Cl, Cu, Sb and Ba, The combination of sea-salt elements (Na, Cl) with tracers from road dust emissions (Cu, Sb, Ba) indicated that this source represents road-salting emissions. However, this source represented the minimum percentage of the variance of the dataset (3%) and did not provide conclusive results when MLRA was applied. Thus, it was concluded that this mixed source was identified by the PCA analysis but its contribution to the PM $_{10}$ mass was too low to be quantified by MLRA.

In order to estimate SCEs by MLRA factor scores with negative effects, which do not have any physical meaning, cannot be allowed into the final source apportionment. For this, two mathematically equal options are available: A) to re-centre the factor scores and B) to eliminate negative coefficients.. Two different source apportionment results were obtained with the two options (Fig. 20). Since it was found that with option A, the contribution of industrial emissions source were overestimated, and that this option overestimates the average contributions (especially at lower levels, $PM_{10} < 75$ µg/m3), option B was preferred.
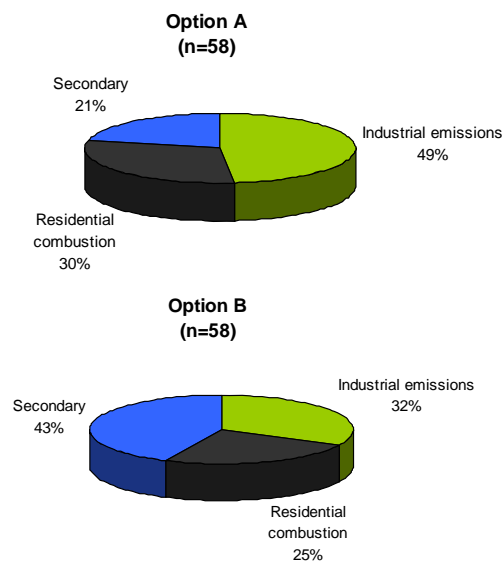
Fig. 20 – Two different source apportionments results obtained with PCA-MLRA. Option A: re-centring the factor scores; Option B, eliminating negative factor scores.

With option B the fit between observed and modelled data for the 5 monitoring sites was significantly high (R^2=0.966), showing that the model is able to reproduce the observed results with great accuracy (Fig. 21). Furthermore, the fit for the individual monitoring sites was also very good, with R^2 values ranging from 0.910 for the INDU site to 0.996 in Zakopane (data not shown).
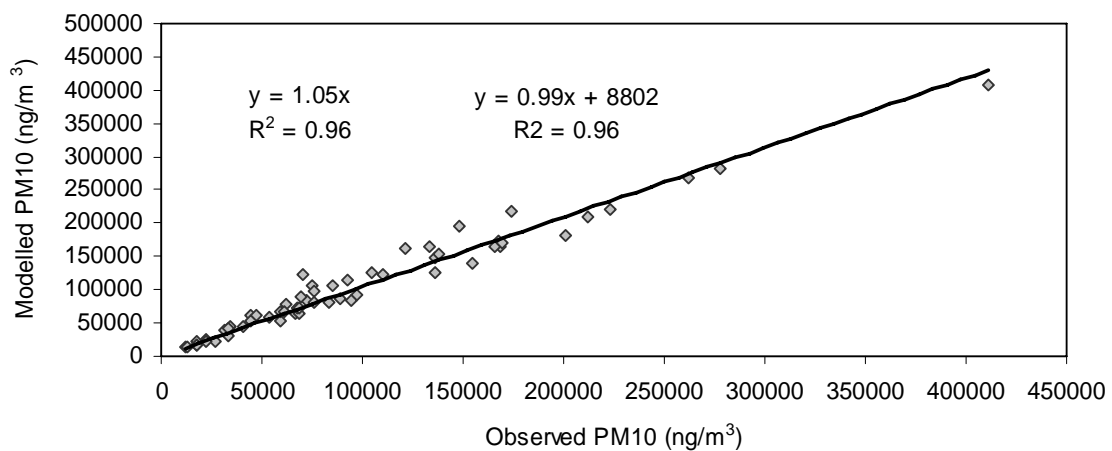
Fig. 21 – Plot of modeled vs. observed PM10 concentrations by PCA-MLRA.

The source contributions calculated for the average of all measurement sites and for each of the monitoring sites are shown in Table 2. The main conclusion obtained is that, whereas the three main emission sources contribute to the levels of PM10 in Krakow, only two are detected in the regional site of Zakopane: the secondary and combustion sources. Industrial emissions do not appear to be registered at this site. Conversely, combustion processes (mostly household-heating) account for almost 80% of the PM10 mass.

Table 2 – Percentage source contributions obtained by PCA-MLRA.

PCA-MLRA	All stations	ZAKO	POLI	AGRI	TRAFFI	INDU
Industrial+	25%	-	27%	17%	36%	31%
Secondary+others	43%	21%	38%	61%	45%	47%
Combustion+traffic	32%	79%	35%	22%	19%	22%
Road-salting	<1 %	<1 %	<1 %	<1 %	<1 %	<1 %

The opposite situation is observed at the TRAFFI site (combustion=19%), suggesting that gasoline is only a minor component of this source and confirming the mostly residential origin of this source. As regards the Krakow sites, the TRAF and INDU stations present relatively similar source contributions dominated by the industrial (45-47%) and secondary (31-36%) sources, while PM at the AGRI station is clearly dominated by the secondary source (61%) due to regional-or long-range transport of pollutants. Moreover, it is interesting to note that the road-salting source observed by PCA but to low to be quantified by MLRA was also detected by CMB and CMF, which estimated a contribution of approximately 2% of the PM10 mass, respectively.

Table 3 - SCE (ng/m3) for compounds regulated by the EU Air Quality directive.

	B(a)P	Pb	Cd	Ni	As
Industrial	5.6	22	0.7	1.2	-
Secondary+others	7.6	51	1.4	1.5	1.4
Combustion+traffic	22.6	20	0.5	-	-

Table 3 shows the source contributions of the three main PM sources identified by PCA-MLRA to the levels of elements of environmental concern, regulated by the EU Air Quality Directive and 2004/107/CE. Results show that in the cases of Pb, Cd, Ni and As, secondary aerosols mixed with others sources is the main factor, whereas combustion+traffic is the main factor for B(a)P. These results are not in agreement with the findings of CMF (Table 4 and Table 5), which may be explained by the mixed nature of the PCA-factors. Secondary aerosols is typically interpreted by receptor modelers as being of regional origin though long-range transport. However during the studied episodes in Krakow when the PM pollution build up during a number of consecutive days with very low wind-speeds (Fig. 7) significant contributions from long-range transport is excluded, which is also confirmed by the back-trajectory calculations (Appendix 9). On the contrary, as already discussed for the CMB modelling, it is likely that local high efficiency coal combustion sources with their very high emissions of SO_2 and NO_X contribute significantly to secondary aerosol. Indeed this may explain the fact that arsenic showed a consistent correlation with NO_3^-, NH_4^+ and SO_4^{--} throughout the different PCA analyses performed, which would not be expected if these ions were of a purely regional origin. The fact that the sum of the contributions adds up to >100% for B(a)P, Pb, Cd and Ni is due to an overestimation by the model.

The day-to-day variation of the SCEs is shown for each site in Fig.22 and compared to back-trajectory data in Fig. 25. It is clear that for the four Krakow stations the PCA-MLRA calculations distinguish the two episodes into one with considerable influence by the mixed source factor designated 'Industrial' (week 1)
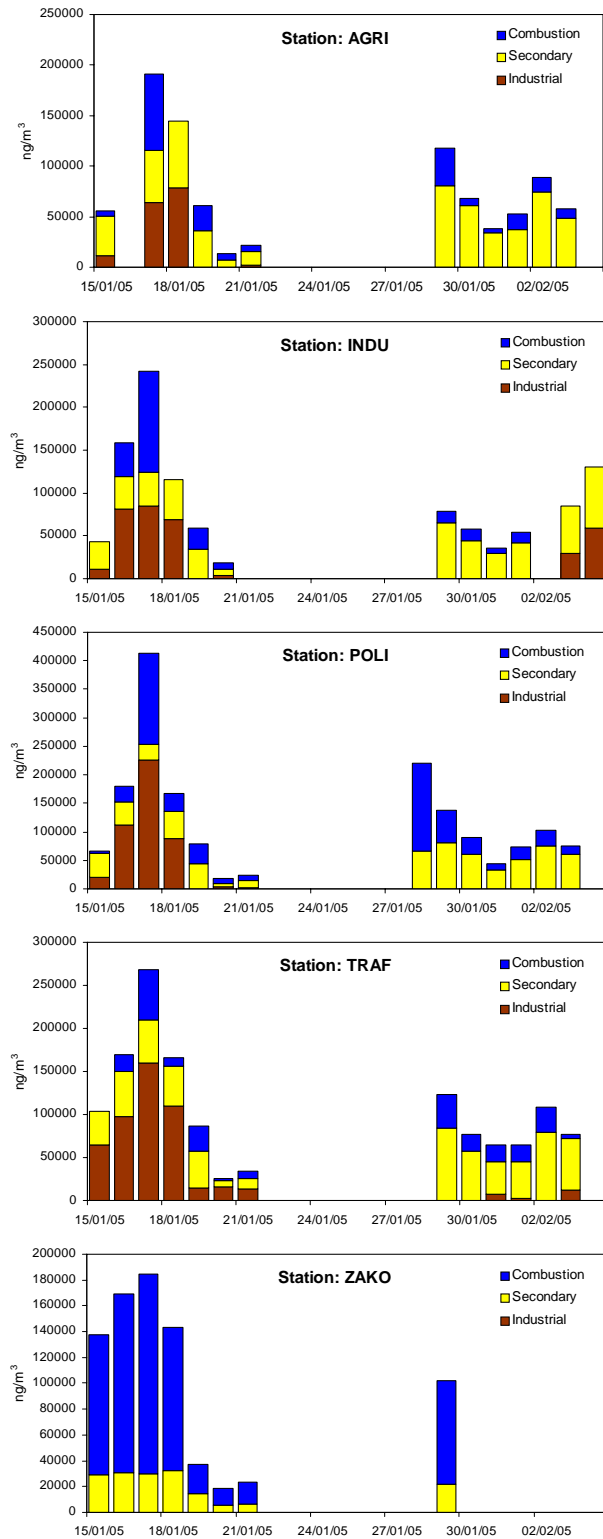
Figure 22 - The day-to-day variation of the PCA-MLA SCEs for each site.
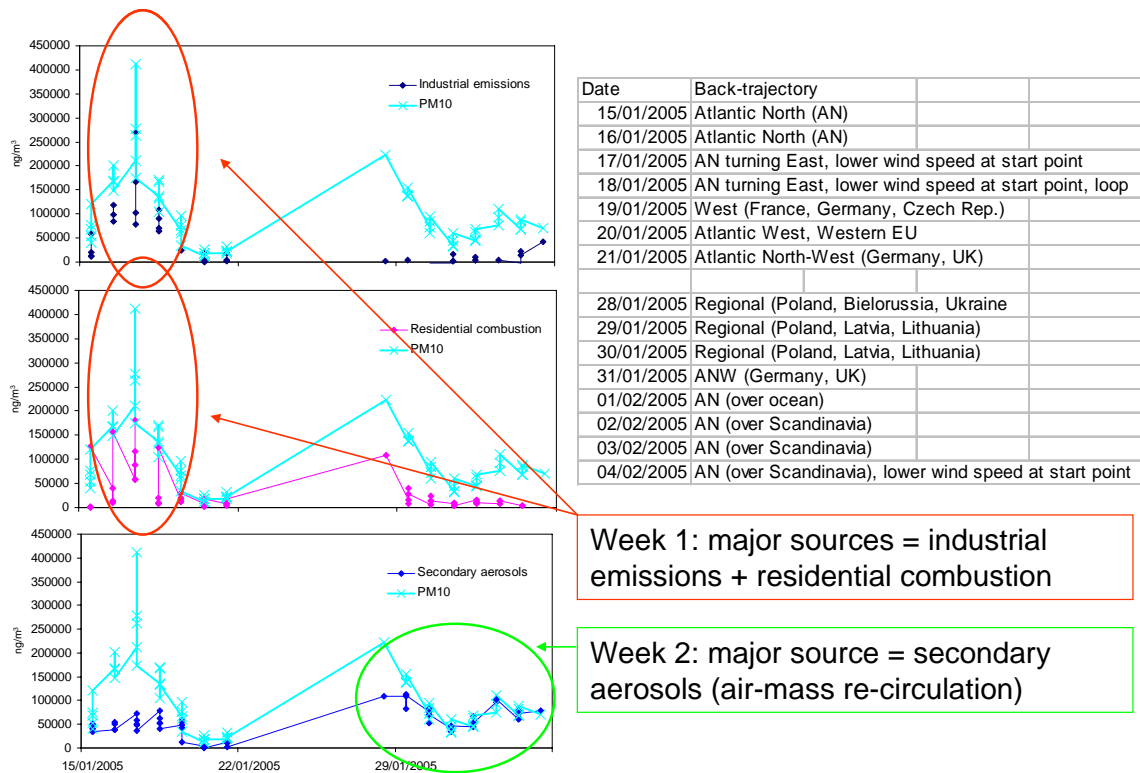
Figure 23 – Back-trajectory analysis of the day-to day variations.

and one with considerable influence by the mixed source factor designated 'Secondary aerosol'. As explained in figure 27 during the days with lower PM_{10} concentrations during the second week it cannot be excluded, that a proportion of the 'secondary aerosol' factor may derive from regional sources in Poland, Latvia, or Lithuania. The third mixed source factor designated 'combustion' becomes important at the days with peak concentrations of $PM_{10,}$ and is always the major factor in Krakow.

5.3 Edge analysis

Edge analysis was carried out with the US EPA UNMIX 6.0 software. Edge analysis seeks to solve the general mixture problem where the data are assumed to be a linear combination of an unknown number of sources of unknown composition, which contribute an unknown amount to each sample. UNMIX also assumes that the compositions and contributions of the sources are all positive. UNMIX assumes that for each source there are some samples that contain little or no contribution from that

source. Using concentration data for a given selection of species, UNMIX estimates the number of sources, source compositions, and source contributions to each sample. If the data consists of many observations of M species, then the data can be plotted in an M-dimensional data space where the coordinates of a data point are the observed concentrations of the species during a sampling period. If there are N sources, the data space can be reduced to an N-1-dimensional space. It is assumed that for each source there are some data points where the contribution of the source is not present or small compared to the other sources. These are called edge points and UNMIX works by finding these points and fitting a hyperplane through them; this hyperplane is called an edge (if N = 3, the hyperplane is a line). By definition, each edge defines the points where a single source is not contributing. If there are N sources, then the intersection of N-1 of these hyperplanes defines a point that has only one source contributing. Thus, this point gives the source composition. In this way the composition of the N sources are found, and from this the source contributions are calculated so as to give a best fit to the data (Henry, 2003).

The application of UNMIX to the combined dataset was done after the addition of 10% to the analytical uncertainties and including the PM mass as receptor species. Preliminary runs produced very high residuals for Na, As and the most volatile PAH compounds (the same that were indicated by SOM to be outliers), and an physically unexplainable factor with azaarenes, which were thus, excluded from the dataset. Finally, the highest PM_{10} value was removed from the dataset because it caused a significant negative intercept. The *UNMIX* model yielded three factors (Fig. 24), which were interpreted as mixed source profiles similar to the three main factors described for PCA (with a slightly different source designation) and with similar contributions to the PM_{10} mass (Fig. 25).

The day-to-day variation of the SCEs for UNMIX (Fig.26) are very similar to those for is shown for PCA (Fig.22). Both models estimated secondary aerosols (mixed with other coal related sources) to be the dominating source at the rural station (AGRI) and residential heating to be the dominating source in Zakopane. Both models also found similar source contributions to the traffic site (TRAFFI) and the industrial site (INDU). As it appears in the following, the SCEs are not comparable with the CMB and CMF models, which may be explained by the mixed nature of the PCA and UNMIX source profiles caused by their lower resolution power.
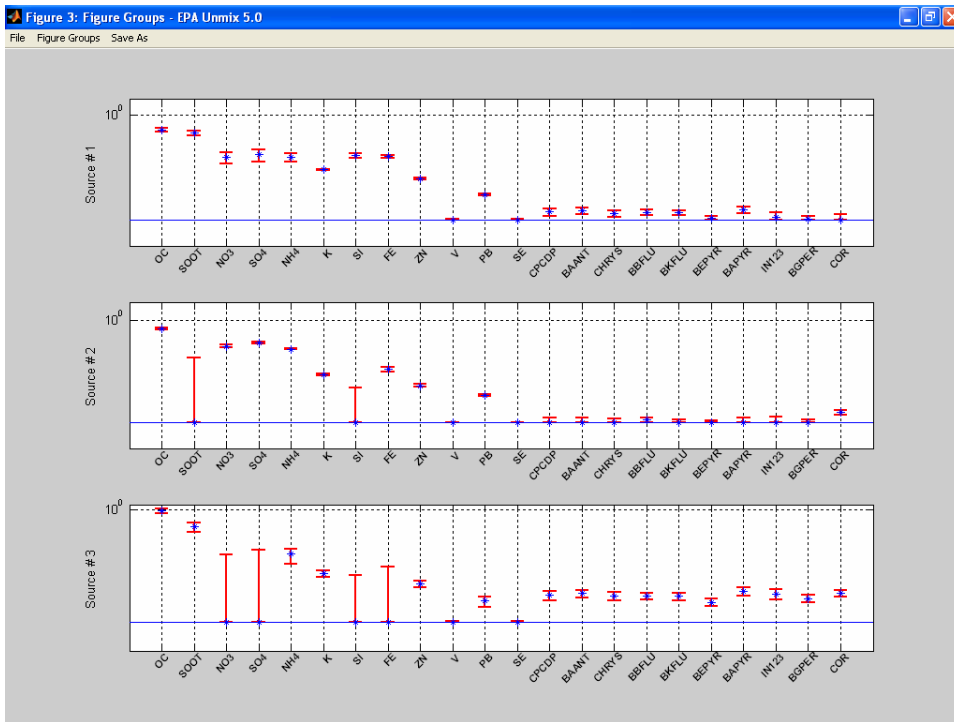
Fig. 24 - The chemical composition and loadings of the three UNMIX factors.
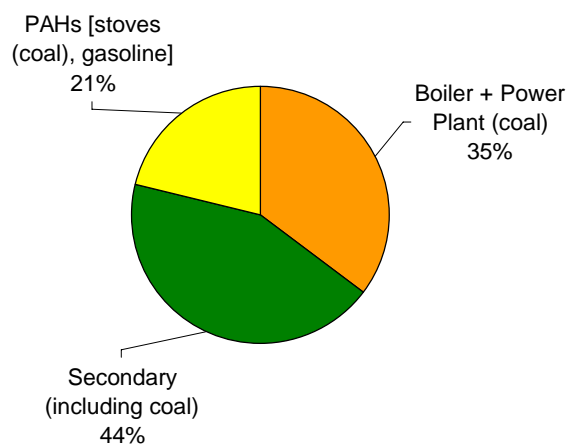
Fig. 25 – The source apportionments results obtained with UNMIX.
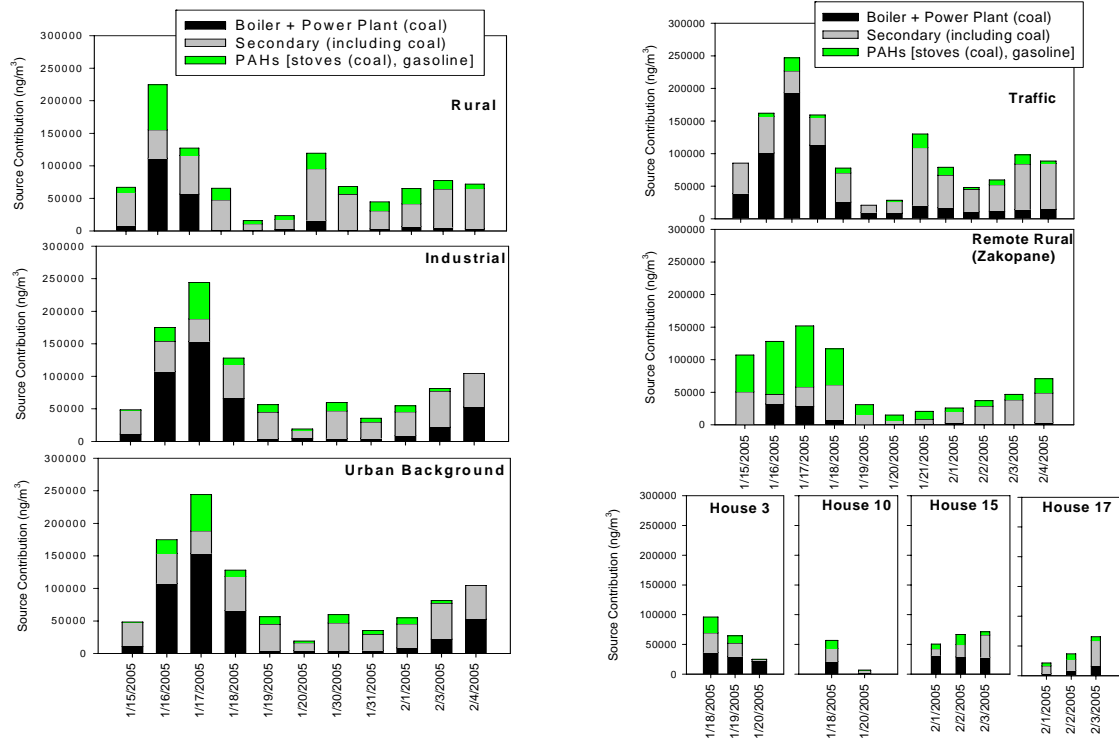
Figure 26 - The day-to-day variation of the UNMIX SCEs for each site.

5.4 Positive Matrix Factorization.

For PMF analysis the US EPA PMF 1.1 software was used. PMF solves the general receptor modelling problem using constrained, weighted, least-squares. The general model assumes there are p sources, source types or source regions (termed factors) impacting a receptor, and linear combinations of the impacts from the p factors give rise to the observed concentrations of the various species. Mathematically stated in Equation 2,

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

Eq. 2

where x_{ij} is the concentration at a receptor for the jth species on the ith day, g_{ik} is the contribution of the kth factor to the receptor on the ith day, f_{kj} is the fraction of the kth

factor that is species j, and e_{ij} is the residual for the jth species on the ith day. In EPA PMF, it is assumed that only the x_{ij}'s are known and that the goal is to estimate the contributions (g_{ik}) and the fractions (or profiles) (f_{kj}). It is assumed that the contributions and mass fractions are all non-negative, hence the "constrained" part of the least-squares. Additionally, EPA PMF allows the user to say how much uncertainty there is in each x_{ij}. Species-days with lots of uncertainty are not allowed to influence the estimation of the contributions and profiles as much as those with small uncertainty, hence the "weighted" part of the least squares. The task of EPA PMF is to minimize Q (sum of squares) in Equation 3.

$$ Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{s_{ij}} \right)^2 $$

Eq. 3

where s_{ij} is the uncertainty in the jth species for day i. EPA PMF operates in a robust mode, meaning that "outliers" are not allowed to overly influence the fitting of the contributions and profiles (Paatero, 1997).

The application of *PMF* to the combined dataset was done with the same compounds as UNMIX with the exception of diB(ah)A that was excluded due high residuals in the preliminary runs (again a compound indicated as outlier by SOM). As uncertainty input to the model, the analytical uncertainties for the PM_{10} components plus ten percent were used. Based on the bilinear model fit evaluation including the block bootstrap uncertainty data a model with five factors was chosen. The composition of the five factors (Fig. 27) did not match the chemical composition of any of the sources characterized in the present study or any source profiles available in literature so they were interpreted as mixed sources.

Fig. 27 - The chemical composition and loadings of the five PMF factors.

Fig. 28 – The source apportionments results obtained with PMF.
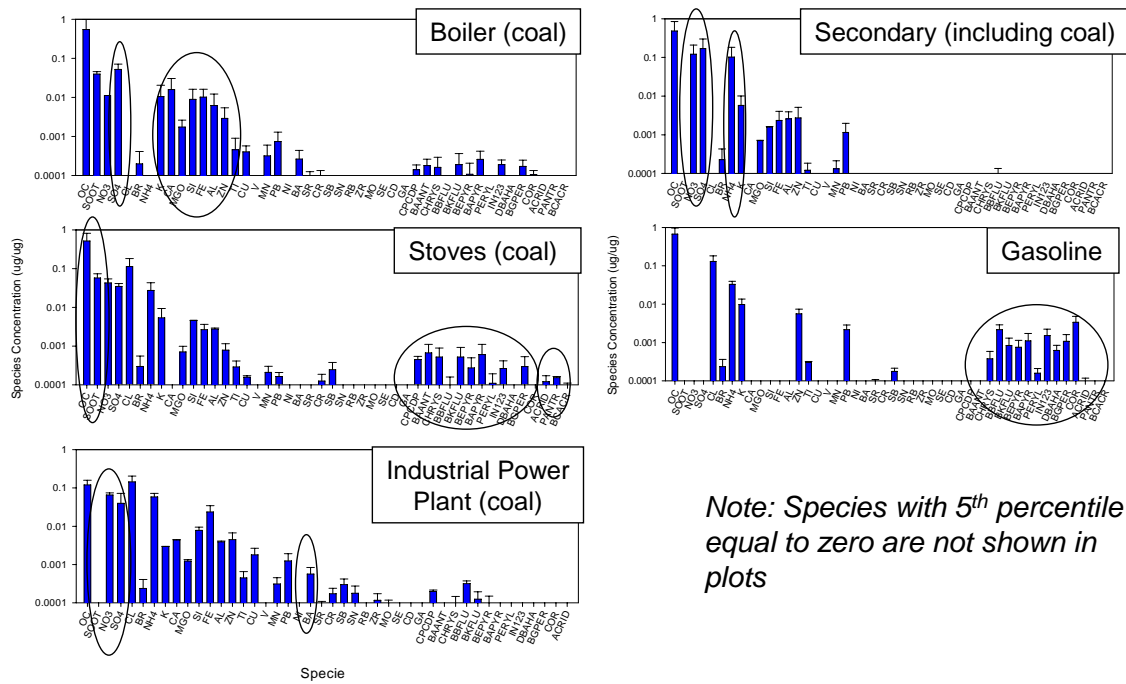
PMF Factor 1 showed high concentrations of PAHs and was the only factor containing azaarenes. It had resemblance to the CMB profile for coal combustion in small stoves and boilers. However, it missed Ca, contained high concentrations of NH_4NO_3 (not emitted by small stoves and boilers), and was enriched for Si, Fe, Al, and to some extend for Mg, Zn, Cu, Mn, Pb, Cr, Sn indicating contribution from other sources such as coal combustion in low efficiency boilers. The SCE from this mixed coal combustion profile amounted to 21% (Fig. 28).

Factor 2 was similar to Factor 1 but further enriched with the metals Si, Fe, Al, Mg, Zn, Mn Pb, and Ba. With is lower concentrations of PAH, Factor 2 showed more resemblance to the CMB profile for low efficiency boilers than to the CMB profile for small stoves and boilers. However contributions from NH_4Cl, Cr, and Sn were totally missing. The SCE from this factor amounted to 28% (Fig. 28).

Factor 3 was different from the former two factors by the zero contribution of EC and the almost absence of PAH. This factor also contained higher concentrations of Cr, Sn, and Zr, all of which indicated contributions from HE coal burning. The enrichment with Cu, Sb, and Ba indicate that also vehicle emissions contribute to this factor, which was further confirmed by the site-to-site variation of the SCEs from factor 3. The SCE from this mixed profile amounted to 13% (Fig. 28).

Factor 4 contained just a few elements, namely OC, NH_4^+, NO_3^-, and SO_4^{--} in high concentrations plus Si, Al, Fe, Zn, and Pb in lower concentrations. This points to secondary aerosol (including a SOA component) mixed with re-suspended soil/dust as sources. The SCE from this mixed profile amounted to 29%.

Factor 5 also contained just a few elements, namely OC, Cl^-, NH_4^+, K^+, Pb, Zn, and all PAH in high concentrations plus Br, Ti, and Sb in lower concentrations. There is no known source profile matching to such a composition, and it possible that this factor is an artifact, a so-called split-factor, which are known to occur in PMF, when too many factors are forced into the solution (see Lanz et al., 2007 and references cited herein). Due to the high concentration of PAH in this Factor, it was initially suggested that emissions from gasoline vehicles were associated with this profile. However, a closer look at the site-to-site variation makes this highly unlikely in the view of the zero contributions of this factor at the traffic site. In any case with a SCE of 8% Factor 5 is a minor compared to the other four (Fig. 29).
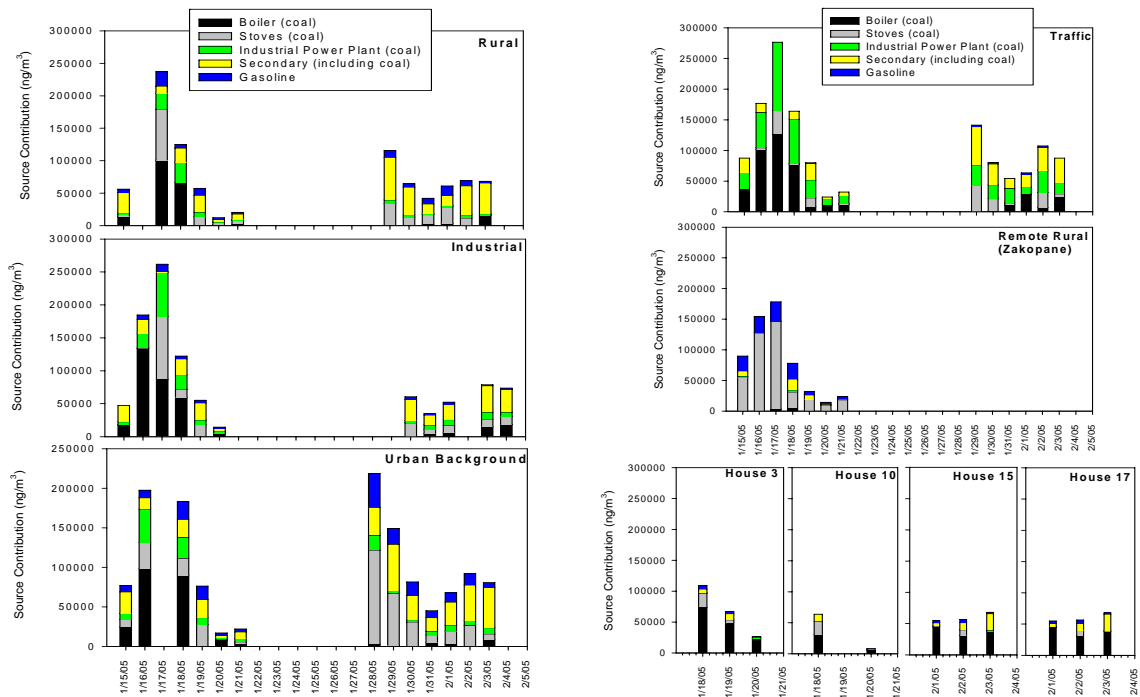
Figure 29 - Day by day PMF source contribution estimates compared to the gravimetrically determined PM$_{10}$ concentrations.

5.5 Chemical mass balance.

CMB modelling was carried out with the software package offered by the U.S. EPA (CMB 8.2). This model find a statistical solution to over determined set of linear equations that express each receptor chemical concentration as a sum of products of source profile abundances and source contributions (Eq. 1) as . For each run CMB fitted the speciated data from the 20 Krakow sources plus additional sources described in literature group of to corresponding data from each 24 hour PM_{10} sample collected at the five receptor sites. The source profile abundances or chemical fingerprints (i.e., the mass fraction of the 52 analyzed particle matter components) and the receptor concentrations, with appropriate uncertainty estimates, served as input data to CMB. The output consisted of the estimated amount ($\mu g/m^3$) contributed by each source type represented by a profile to the total mass, as well as to each chemical species. CMB was used to compute values for the contributions from each source and the uncertainties of those values. The statistical theory behind this model has been described in details elsewhere (Friedlander, 1973; Henry et al., 1984; Watson et al., 1984; Hopke, 1985).

As estimates of the uncertainty on the input data (receptor and source mass fractions) for non-volatile compounds, such as EC, OC, trace elements and ions we assumed a 20 % overall uncertainty encompassing the analytical chemical uncertainty and all approximations of assumptions for CMB which are: constant compositions of source emissions over the period of ambient and source sampling; non-reactivity between chemical species (*i.e.* they add linearly); identification of all significant sources; normal distribution of random, uncorrelated measurement uncertainties. Hence, the overall uncertainty, S_{ij} for compound *j* in sample *i*, was calculated according to Equation 2.

$$S_{ij} = \Lambda_j + 0.20 \, C_{ij} \qquad \qquad \text{Eq. 2}$$

Furthermore, the uncertainty, S_{ij}, for semi-volatile PACs, which may be affected by temperature dependant partitioning was estimated by Equation 3-6

$$S_{ij} = \frac{\Lambda_j + 0.2 C_{ij}}{\Phi_{ij}} \qquad \qquad \text{Eq. 3}$$

$$\Phi = \frac{KpC_{PM}}{(1+KpC_{PM})} \qquad\qquad \text{Eq. 4}$$

$$\log Kp = m \log p_{Ls}^{o} + b \qquad\qquad \text{Eq. 5}$$

$$\log p_{Ls}^{o} = \log p_{L}^{o} + \frac{\Delta H}{R}\left(T^{-1} - T_{s}^{-1}\right) \qquad\qquad \text{Eq. 6}$$

In which, Λ_j nominates the detection limit of compound j, C_{ij} the concentration of compound j in sample i, Φ_{ij} the partition of compound j in particulate phase in sampling temperature of sample i, Kp the temperature corrected partitioning coefficient, C_{PM} the concentration of PM, P_{Ls}^{O} the temperature corrected subcooled liquid vapor pressure, m and b are, constants (Fernández et al., 2002) , and T the sampling temperature.

A number of source profiles used in this study were composite profiles. For these, the uncertainties were 1σ variations in fractional abundances among members of the composite or the uncertainties specified in Eq. 2 and 3, whichever was larger.

5.5.1. CMB Source profiles. Chemical mass balance analysis involved procedural choices for the selection of source composition profiles and fitting species in the CMB calculations. In order to obtain a solid basis for choices preliminary computations were carried out with the source elimination option in the CMB 8.2 software turned on, so that collinear profiles were automatically eliminated in the successive iterations of the least-square calculations. These computations were carried out on a data set consisting of the average ambient concentrations over the complete study period for each receptor site. When only profiles (chemical fingerprints) for the known source in Krakow (Table 1) were used as input, it was evident that sufficient mass coverage could not be obtained, and therefore the in-data needed to be complemented with other source profiles. These were obtained from previous source characterization studies carried out in JRC's vehicle testing laboratories, from the U.S. EPA SPECIATE database and from the literature. The additional profiles represented secondary aerosols, vehicle transport and re-suspended PM. A total of 65

additional profiles were tested. With the criteria of optimizing the PM_{10} mass coverage in the source apportionment while only including source profiles that resulted statistically significant a subset of source profiles was selected. This subset was utilized for the 58 individual CMB computations of the PM_{10} samples collected at the five receptor sites and the 11 individual CMB computations for the indoor receptor sites. For each individual CMB computation, all the candidate source profiles were tested manually. This is a cumbersome process; however it ensured that the highest possible mass coverage was attained for each site and day. For the transition days between pollution episodes and clean air, the criteria of only including sources, which resulted statistically significant was relaxed to maintain these sources if the SCEs resulted higher than associated standard error of the estimates. In the preliminary tests, a number of individual source profiles resulted collinear and thus either one of these or a composite profile of these was used, whichever gave the highest PM_{10} mass coverage. Finally, for each site on a limited number of days which represented pollution episodes and clean conditions, the collinearity issue was readdressed by further CMB computations using all the individual profiles. In the end the following source fingerprints were included

Residential stoves/boilers (coal). A composite profile constructed as the average of three individual profiles (N1, N2, N10; Table 1) of PM emitted from coal combustion in small stoves and boilers in Krakow and Zakopane.

Residential stoves/boilers (wood). A composite profile constructed as the average of three individual profiles (N5, N6, N9) of PM emitted from mixed wood combustion in small stoves and boilers in Krakow and Zakopane.

Low efficiency boilers (coal). A composite profile constructed as the average of three individual profiles (N3, N4, N7) of PM emitted from coal combustion in small (<5MW) boilers in Krakow fuelled manually or automatically. *Low efficiency boilers (fuel).* Individual profile (N8) of PM emitted from heavy fuel combustion in a small (<5MW) boiler in Krakow.

SteelworksPP and Steelworks. Only four profiles from the steelworks operation resulted significant in the CMB computations. Two came from the >50 MW power plants, namely the steelwork coal (and coke gas) fuelled power plant (N14) and the steelwork coke gas (and coal) fuelled power plant (N12). These profiles resulted collinear and were represented arbitrarily by the former, *SteelworksPP,* which generally produced slightly higher mass coverage. The two other significant profiles

came from the coke fuelled blast furnace (N13) and the (coke fuelled) basic oxygen furnace steel plant (N15). Also in this case were the profiles collinear, and the final apportionment of these sources was carried out case by case with the one, which produced the highest mass coverage. It must be noted that also the public power plant coal combustion profiles were collinear with *SteelworksPP*. Power-generation resulted significant (albeit with a small contribution), only at the INDU site and since the wind during most of the days with episodes was carrying PM from the steelworks to the receptor site this was attributed to *SteelworksPP*. Indeed, tests with all power generation profiles gave highest mass coverage for this profile.

Vehicles. For obvious reasons, source profiles for traffic (road transport) are difficult to obtain by direct in-field source characterizations. Previous approaches include construction of composite profiles from a large number of emission profiles for individual vehicles typical for the source apportionment site (e.g. Chow et al., 2006; Fujita et al., 2007) and characterization of particle compositions in tunnel studies (e.g. Lanz et al., 2007). The main uncertainty of both approaches is connected with the question about the source profile representation. In the present study, eight composite profiles were tested. Four EPA-SPECIATE profiles (light duty and heavy duty gasoline vehicles with and without catalyst as well as heavy and light duty diesel vehicles) were supplemented with PAH emission data from Sagebiel et al. (1997) Miguel et al. (1998) and Marr et al. (1999). Other four profiles were build by combining a profile for traffic-generated PM (vehicle exhaust + brakes) sampled close to a main street in the city of Copenhagen, Denmark (Wåhlin et al., 2006) with PAH emission data for Euro 2 -3 light duty and heavy duty diesel vehicles and Euro 2-3 light duty diesel vehicles obtained from vehicle testing studies in our laboratories (Larsen et al., 2000; Farfaletti et al., 2005) and from a mixed traffic tunnel study (He et al., 2006). All the eight composite sources were collinear for most CMB computations, and resulted in comparable SCEs. Best statistical performances (chi-square, T-value, standard error on SCE) were obtained with the profile for traffic-generated PM combined with PAH data from the mixed traffic tunnel study. It is possible that, this may be explained good similarities in the vehicle fleet of Krakow and Copenhagen compared to the SPECIATE data, which is obtained with vehicles typical for U.S.A. However, it may also be explained by the fact that profiles derived from field measurement of mixed traffic better represent real driving conditions.

Ammonium sulfate, ammonium nitrate, and ammonium chloride. As profiles for secondary aerosol we used $(NH_4)_2SO_4$ and $(NH_4)NO_3$ (stoichiometric composition), which are known to be ubiquitously present in ambient PM as a result of atmospheric oxidation of sulfur and nitrogen containing gaseous precursors (Putaud et al., 2006). Preliminary CMB computations made it clear that a further secondary aerosol profile containing chloride was needed to obtain good mass coverage. Compared to the vast data available in literature on PM from kerbsites, urban, rural and background sites in Europe (Putaud et al., 2006 and references herein) this is very unusual, and can only be explained by the gaseous emissions of chloride (probably in the form of HCl). It is well know, that combustion of coal which contains impurities of chlorine such as the Krakow hard-coal (Jimenez and Niedzialek, 2006) lead to gaseous emissions of HCl (e.g. Jaszczur et al., 1995) and all observations in the present study points to coal combustion as the dominating source for the third secondary aerosol component, which was modeled in CMB as $(NH_4)Cl$ (stoichiometric composition).

Rock, Lime, Cement, and *Sodium chloride.* A few profiles with minor source contributions (< 3 %), were added to maximize the mass coverage, which all represented diffuse, re-suspended road dust or road salt. For a number of samples the CMB runs showed mutual collinearity for these profiles, and in each case the one, which gave the best PM mass coverage was arbitrarily selected. The *Rock* profile corresponds to igneous rock by Kaye and Laby (1959) and the *Lime* profile is equal to the $CaCO_3$. In most CMB runs, the *Rock* profile resulted collinear with various pavement profiles obtained from the SPECIATE database. The *Cement* profile was obtained from the characterization of PM emitted at the Krakow cement kiln (N19). In a number of CMB runs *Cement* resulted collinear with *Lime* and with the profile from the production of fire-proof material at the steelworks, and it is actually not possible by CMB to distinguish between these three sources, which all have calcium as marker compound. Sodium chloride represents re-suspension of road salt used for road de-icing operations. Different profiles were tested from pure sodium chloride to average sea salt without any significant difference in the resulting source contribution, which in any case remained very small and only obtained statistical significance at a few days at the traffic site.

5.5.2. CMB results. The day-by-day SCEs (and propagated standard error) for the five sites are plotted in Figs. 30 – 34 together with the gravimetrically determined PM_{10} concentrations. A good mass coverage is observed for all days and sites, however, with a tendency for the source apportionment to underestimate the PM_{10} levels (Predicted PM_{10} = 0.82 * Measured PM_{10} + 0.3; R^2 = 0.93; Fig 39). Whether this indicates that a significant source has not been considered in the study, or that the discrepancy can be explained by the statistical error of the CMB approach (including analytic errors and unfulfilled basic assumptions such as e.g. mass conservation as described in the introduction) is not easy to say. However, considering that the average propagated standard error for all days and sites was 15% the obtained underestimation of 18% is hardly significant.
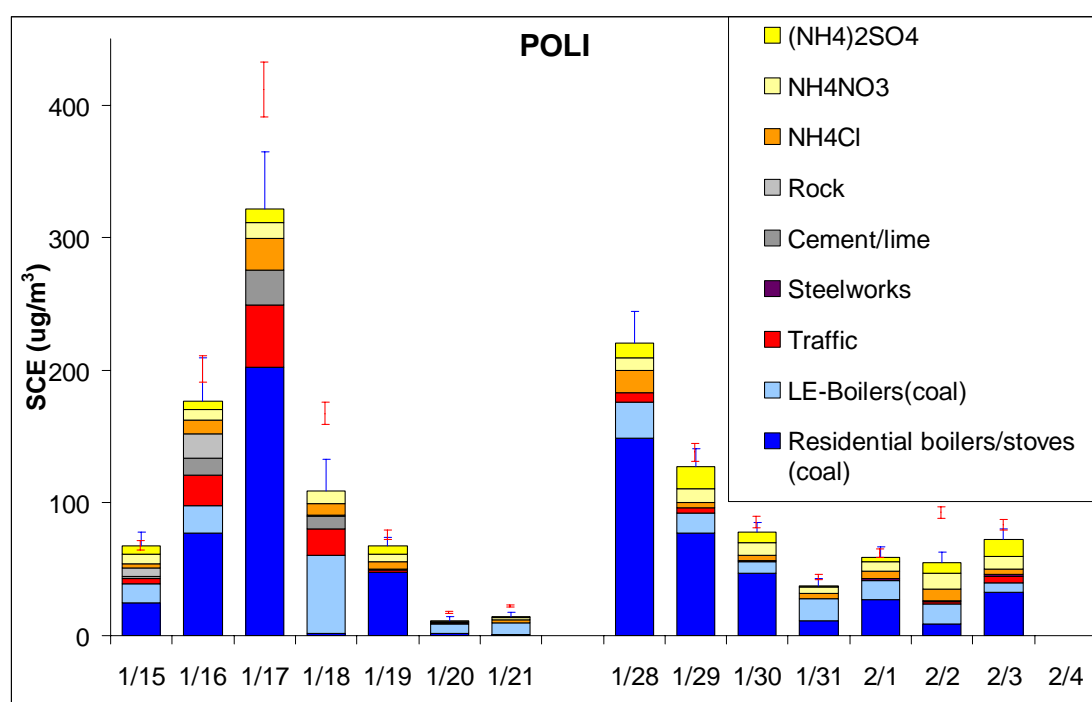
Figure 30 - Day by day CMB source contribution estimates (propagated standard error: blue bars) compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error: red bars) for the POLI site.
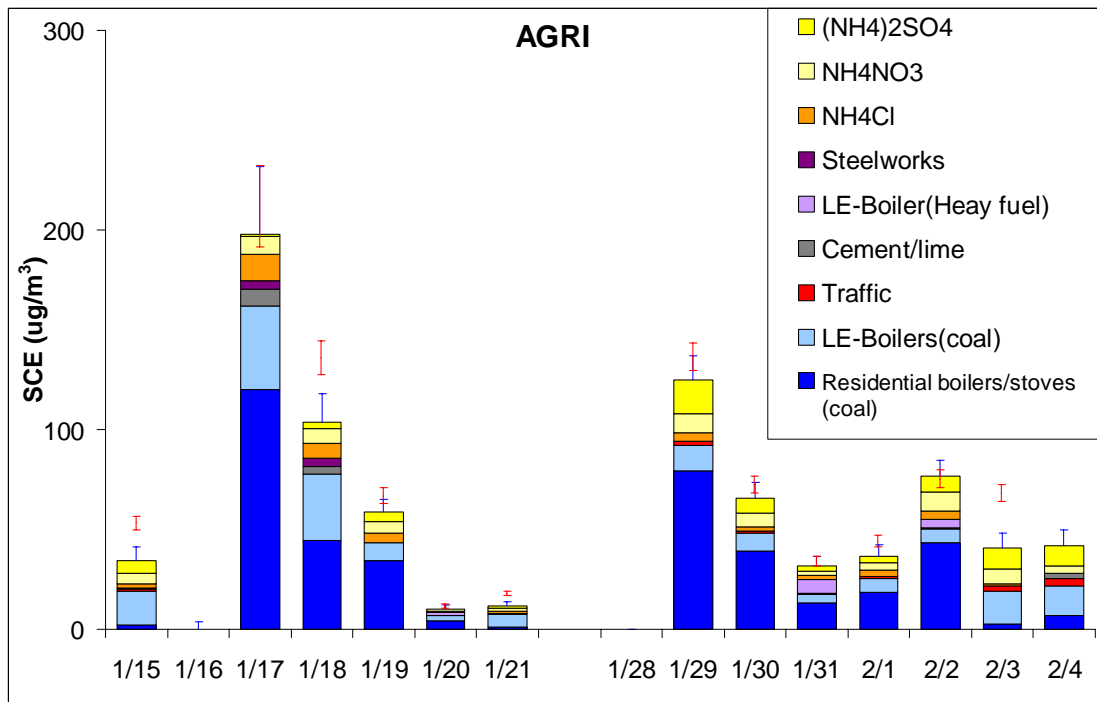
Figure 31 - Day by day CMB source contribution estimates (propagated standard error: blue bars) compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error red bars) for the AGRI site.
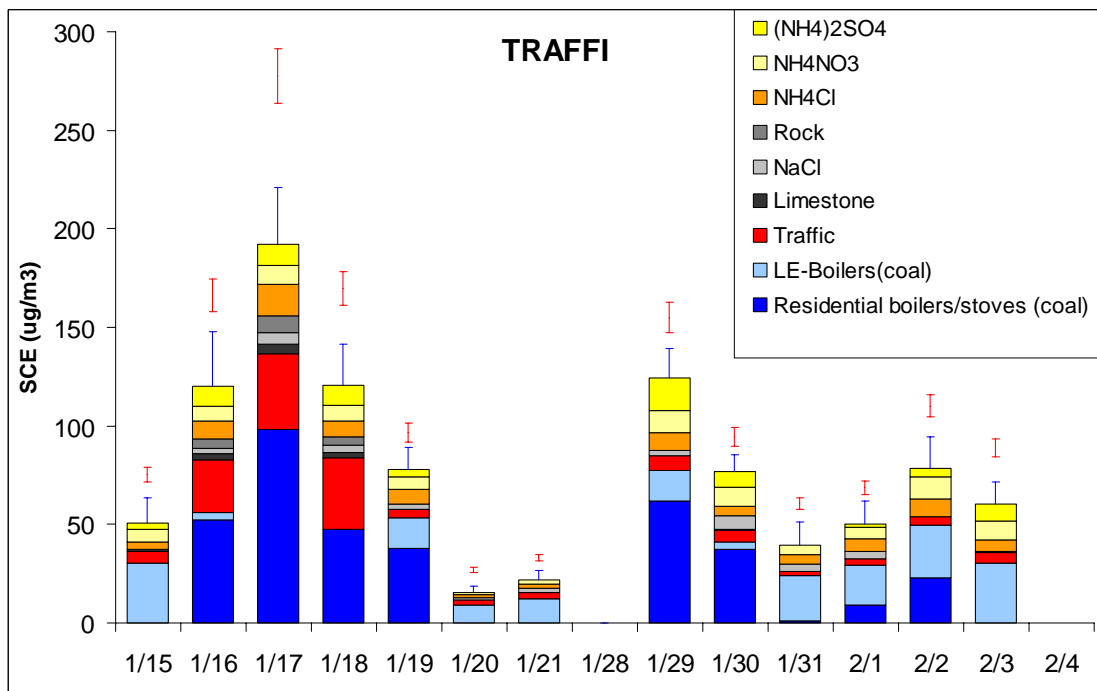
Figure 32 - Day by day CMB source contribution estimates (propagated standard error: blue bars) compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error red bars) for the TRAFFI site.
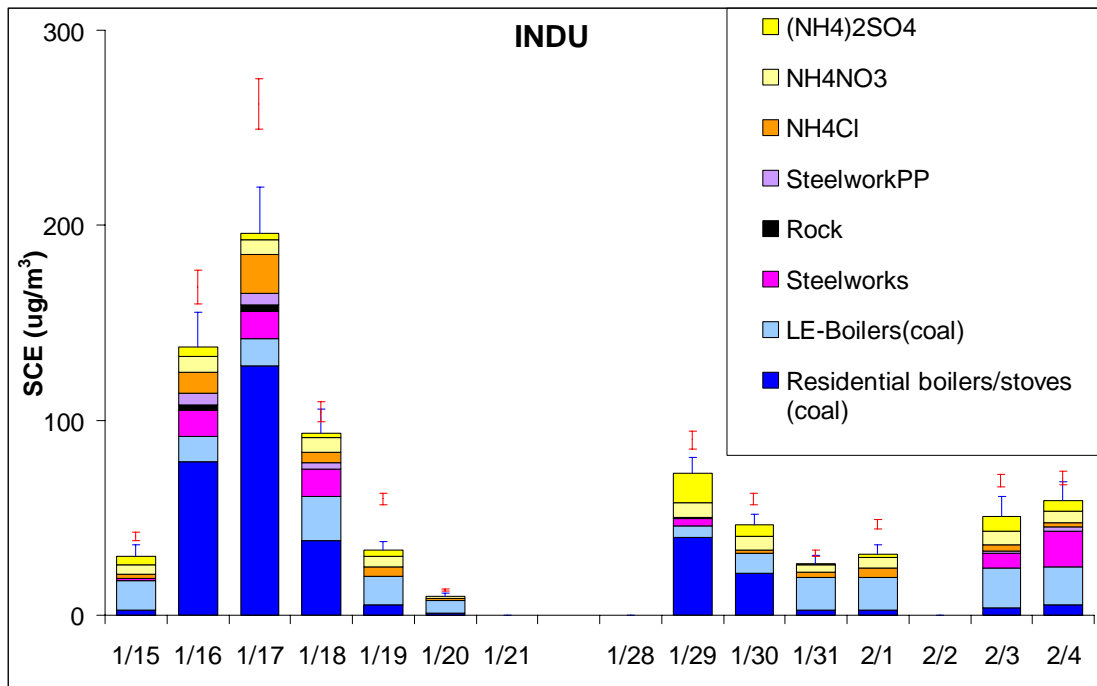
Figure 33 - Day by day CMB source contribution estimates (propagated standard error: blue bars) compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error red bars) for the INDU site.
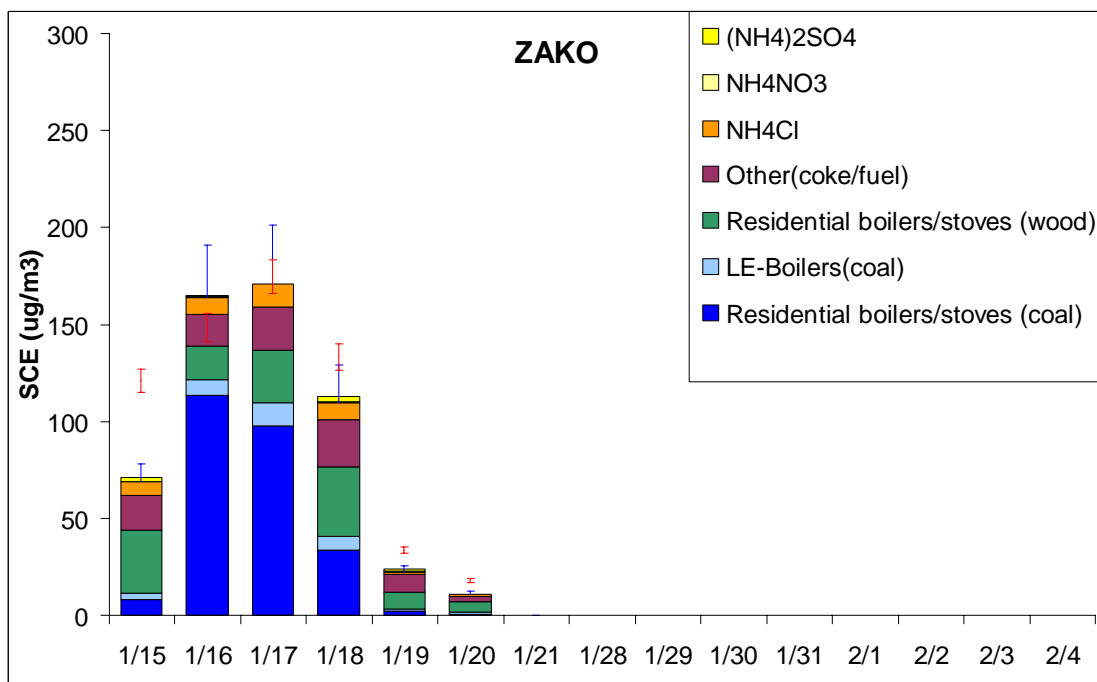
Figure 34 - Day by day CMB source contribution estimates (propagated standard error: blue bars) compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error red bars) for the ZAKO site.

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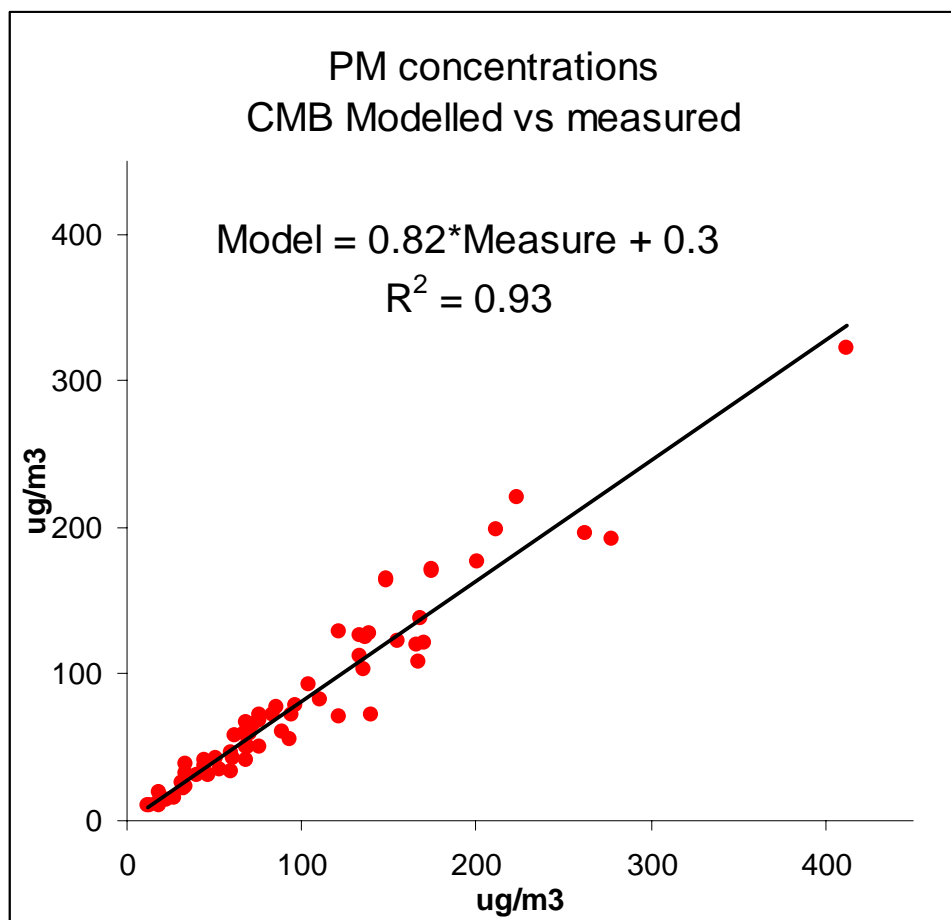
Fig. 35 – Plot of modeled vs. observed PM10 concentrations by CMB.

It is evident in Figs. 30 – 34 that on all days the contribution to the atmospheric pollution with PM_{10} is dominated by coal combustion in stoves and small boilers, with the exception of the few days in Zakopane, when wood combustion also plays and important role. It is also evident from the SCEs of ammonium sulfate and ammonium nitrate that secondary aerosol contribution is significantly higher at the Krakow sites than in Zakopane (almost absent), which strongly point to local sources for this secondary aerosol, such as industry, power generation and possibly road transport, which all are major emitters of SO_2, NO_X or both. In Krakow, these sources contributed on average with 14 ($\pm$ 7) % of the PM_{10} mass concentrations, and tended to be relatively more important in the second period, which had different meteorological conditions that the first period, as will be discussed in the following. The third secondary aerosol component, ammonium chloride, contributed on average with 7 ($\pm$ 4) % of the PM_{10} mass concentrations and was not only significant in

Krakow but also in Zakopane, where industrial sources are absent, which strongly suggests coal combustion in stoves and small boilers as the major source. This is sustained by the fact that ammonium chloride tended to prevail on days with high source contributions from these sources.

It is interesting to compare these results with the SCE obtained with PMF for secondary aerosol (29%), which in contrast to the CMB profiles includes both inorganic and organic secondary components. The SCEs for inorganic secondary aerosol and for re-suspended soil/dust obtained with CMB contributed with 17-18% and 2%, respectively, for the combined dataset. This leaves contribution from secondary organic aerosols (SOA) of approximately 10%. The secondary aerosol profile in CMB and CMF (as well as PCA) contains Cl⁻, which was missing in the CMB Factor 4. If this is taken into consideration, the estimate of SOA increases by 3-5%.

It is also evident in Figs. 30 – 34 that, as expected, sources related to road transport (traffic and re-suspension) contributes most at the two sites which are situated near the city centre (TRAFFI > POLY) and are insignificant at other peripherical sites (AGRI, and INDU) and the remote site (ZAKO). Moreover, in good agreement with what would be expected, the sources from steelwork activities are only important at the INDU site, and home heating by combustion of wood is only important at the site (ZAKO) where it is easily available from the surrounding forested area.

All the above mentioned findings add credibility to the entire CMB exercise, which is further sustained by the fact that the time evolution of the source contributions to each receptor site could be explained nicely by local-scale transport phenomena driven by the prevailing meteorological conditions. The meteorological conditions were analyzed from back-trajectory plots constructed for each site and day (Appendix 8) in addition to the recorded temperature and wind observations at the measurement sites. During the build-up phase of the first episode, weak (< 1.5 m/s) synoptic winds from the west turned northerly and slowly died out on the January the17[th] while the temperature dropped (inversion), which caused the severe pollution peak. At the end of the episode, the winds were southerly and increased in intensity. The second episode of the measurement campaign started with cold days (inversion) with very weak (< 0.5 m/s) local winds turning from south over west to north. At the end of the period, the winds turned westerly (synoptic) and increased in intensity.

Interestingly, CMB computations were able to reveal local-scale transport by minor, yet significant, contributions from non-local sources to the sites in Krakow. Hence, only during the days with westerly winds small contributions from an industrial source (quantified as "steelworks") was revealed at the AGRI site, which is in good accordance with the presence of an industrial area west of Krakow. Likewise, at the INDU site, the contribution from the steelworks activities could not be detected during the days with winds from south, whereas the contributions from home-heating were strongest felt during the meteorological conditions when this site was downwind the city center. Finally, the contribution from coal combustion in small stoves (which is a source type concentrated around the city centre) relative to the contribution from coal combustion in LE-boilers (which is distributed all over the Krakow area) can also be explained by the meteorological conditions. Expectedly, on days with very stable conditions and insignificance local-range transport the contribution from small stoves dominated at two sites near the city centre (POLI and TRAFFI) and on windy days the contribution from boilers increased. At the remote site in Zakopane these transport phenomena were not observed due to the absence of sources in the vicinity.

The receptor modelling results for the combined Krakow-Zakopane dataset appears in Fig 36. The individual source apportionment results for PM$_{10}$ in Krakow and Zakopane will be discussed in the next chapter together with the CMF results.
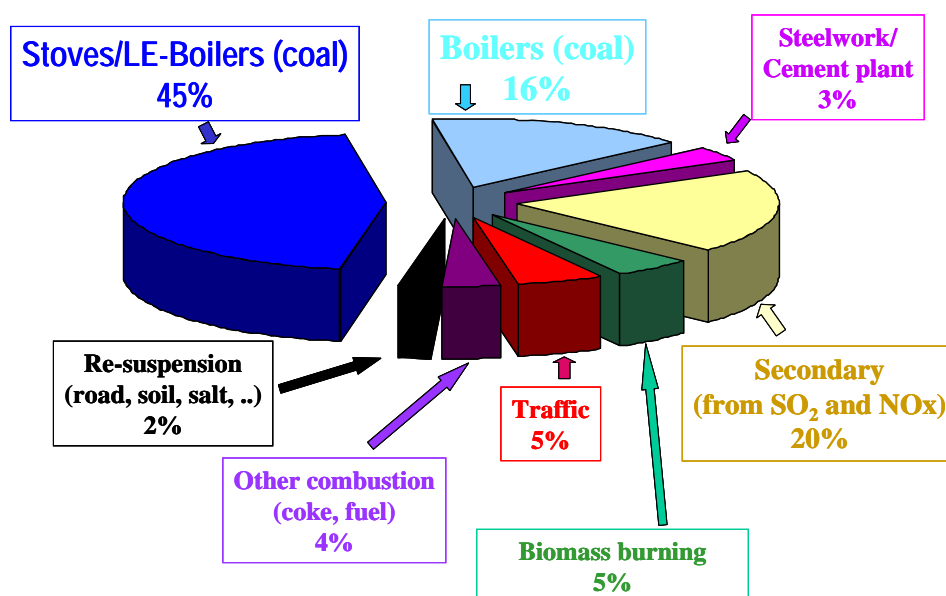
Fig. 36 – The source apportionments results obtained with CMB.

The receptor modelling results for the indoor air in the four investigated apartments in Krakow yielded the same main sources as outdoor air from nearest receptor site with an expectedly higher contribution from residential coal combustion. For the four apartments the average (± SD) source contribution estimates were ($\mu g/m^3$, CMB data): residential coal combustion in small boilers and stoves (50 ± 20.4); Secondary aerosols (5.3 ± 3.1); traffic (2.6 ± 1.9); re-suspension (1.0 ± 0.6). The mass coverage was higher than 85% for all individual apartments

5.6 Constrained matrix factorization.

CMF can be regarded as a hybrid of CMB and bilinear models solved by PMF. In CMB, the source profiles have to be known in advance, whereas bilinear models give estimates for an assumed number of source profiles without any a priori knowledge about emission sources. Hybrid models are promising when bilinear un-mixing techniques fail and partial *a priori* information about emission sources is available. As an intermediate between factor analysis and CMB, a method called target transformation factor analysis (TTFA) has been used (Hopke, 1988). In TTFA, the user specifies likely target shapes for the composition factors. The algorithm attempts to rotate the computed solution so that the target shapes are reproduced as well as possible. Although TTFA has been successful in many practical problems, it suffers from the fact that rotations are performed a posteriori, after choosing the subspace with an eigen-analysis (Paatero et al., 2002). Another application of a hybrid receptor model was developed in the early 90ties by Wåhlin (Wåhlin, 1993, Lee et al., 1999, Wåhlin et al., 2001) to tackle the classical problem with residual arbitrariness, which all factorization models suffer from. The arbitrariness can be reduced by using *a priori* knowledge about the source profiles. In Wåhlin's COPREM model (Wåhlin, 2003) and in CMF an initial source profile matrix ($g_{in.}$ in Eq. 1) is used for the fit, in which some profiles, or parts of these, are constrained in the iteration process to constant ratios between the compounds. Source profiles with fixed ratios are consistently used with the CMB approach, which is the most objective way of doing a source apportionment. As more constraints (i.e. knowledge about the real sources) are added to the source profiles, the model can be gradually changed from a factorization model to a CMB model. Finally a multiple weighted linear regression analysis, in

which all constraints are ignored, is performed after the last iteration step. CMF takes advantage of the multi-linear engine ME-2 model tool developed by Paatero, (1999), which facilitate the running of PMF in various constrained modes. We have originally developed and tested this approach for the source apportionment of volatile organic compounds (Latella et al., 2005; Juninnen et al., 2005) and it has been further developed and described in mathematical details for organic aerosol source apportionment (Lanz et al., 2007; 2008). In this study we tested a new approach for constraining some of the factors. Instead of a freezing the ratios of certain elements in the constrained factors ('hard locking'), these ratios were allowed to vary between given intervals in the iterative solution to Eq. 1 ('soft locking'). This approach addresses one of the fundamental assumptions of receptor models discussed in the introduction, namely question of source profile representation, and the basic idea is to allow CMF to slightly modify some elements in a constrained profile, without loosing the main features of this profile. There is no objective measure of how broad the soft locking interval of a constrained element should be, so for each element a number of different intervals were tested with the main criterion to have as wide soft locking intervals as possible, and to obtain a small as possible Euclidian distance from the soft-locked modified factor to the source profile it was constrained to, while maintaining the highest possible mass coverage and the lowest possible residuals for the individual receptor elements. Before finding the final solution a total of 23 test trials were conducted with different soft locking approaches. In order to compute the SCEs and estimate their uncertainty, the final CMF solution was subjected to a bootstrapping procedure, by which the model was run repeatedly 100 times, each time on a randomly chosen 80% subset of the receptor samples. From run to run all factors were constrained to the previous one (with a 40% soft-locking interval for all elements). This was repeated 100 times and the final source factors were computed as the averages of these 100 bootstrap runs. The uncertainties of the SCEs were calculated as the standard deviations of the 100 bootstrap runs. The designation of sources to the non-constrained CMF factors, Euclidean distances were calculated to the source profiles described for the CMB modelling, and the closest source profile was assigned to each CMF factor. This approach was taken to minimize the subjectivity element in the source designations.
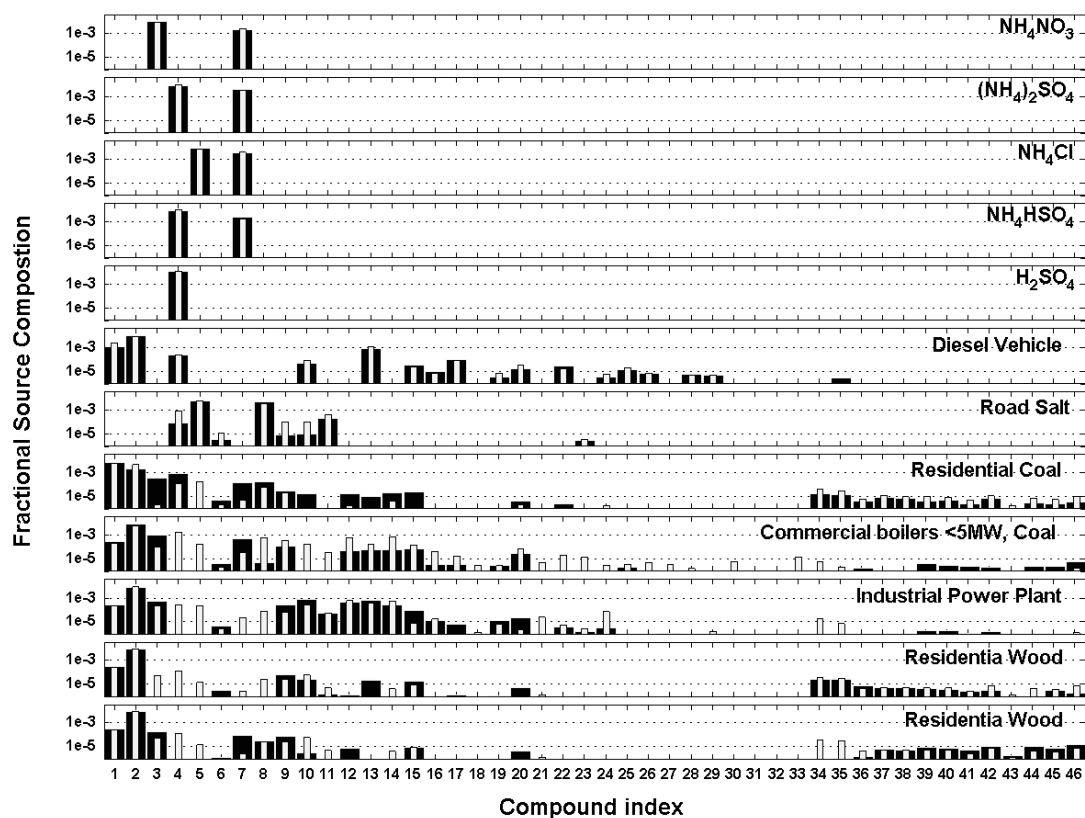
Figure 37 - Comparison of CMF factors (black bars) and measured source profiles used in CMB model (white bars). The closest profiles in a Euclidian distance are presented. Chemical compound numbers are given in Fig. 38.

The Krakow dataset is characterized by very high EC and OC concentrations and all other components are low compared to them. In a pure factorization model such as e.g. PMF, most of the variance in the dataset will derive from EC and OC and profiles dominated by these components, which may mask the variability of minor components and factors driven by them. Two PACs (diB(ah)A; diMPhe) where very close to their detection limit in all of the samples and produces high residuals in the preliminary runs, so they were excluded from CMF. A large number of exploratory model runs were conducted with completely and partially constrained factors, for which *a priory* information was available. The selection criteria were the optimization of mass coverage and minimization of residuals for PM_{10} as well as single components. The most satisfactory model contained in total 12 factors, six factors for which all elements are constrained, two factors with some of the elements constrained, and four non-constrained factors (Fig.37). A higher number of factors

resulted in factor splitting and yielded meaningless profiles, whereas, a lower number of factors deteriorated mass coverage and residuals.

Secondary aerosol. It was assumed that secondary aerosol contributed to all receptor samples. Thus five common secondary aerosol components were included (NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, NH_4Cl, and H_2SO_4) as constrained factors by freezing concentrations of the intrinsic compounds (NH_{4+}, NO_3^-, SO_4^{2-}, Cl^-) to their respective stoichiometric ratios. Test runs revealed better results by allowing the composition of these factors to vary between a $\pm$ 2% soft-locking interval for all intrinsic compounds (Fig 37).

Vehicles. The large contributions from coal combustion related sources, made it necessary to partially constrain the profile for vehicle emissions. This was done with the same literature data as in CMB, with the exception that for CMF an average composition of all available profiles was used with 2 times the standard deviation of the averaged profiles as soft-locking interval in the constraints (Fig. 37). Not all the profiles had PAH measured. In the test runs with constrained PAHs, especially coronene caused distortion and the best results were obtained without constraining the PAHs. The soft-locking procedure yielded a profile, which was still without significant concentrations of PAH, and which had a very small Euclidian distance to a diesel exhaust profile. Yet, the Euclidian distances to other vehicle exhaust profiles of mixed diesel and gasoline exhaust, were also small and although it is likely, that the major contribution to PM_{10} from vehicles comes from diesel exhaust as e.g. demonstrated with COMPREM analysis in Copenhagen (Wåhlin et al., 2006), the mere fact that the closest source profile to this CMF factor is diesel exhaust, does not exclude that gasoline vehicles also contribute to PM_{10} in Krakow. The latter source can be distinguished from diesel exhaust in the PAH fingerprint (Fujita et al., 2007), in particular 5-6 ring compounds. However, these compounds are emitted in high quantities by the coal combustion sources. It is therefore probable, that in the CMF computations gasoline exhaust may me masked by coal combustion.

Road salt. Road salt is a minor source and best results were obtained by constraining this profile to the composition of sea salt. Since it is not clear how similar the road salt is to pure sea salt, large soft-locking intervals were allowed for these all elements in this constrained profile (50%-200%). In practice, with this kind of constraint the mass ratios of the compounds that are known to be present in sea salt were allowed to vary in the iterations, but other compounds were blocked from

entering into the profile (Fig 37). The soft-locking procedure resulted in the enrichment of the profile with SO_4^{--}, Br^-, Ca^{++}, Mg^+, and K^+, which may not only be due to a different composition of the utilized road salt, but also may derive from road dust.

Combustion sources. Although, constraining a factorization model largely reduces the rotational ambiguity it will not remove it totally. Remaining factors can still have rotational ambiguity among themselves if they have a high degree of collinearity, which is very much the case of the Krakow data. The remaining major sources are likely to be combustion sources and thus, are all just a little different in their composition, The best results were obtained with four non-constrained factors together wit a partly constrained profile for *residential coal combustion* based on the source profile N10 (small stoves; Table 1). The constrained components were EC (hard-locked) as well as OC and PAHs (± 40% soft-locked) (OC and PAHs). This containment approach yielded a factor profile very similar to the original source profile, although somewhat enriched for ammonium nitrate and soil minerals (Si, Fe, Al, and Zn) and depleted for Cl^- and to some extent the 5-6 ring PAHs. The profiles that CMF estimated for the four non-constrained factors had Euclidian distances closest to two CMB source profiles for coal combustion: *Low efficiency boilers (coal) SteelworksPP,* and two CMB profiles for wood combustion: *Residential wood combustion in small stove (N5)* and *Residential wood combustion in small stove (N6).* However, as already discussed in the CMB chapter the existing collinearity between these profiles and other combustion profiles makes the source designation ambiguous. Thus, for the final listing of the source apportionment results in comparison with the CMB results (Table 2 and 3) individual SCEs are pooled into broader source categories without distinguishing between collinear sources. In the comparison of the non-constrained CMF factors with the designated CMB source profiles (Fig. 37) discrepancies are evident for SO_4^{--} and Cl^-, which are practically missing in the four CMF factors and for NO_3^-, NH_4^+, and Na^+ which are significantly underestimated. These elements are major contributors in the constrained factors for secondary aerosols and road salt and even though the overall model performance for all these elements is very good (R^2 >0.95; Fig. 38) it is clear that the used CMF approach with the relatively little data available for estimation of 12 sources does not manage to handle the primary contributions for these compounds. Two PAHs are also behaving strangely in Fig. 38, namely fluoranthene and pyrene (the ones that were indicated as

outliers by SOM). These are the most volatile compounds in the entire dataset, and it is possible that that in their case the fundamental assumption for receptor modelling of mass conservation is not fulfilled.
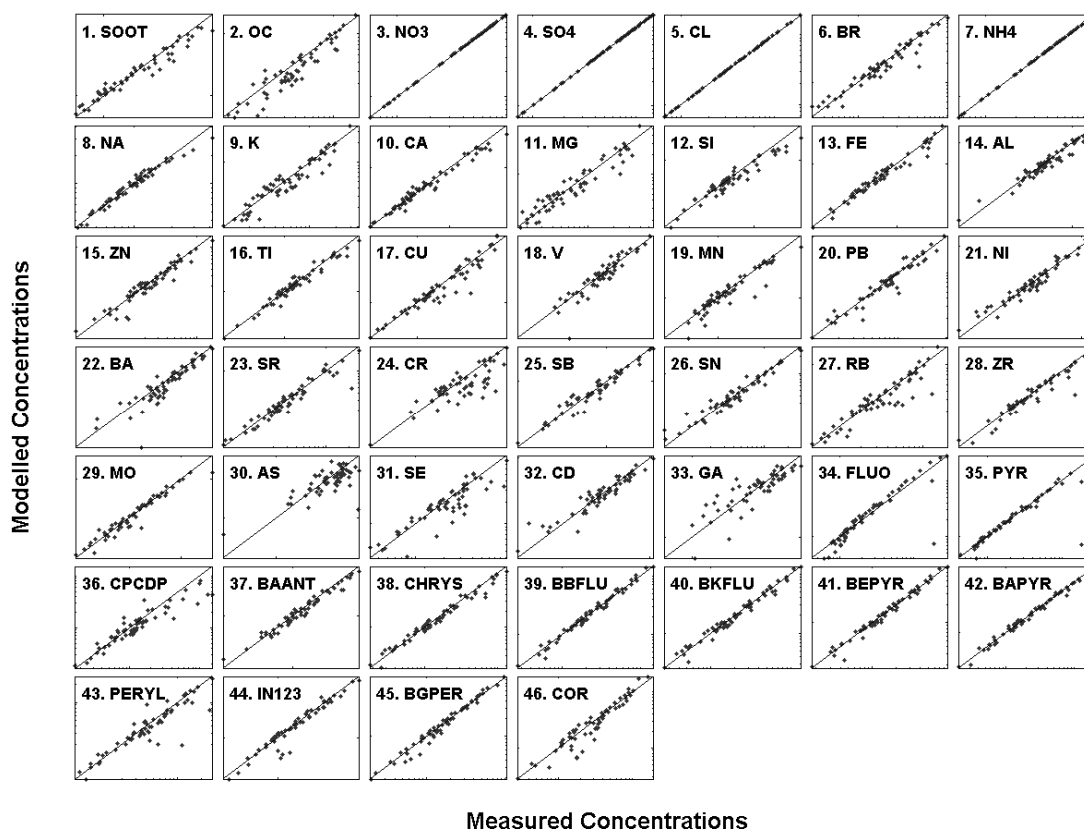
Figure 38 - CMF model performance for each receptor compound. All subplots have log-log axes.

The day-by-day variation of the SCEs for the five sites is plotted in Figs. 43 – 47. In the figures it appears that that on all days the contribution to the atmospheric pollution with PM_{10} is dominated by coal combustion in stoves and small boilers, with the exception of the few days in Zakopane, when wood combustion also plays and important role. This is in good accordance with what was found by CMB. It is also evident that the inorganic secondary aerosol contribution is significantly higher at the Krakow sites than in Zakopane, which strongly point to local sources for this secondary aerosol, such as industry, power generation and possibly road transport,
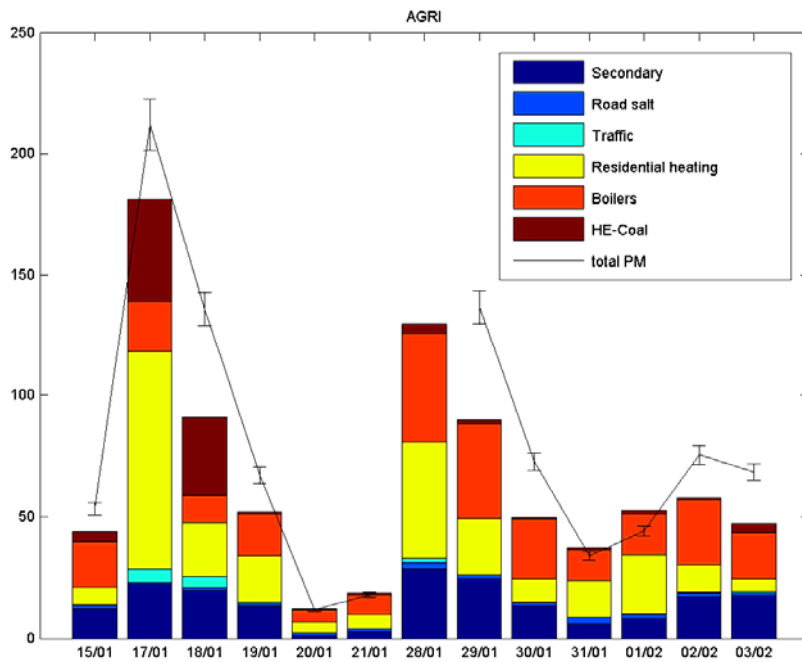
Figure 39 - Day by day CMF source contribution estimates compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error: black line) for the AGRI site.
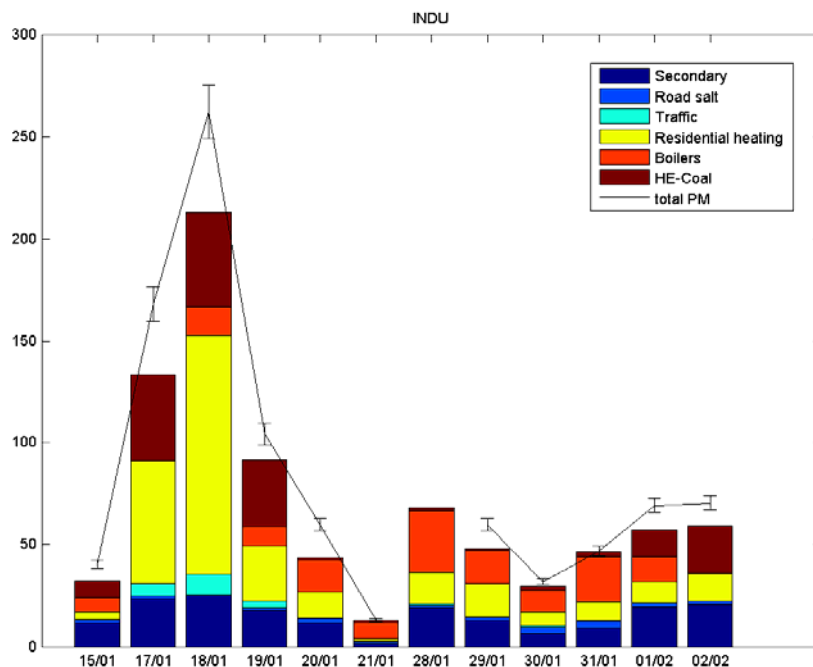
Figure 40 - Day by day CMF source contribution estimates compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error: black line) for the INDU site.
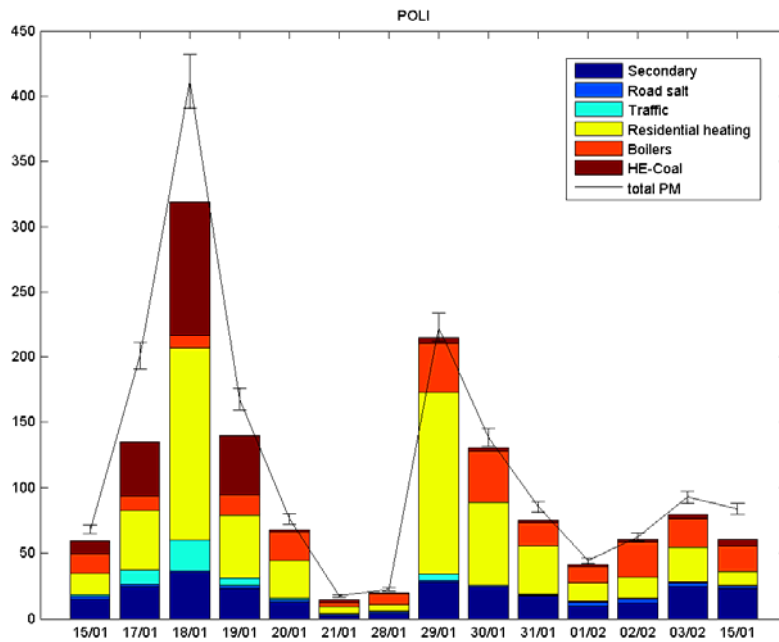
Figure 41 - Day by day CMF source contribution estimates compared to the gravimetrically determined PM$_{10}$ concentrations (± 5% standard error: black line) for the POLI site
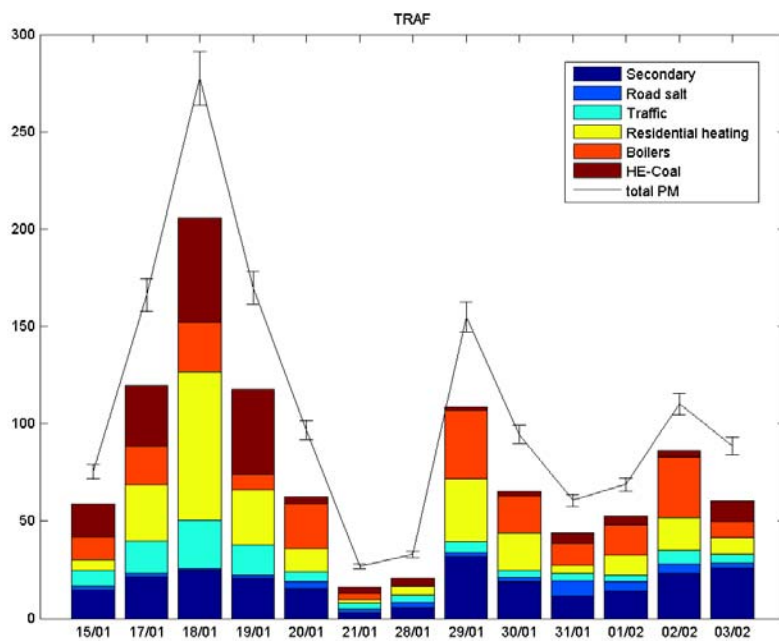
Figure 42 - Day by day CMF source contribution estimates compared to the gravimetrically determined PM$_{10}$ concentrations (± 5% standard error: black line) for the TRAFFI site.
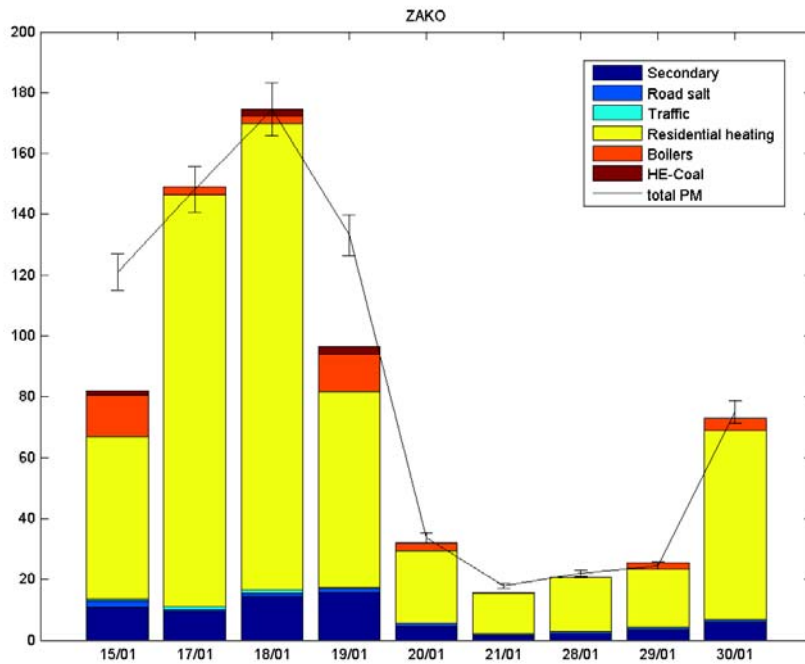
Figure 43 - Day by day CMF source contribution estimates compared to the gravimetrically determined PM_{10} concentrations (± 5% standard error: black line) for the ZAKO site.
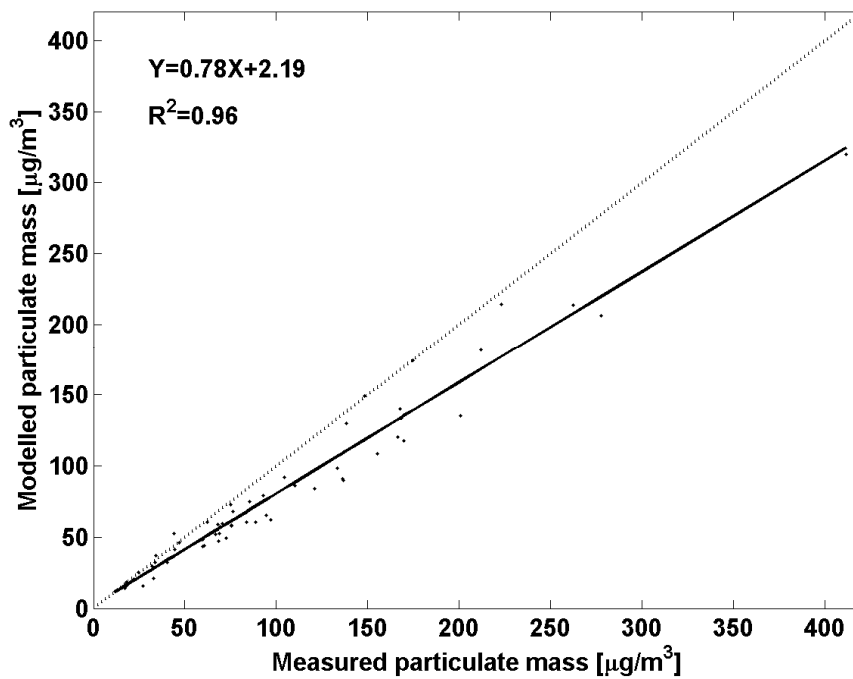
Fig. 44 – Plot of modeled vs. observed PM_{10} concentrations by CMF. Best fit (solid line) and one-to-one line (dashed line).

which all are major emitters of SO_2, NO_X or both as already discussed for the CMB modelling.

It is also evident in Figs. 30 – 34 that, as expected and also seen for CMB, the sources related to road transport (traffic and re-suspension) contributes most at the two sites which are situated near the city centre (TRAFFI > POLY) and are insignificant at other peripherical sites (AGRI, and INDU) and the remote site (ZAKO). Moreover, in good agreement with what would be expected, the sources from steelwork activities are only important at the INDU site, and home heating by combustion of wood is only important at the site (ZAKO) where it is easily available from the surrounding forested area.

The final source apportionment results for PM_{10} in Krakow and Zakopane are shown in Table 4 for CMB and CMF. Generally, good mass coverage and predictability (R^2) are observed for both models together with a very good mutual agreement for the estimated SCEs. Both models compute the highest primary contributions to the PM_{10} pollution in Krakow and in particular Zakopane from *Home heating* with some differences in the breakdown of the SCEs into combustion of coal, and wood/coke/oil due to the discussed collinearity of these sources. In Krakow the SCEs from this source category (mainly coal combustion) correspond to 30-50% and in Zakopane (mainly wood and coal) to 80-90%, which is in accordance with high number of small stoves in Krakow and Zakopane (> 20.000; Turzanski and Pauli, 1999). The second highest primary contribution was estimated by both models to come from *industrial power generation (coal)*, with SCEs that correspond to 30-40% in Krakow and 5-10% in Zakopane (mainly wood and coal) to 80-90%. Within this category combustion of coal in low efficiency boilers was the major source. When the PM emission rates from the HE-coal combustion sources are taken into consideration (Table 1) this finding may seem surprising. However, the HE-coal combustion sources are all emitting through very high stacks, which are constructed to assure minimum fallouts in the Krakow area and during the measurement campaigns the mixed boundary layer (MBL) was often so shallow, that the stack emissions occur above the MBL (Marelli et al., 2008). *Traffic and re-suspension* was estimated by both models to lowest primary source with SCEs that correspond to 8-10% in Krakow and less than 2% in Zakopane. At first thought this finding may appear surprising for a metropolitan area. However, it should be seen in the light of large intensities of the

Table 4 – Source Contribution Estimates (± 95% confidence interval) for PM$_{10}$ in Krakow and Zakopane (units µg/m^3).

		Krakow		Zakopane	
		CMB	CMF	CMB	CMF
Home heating	Residential coal combustion in small stoves and boilers	*38 ± 11	11 ± 5	43 ± 40	16 ± 16
	Residential heating (wood, coke, oil)		13 ± 6	46 ± 20	58 ± 31
Industrial power generation (coal)	LE-Boilers (coal)	16 ± 3	17 ± 3	5.4 ± 3.5	5.5 ± 4.4
	HE-Coal combustion	3.5 ± 1.2	13 ± 5	Not significant	1.1 ± 0.9
Secondary aerosol (inorganics)	Sulfates, nitrates and chlorides	16 ± 2	16 ± 2	7.7 ± 3.7	9.4 ± 4.4
Traffic and re-suspension	Vehicles	5.8 ± 2.0	3.7 ± 1.5	Not significant	0.5 ± 0.4
	Re-suspension (incl. road salt)	2.1 ± 0.3	2.0 ± 0.3	Not significant	1.2 ± 0.4
	Mass coverage	82 %	84 %	91 %	82 %
	R^2	0.94	0.96	0.89	0.89

* In a large number of CMB runs, profiles for residential heating (coal , wood, coke, oil) resulted collinear and were estimated as coal.

coal combustion sources in the area. The SCE of 3.7 - 5.8 $\mu g/m^3$ obtained for Krakow is in the same order of magnitude as road traffic SCEs in many European metropolitan areas such as e.g. Zurich (Gehrig et al., 2001). The contribution from *secondary aerosols* was estimated by both models to contribute with 20-21% in Krakow and less than 8-10% in Zakopane. Secondary aerosols are formed in the air by chemical transformations of gaseous pollutants as these transported to the receptor site, and as such are much better dealt with by source-oriented chemical transport models (e.g. Pekney et al., 2006; Kleeman et al., 2007). Receptor modelling cannot attribute sources for the proportion of PM made up by secondary aerosol, and modelers are limited to merely interpret the source factors which contain high loadings of SO_4^{--}, NO_3^-, and NH_4^+ as 'secondary aerosol, even though in some cases this may been useful in the estimate of contributions from secondary organic carbon (Yuan et al., 2006). The SCE of 16 $\mu g/m^3$ inorganic secondary aerosol is high compared most other European data (Putaud et al., 2004; Querol et al., 2007), and strongly indicates that a significant proportion of this source is local/regional rather than remote. This may derive from all sources and the applied receptor models cannot apportion this. However, based on the very high emission factors for SO_2 and NO_X measured in the present study for industrial power generation (Table 1) it is likely that this source category is a major contributor to secondary aerosols. Only the inorganic part of secondary aerosol could be quantified by CMB and the used CMF approach. It is well-known, that organic carbon emitted in the gas-phase at the high source temperatures may condense onto existing PM in the atmosphere, and thus, a part of the PM mass attributed to primary sources in the present study, may actually derive as secondary aerosol. OC is one of the few PM_{10} components that did not have such as good model performance (Fig. 37), which may very well be due to a role played by secondary organic aerosol that cannot be handled with the present CMB and CMF approach. The use of aerosol mass spectrometry as demonstrated by the group of Prevot (Lanz et al., 2007, 2008) in future source apportionment studies of areas dominated by coal combustion may solve the ambiguity in the OC apportionment.

3.2.4. Regulated air pollutants. Receptor models can produce source contribution estimates not only for the PM_{10} mass, but also for the individual chemical compounds. Whereas, the SCEs for the PM_{10} mass are obtained in an iterative process, which aim to minimize the overall difference (sum of least squares) between measured and modeled concentrations of all the included receptor compounds, this does not imply, that the solutions are optimal for each individual compound. Thus the value of source apportionment from single compounds depends very much on the model performance for these compounds. CMF produced the best performance for the regulated compounds, and was therefore preferred over CMB for single compound source apportionment.

As seen in fig. 37, CMF performed very well for B(a)P (R=0.99 p=0.000). The single compound source apportionment for B(a)P (Fig. 45) revealed, that for all receptor sites, residential heating is the dominant source, which together with (low efficiency boilers) contribute with more than 90% for this toxic air pollutant. The remaining 10% derive mainly from High efficiency coal combustion (e.g. power generators). The contribution from road transport (+ re-suspension) is only significant at the traffic site, and even here it contributes with less than 3%.
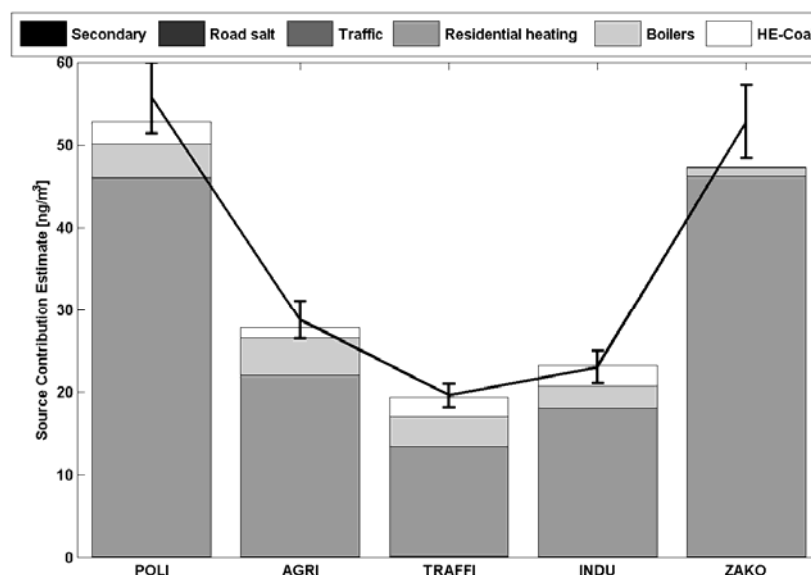
Figure 45 - SCE for benzo(a)pyrene calculated by the CMF model for each site. The black line represents the measured average concentration (±SD).

CMF performed well for Pb (R=0.96 p=0.000) and Cd (R=0.96 p=0.000). However, the performance for Ni (R=0.82 p=0.000) and As (R=0.36 p=0.000) was not as good as for the other regulated compounds, which may indicate that sources for these two trace compounds may not have been detected by the CMF model. The single compound source apportionment for these compounds is shown for each site in Fig. 46-49.
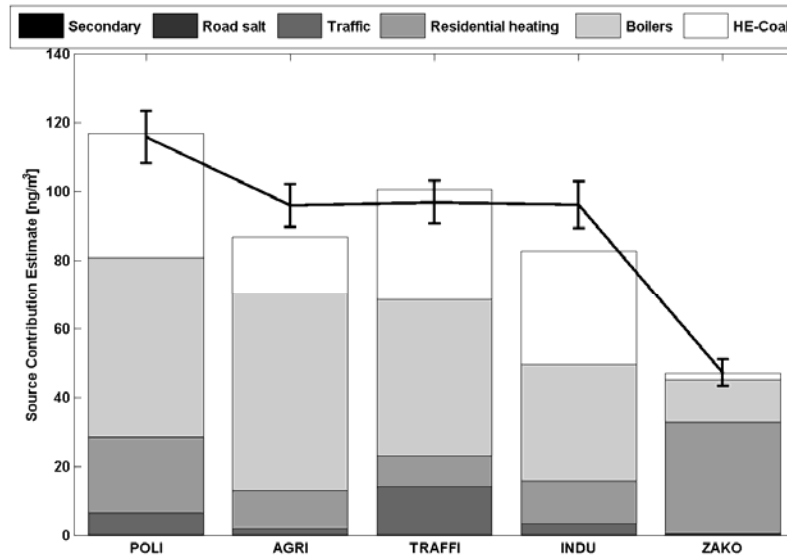
Figure 46 - SCE for Pb calculated by the CMF model for each site. The black line represents the measured average concentration (±SD).
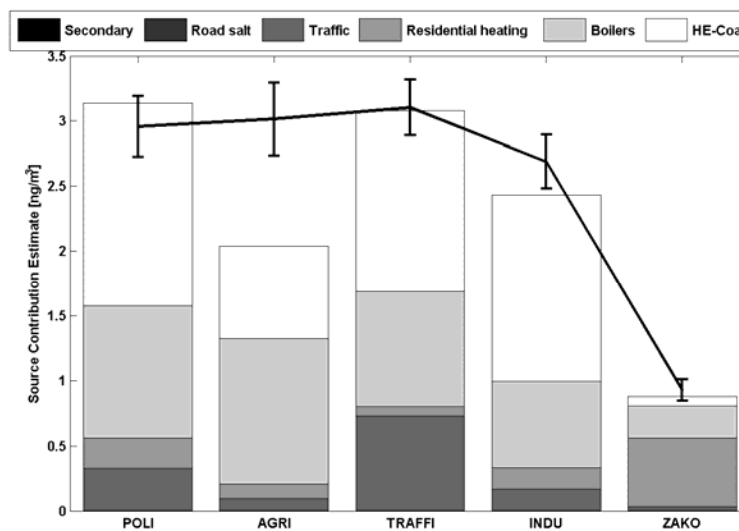
Figure 47 - SCE for Ni calculated by the CMF model for each site. The black line represents the measured average concentration (±SD).
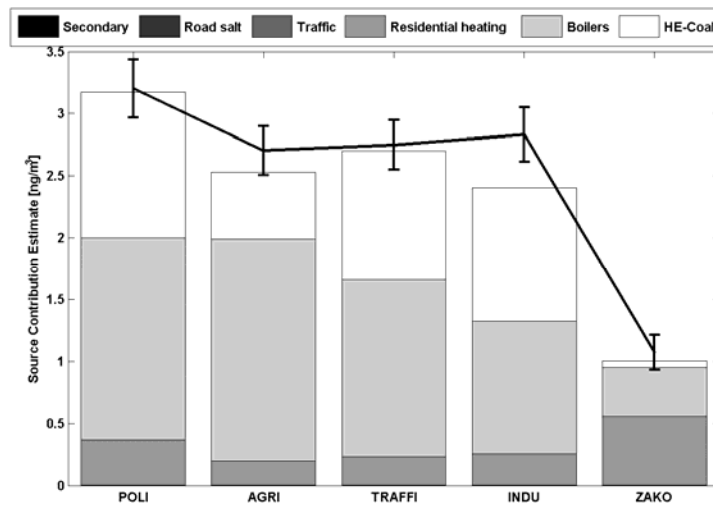
Figure 48 - SCE for Cd calculated by the CMF model for each site. The black line represents the measured average concentration (±SD).
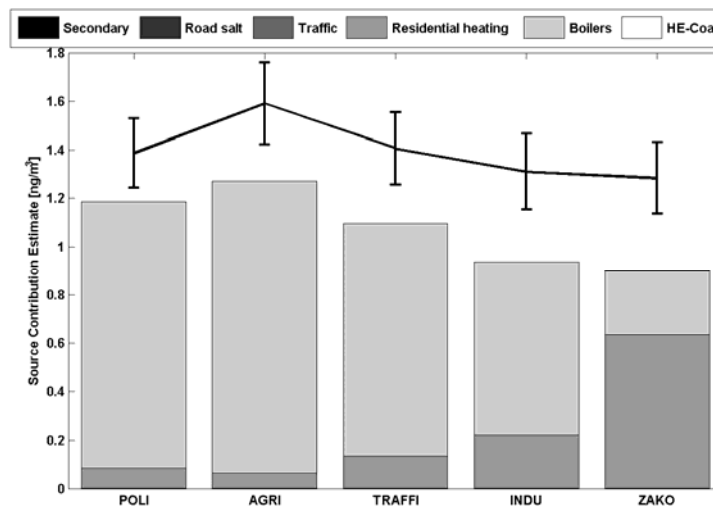
Figure 49 - SCE for As calculated by the CMF model for each site. The black line represents the measured average concentration (±SD).

A very similar trend in the SCEs at the 5 five different receptor sites is observed for Pb, Ni, and Cd for which HE-Coal combustion and Boilers (coal) are the main sources in Krakow and Boilers (coal) and residential heating are the main sources in Zakopane. For these Pb and Ni (an exclusively for these two compounds) Traffic played an import role only at the sites TRAFFI and POLI.

A different trend was seen for As, which derives mainly from boilers in Krakow and residential heating in Zakopane.

TABLE 5. Source apportionment for regulated air pollutants in PM$_{10}$: Average SCE (ng/m^3) of all five receptor sites ± (95% confidence interval).

	B(a)P	Pb	Cd	Ni	As
Home heating (coal)	28±4	17±2	0.3±0.04	0.2±0.03	0.20±0.03
LE-Boilers (coal)	3.4±0.4	43±5	1.3±0.1	0.8±0.1	0.9±0.1
HE-Coal combustion	1.9±0.4	25±5	0.8±0.2	1.1±0.2	Not significant
Traffic and re-suspension	0.04±0.01	5.6±1.0	Not significant	0.3±0.1	Not significant
Mass coverage	99%	97%	100%	96%	85%
R^2	0.98	0.92	0.92	0.67	0.32

The source contributions for Pb, Cd, Ni, and As are compared in Table 5 for the four main source categories as average of all five sites. It is seen that these compounds derive mainly from the industrial sources boilers and high efficiency coal combustion (e.g. power generation). Although none of the above mentioned heavy metals at present are found at critical levels compared to the EU air quality limits, a future shift in energy strategy for home heating from low efficiency coal combustion in small stoves and boilers to power generators, needs careful monitoring for heavy metals.

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The Krakow receptor modeling inter-comparison exercise:

Supporting information

APPENDICES

Appendix 1. The emission rates for each individual source.

Appendix 2. PM sampling.

Appendix 3. Chemical analysis.

Appendix 4. Database for the receptor modeling exercise.

Appendix 5. Quality control of the dataset.

Appendix 6. PCA and apportionment analysis with data for metals as oxides.

Appendix 7. PCA and apportionment analysis with data for metals as elements.

Appendix 8. Back trajectories for Krakow and Zakopane.

Appendix 1. Emission rates for each individual source

Source	Boilers	Sample identification	gas flow m³/h	PM - on the filter g	PM - raw flue gases g/m³	PM - Emission rate (g/h)	PM - standard conditions g/m³	SO2 - raw flue gases mg/m³	SO2 - Emission rate (kg/h)	SO2 - standard conditions mg/m³	CO - raw flue gases mg/m³	CO - Emission rate (kg/h)	CO - standard conditions mg/m³	NOx - raw flue gases mg/m³	NOx - Emission rate (kg/h)	NOx - standard conditions mg/m³	sulphur in fuel %	coking gas m3/h	coal Kg/h	sawdust kg/h	wood kg/h
Coal and gas burning Public Power.	Boilers > 50 MW	12/Q/1	1016582	0.02	0.004	3761	0.0158	164.0	167	705.3				116.3	118	500.1	0.59	9000			
Coal burning	Boilers > 50 MW	12/Q/2	1016582	0.012	0.001	1423	0.0061	204.9	208	879.9				125.1	127	536.9	0.59	9000			
Coal and gas burning	Boilers > 50 MW	14/Q/2	327024	0.04	0.004	1275	0.0111	254.6	83	730.3				248.7	81	713.4	0.67	2000			
Coal burning	Boilers > 50 MW	20/Q/2	476845	0.017	0.003	1526	0.006	815.1	389	1527.9	8.5	4.1	15.9	280.1	134	525.1	0.56				
Coal burning	Boilers > 50 MW	20/Q/2	477491	0.025	0.005	2483	0.0098	1139	544	2138.4	8.5	4.1	15.9	282.3	135	529.8	0.56				
Coal burning	Boilers > 50 MW	21/Q/1	476845	0.039	0.008	3862	0.0152	1141	544	2138.4	8.5	4.1	15.9	282.7	135	529.8	0.56				
Coal burning	Boilers < 5 MW	3/Q/1	6199	0.046	0.019	120	0.1569	89.9	1	727.8	19.6	0.1	158.7	57.2	0	461.5	0.42		20		
Coal burning	Boilers < 5 MW	7/Q/1	10289	0.105	0.03	310	0.1826	115	1	697.1	344.2	3.5	2086.1	64.7	1	392.3	0.79				
Coal burning	Boilers < 5 MW	7/Q/2	10289	0.15	0.043	439	0.2588	150.4	2	911.6	405.3	4.2	2456.3	64.7	1	392.3	0.79				
Coal burning	Boilers < 5 MW	4/Q/1	17631	0.062	0.023	398	0.084	386.6	7	1439.3	272.2	4.8	1013.2	157.2	3	585.2	0.57				
Coal burning	Boilers < 5 MW	4/Q/2	17657	0.073	0.026	466	0.0982	252.5	4	941.1	179.4	3.2	668.5	114.4	2	426.5	0.57				
residential plant, coal burning	Boilers < 50 KW	1/Q/1	30	0.052	0.093	3	0.4654	359.6	0	1808.9	1499	0.0	7540.5	114	0	573.6	1.39		1.7		
residential plant, coal burning	stove < 50 KW	2/Q/1	166	0.125	0.404	67	2.9183	68.2	0	492.8	749.9	0.1	5423.9	107	0	773.9	0.61		0.5		
residential plant, coal burning	stove < 50 KW	10/Q/1	176	0.328	0.06	11	0.3615	11.8	0	71.5	845.1	0.1	5113.1	72.3	0	437.7	0.42		2.3		
residential plant, wood burning	Boiler < 50 KW	5/Q/1	671	0.119	0.049	33	0.45		0		316.9	0.2	28930.2	29.1	0	265.9	0.12				3
residential plant, wood burning	Fire place < 50 KW	6/Q/1	40	0.119	0.029	1	0.1115		0		1087	0.0	4176.7	46.4	0	178.3	0.05				1.5
residential plant, wood burning	stove < 50 KW	9/Q/1	174	0.087	0.032	6	0.1767		0		944.3	0.2	5170.4	23.2	0	127.2	0.03				3.3
~~Heavy oil burning~~	~~boiler~~	~~8/Q/1~~	~~11269~~	~~0.025~~	~~0.009~~	~~103~~	~~0.0236~~	~~288.2~~	~~3~~	~~744.6~~		~~0.0~~		~~133.1~~	~~1~~	~~343.9~~	~~0.66~~				
Heavy oil burning	boiler	8/Q/2	11269	0.048	0.019	215	0.0495	334.7	4	864.7		0.0		155.3	2	401.2	0.66				
						159			4			0			2						
Iron ore sintering plant		11/Q/1	424976	0.031	0.022	9349	0.0389		0		7904	3359	8655	168.3	72	297.1					
Iron ore sintering plant		11/Q/2	424976	0.071	0.031	13089	0.0544		0		4904	2084	8655	168.3	72	297.1					
Reheating furnace steel and iron		17/Q/1	155486	0.117	0.008	1291	(?) 0.018	15.6	2	34.3	5.7	0.9	12.5	7.5	1	16.4		22000			
Reheating furnace steel and iron		17/Q/2	155486	0.142	0.01	1586	0.0226	14.3	2	31.5	6.8	1.1	15	13	2	28.7		22000			
Cement production		19/Q/1	109893	0.128	0.042	4561	0.0752		0		110.4	12.1	200	324.5	36	588.2	0.67				
Cement production		19/Q/2	100417	0.165	0.05	5061	0.0768		0		136.2	13.7	207.5	288.1	29	438.7	0.67				
Production of fireproof materials		18/Q/1	27643	0.571	0.096	2640	0.1531		0		1688	46.7	2707.5	33.2	1	53.3					
Production of fireproof materials		18/Q/2	27620	0.908	0.066	1812	0.1533		0		1364	37.7	2185	40.9	1	65.6					
						2226			0			42			1						
Balst furnace		13/Q/1	1139383	0.031	0.004	5013	0.00052		0		47.3	53.9	56.5	3.4	4	4					
Balst furnace		13/Q/2	1140405	0.048	0.01	10834	0.0115		0		47.3	53.9	56.5	3.3	4	4					
Basic oxigen furnace steel plant		15/Q/1	247710	0.049	0.007	1684	0.0101		0		18.5	4.6	27.5	8.3	2	12.3					
Coke oven		16/Q/1	0.33 m/s	0.009	0.35	1015			0			4.6			2						
Basic oxigen furnace steel plant		15/Q/2	247519	0.009	0.001	347	0.0021		0		18.5	4.6	27.5	8.3	2	12.3					

Appendix 2. PM sampling.

A total of 178 ambient air samples, 54 source samples and 22 indoor samples were collected for the present study. In order to facilitate the chemical analysis of organic and inorganic compounds two kinds of filter material was used in parallel for PM sampling. *i.e.* quartz and mixed nitrocellulose esters. For ambient air measurements, PM_{10} was sampled by means of low-volume samplers (24 h, 2.3 m^3/h) and determined gravimetrically according to the official European Commission method as described in details elsewhere (Marelli et al, 2008). In brief, the sampling filters (47 mm, 5 μm,) were coded and conditioned at controlled humidity (50% RH) and temperature (25 ^{o}C) for 3-5 days (ΔM< 0.00001 g). After final weighing, the filters were loaded into the multiple filter holders, and kept at controlled humidity (50% RH) and temperature (25 ^{o}C) until transportation to the sites and loading into the PM_{10} samplers. After sampling, the filters were recollected and conditioned at controlled humidity (50% RH) and temperature (25 ^{o}C) for 3-5 days before weighing. Finally the filters were stored at -20 ^{o}C until chemical analysis.

For emission source measurements, PM was sampled *iso*-kinetically in the emission stacks following international standards (ISO-9096). Flue gas sampling was performed by the filter-cooler method (approx 120 ^{o}C) and conducted with an automatic, adjusting *iso*-kinetical sampling system. Source sampling and characterization was carried out in duplicate or triplicate at consecutive days during normal operation conditions in order to ensure representative samples.

The sampling of PM_{10} outdoor and indoor was conducted over a three-week period from January 16th to February 8th, 2005 – interrupted for six days (24-28/1) due to heavy snowfall. The indoor sampling was part of a dedicated pilot scale epidemiological/indoor air quality study published, elsewhere (Jimenez and Niedzialek, 2006; Marelli et al., 2008), which included more than 300 apartments distributed over Krakow. In 20 of the apartments (10 heated by coal combustion in small stoves, 10 with district heating) PM_{10} was sampled in parallel in the outdoor air on the apartment balconies. In order to apportion pollution sources for indoor air, four apartments were selected close to the ambient air measurement sites in Krakow (Fig. 1) and the filters collected on three consecutive days were subjected to the full chemical analysis and receptor modeling.

Appendix 3. Chemical analysis

Polyaromatic compounds. The principal stages in the measurement of the particulate-associated polyaromatic compounds (PAC) are sampling, extraction, clean-up and analysis. The method used in this work is based on the EPA method TO13 and ISO/DIN 12844 and has been developed in our laboratories (Astorga et al., 2003). In brief, the PAC in the PM sampled on the quartz filters were extracted in an automatic Soxhlet extractor for 2 h with dichloromethane. The extracts were evaporated to 500 μL and solvent exchanged to hexane using a mild stream of nitrogen and a mild heating (30 $^{\circ}$C). For source samples, the extract was transferred to a solid phase extraction cartridge (PAH-soil™, Supelco) for clean-up. The bulk of non-polar species was removed by elution with hexane and the PAH were eluted with hexane/dichloromethane (40:60) and the azaarenes by acetonitrile (0.1% triethylamine). This clean-up step was not necessary for ambient air samples. After evaporation the samples were collected in toluene containing d_{12}-chrysene as internal standard and analyzed by gas chromatography-mass spectrometry (GC-MS) using electron ionization (for operational details see Farfaletti et al. 2005). The analytical method has been validated by a successful participation in an inter-laboratory comparison using the reference material (NIST SRM 1650 soot) and PM from vehicle exhaust (Larsen et al., 2000). The method has been set up to analyze 39 target compounds (21 azaarenes and 18 PAH). However, due to a combination of relatively high vapor pressures and low concentrations some compounds were excluded from this receptor modeling study. The final set of PACs was: Fluoranthene (Fl), pyrene (P), dimethylphenanthrene (diMPhe), Cyclopenta(cd)pyrene (Cyp(c,d)P), benzo[a]anthracene (B(a)A), chrysene (Chr), benzo[b]fluoranthene (B(b)Fl), benzo[k]fluoranthene (B(k)Fl), benzo[e]pyrene (B(e)P) benzo[a]pyrene (B(a)P), Perylene (Per), indeno[1,2,3-cd]pyrene (Ind(123cd)P), dibenzo[a,h]anthracene (diB(ah)A), benzo[ghi]perylene (B(ghi)Per), benzo[c]acridine (B(c)Acr), Phenanthridine (PhenAnt), Coronene (Cor), dibenzo[a,h]acridine (diB(ah)Acr)).

The analytical recoveries were in the range of 80-110% for the included PACs, the detection limits in the range of 0.01-0.03 μg/g, and the uncertainty of repeated analysis (six individual punches from one filter) in the order of 6-8%. The corresponding detection limits expressed as ng/m^3 were all below 0.5, which was sufficient to analyze all elements in all collected samples in this study.

Trace elements. A total of 27 trace elements were analyzed by the use of proton induced x-ray emission (PIXE) according to the ISO 17025 standard (DANAK, Danish Accreditation no. 411). For that purpose, a circular piece (2 cm^2) was punched from the mixed nitrocellulose filter of each sample and the rest was used for cation and anion analysis. X-ray sample absorption correction was necessary for the lighter elements due to the high mass concentration of PM on the filters. A calculation of the absolute standard deviation for each analyzed element was incorporated in the fit of the x-ray spectrum which resulted in the following typical detection limits (expressed as µg per sample): Al(1.9), Ti(0.02), Zn(0.05), Zr(0.005), Si(2,3), V(0.017), Ga(0.007), Mo(0.006), P(1.8), Cr(0.017), As(0.006), Cd(0.03), S(0.8), Mn(0.012), Se(0.002), Sn(0.04), Cl(0.6), Fe(0.14), Br(0.007), Sb(0.06), K(0.3), Ni(0.012), Rb(0.004), Ba(0.2), Ca(0.6), Cu(0.02), Sr(0.004), Pb(0.014). These values are obtained as the maximum of the average standard deviation of the values in a series of blanks and the standard deviation of the blank values. The corresponding detection limits expressed as ng/m^3 are all below 0.2, which was sufficient to analyze all elements in all collected samples in this study.

The uncertainties depend on the thickness of the filter material (due to the continuous spectral background), its purity and the matrix (interferences from neighbor spectral peaks). The uncertainty of the integrated proton charge and fluctuations of the detector solid angle give rise to an additional standard deviation of 5%, which is geometrically added to the spectral uncertainty. The calibration is permanent (but is regularly controlled), so the calibration uncertainty has no influence on the precision. The calibration uncertainty was 7% in average for all elements, but this uncertainty was not added to the uncertainty of the PIXE results. The resulting overall method accuracy (for measurement distant from the detection limit) was on average 9% for all elements (*i.e.* the geometric sum of 5% and 7%).

Cations and anions. Ion chromatography (IC) was used for the analysis of the anions NO_3^-, SO_4^{2-}, and Cl^-. Automated colorimetric analysis was used NH_4^+, and atomic absorption spectrophotometric analysis for Na^+, K^+, and Mg^{2+}. All these compounds were analyzed according to the ISO 17025 standard (DANAK, Danish Accreditation no. 411) except for Na^+ and Mg^{2+}, which nevertheless were measured using similar standard procedures and quality control as for the other ion analyses.

The detection limits (expressed as µg per sample) and the method uncertainty in repeated analysis was the following: Na^+ (0.5, 7%); Mg^{2+} (0.3, 7%); NH_4^+ (0.4, 7%); NO_3^- (4.7, 5%); SO_4^{2-} (2.4, 5%); Cl^- (3, 7%). The relatively high concentration of these cations and

anions in PM from ambient samples and emission sources posed no problems for the method detection limits and it was possible to analyze all elements in all collected samples in this study.

Elementary and organic carbon (EC and OC). The concentrations of elementary carbon (EC) and organic carbon (OC) in PM from ambient air and emission sources were determined by thermal-optical analysis using a dedicated low-mass PM analyzer (Horiba MEXA 1370PM), which in addition gives quantitative information on the concentration of total sulfur. Small punches (0.2-0.4 cm^2) of the quartz filters containing the PM samples were placed in furnace, slowly heated to 980 ºC in a N$_2$ gas flow. Hereby organic carbon and sulfur compounds are vaporized and after conversion to their gaseous oxides they are quantified as CO$_2$ and SO$_2$, respectively. In a second step oxygen was flowed through the hot furnace, and elementary carbon was oxidized to CO$_2$ and quantified as such. The authors acknowledge that this method does not make any attempt to correct for the inevitable generation of carbon char produced by the pyrolytic conversion of organics into elemental carbon, which may resulting in a an EC overestimation of up to 30% (Min-Suk et al., 2004). However results obtained in preliminary tests with other instruments with options for pyrolysis compensation by optical methods, demonstrated great technical difficulties with the very dark filters (black as coal) encountered in this Krakow study. Due to the advantage of obtaining additional quantitative data on sulfur, the described method was preferred. The choice was also affected by the fact that the results of the EC/OC analysis were designated for receptor modeling source apportionment, by which it is expected that any systematic error in the EC/OC ratio is evened out by the use of the same methodology for chemical fingerprints of sources and receptors. The uncertainty of the method was estimated by duplicate analysis (individual punches) of 10 % of all collected filters and amounted to an average of 8.0% for EC, 5.1% for OC and 6.2% for sulfur. The lower detection limit of this method was around 0.2 µg/cm2 for both OC and EC, which was more than sufficient to analyze all samples in the present project.

Uncertainty estimations. The background data for evaluating the analytical uncertainty on the data is presented in Fig. AP3.1-AP3.5
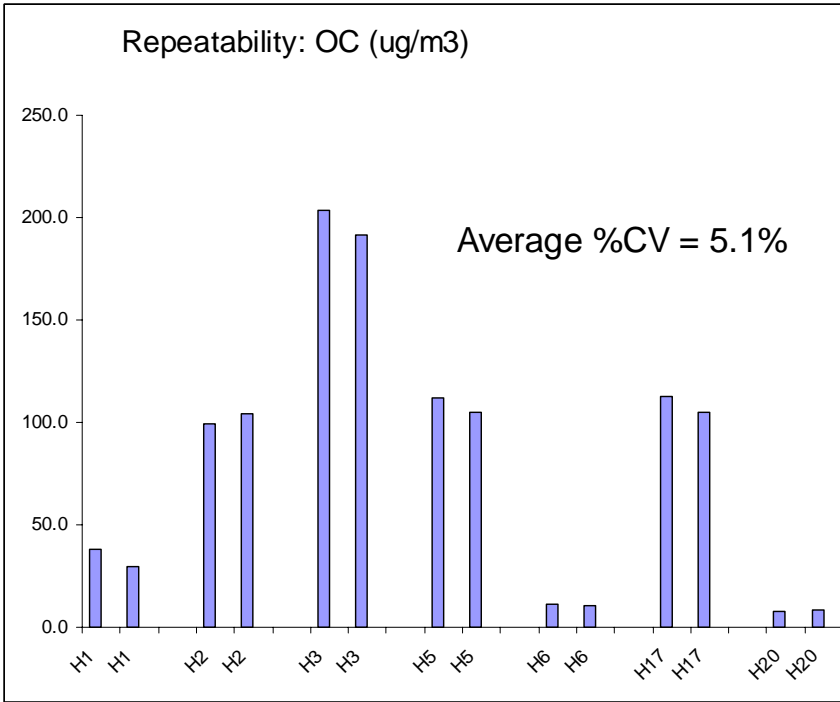
Figure AP3.1 Estimation of the analytical uncertainty for organic carbon (OC).
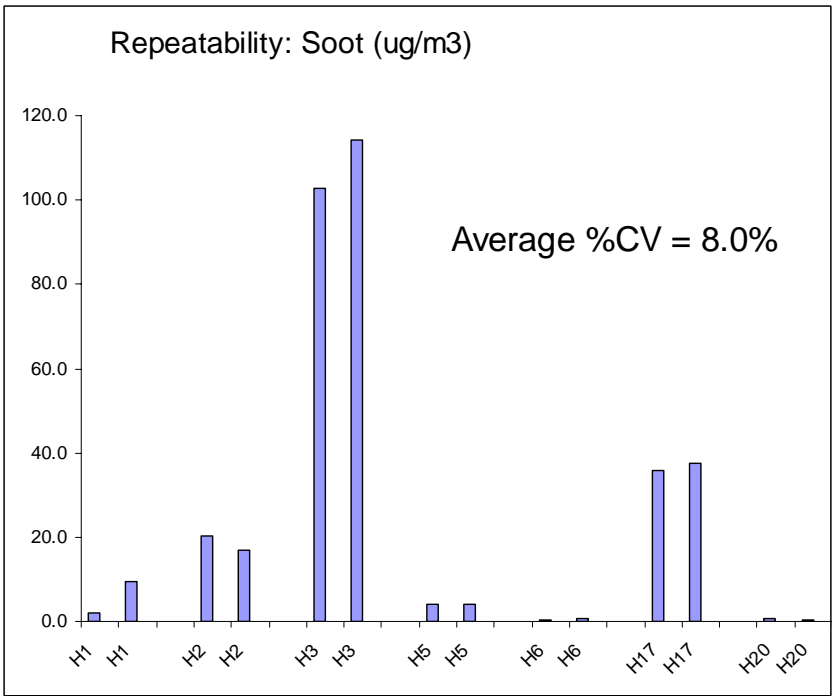
Figure AP3.2 Estimation of the analytical uncertainty for elementary carbon (EC).
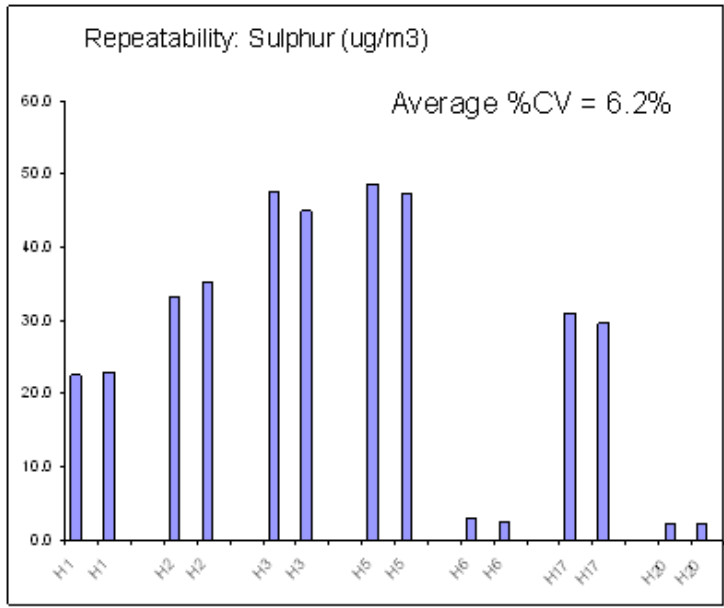
Figure AP3.3 Estimation of the analytical uncertainty for sulfur (S).
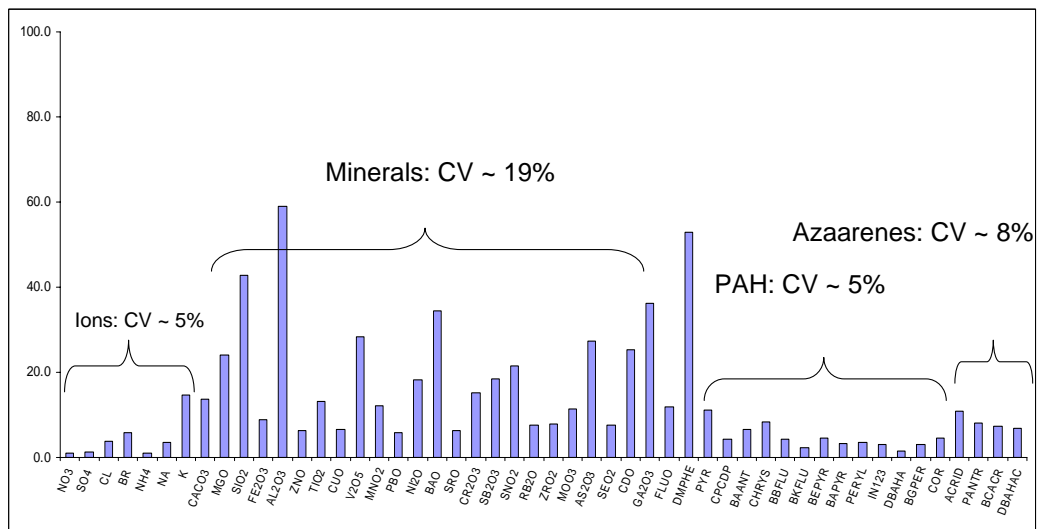
Figure AP3. The uncertainty for the receptor compounds

Appendix 4. Database for the receptor modeling exercise

All ambient concentrations are in ng/m3
The concentrations of PAH and OC/EC are refered to the PM(10 or TSP) mass on the Quartz filters
The concentrations of ions and metals are refered to the PM10 mass on the Nitrocellulose filters
Station 1   Station 2
POLI   AGRI   2
PMNIT means PM10 from nitrocel filters
PM means PM(10 or TSP) from quartz filters
NO3, CL and SO4 means nitrate, chloride and sulfate from IC measurements
an U in front of the name denotes that the column contains the uncertaity of the result

	DATE	PMNIT	UPMNIT	PM	UPM	OC	UOC	SOOT	USOOT	NO3	UNO3
AGRI	1/15/2005	51596	2580	54912	2746	29073	3238	893	71	4072	42
AGRI	1/17/2005	200091	10005	223733	11187	108964	12137	36693	2918	7179	72
AGRI	1/18/2005	136025	6801	219154	10958	94128	10484	13991	1113	6270	63
AGRI	1/19/2005	66346	3317	67502	3375	42849	4773	1356	108	4786	49
AGRI	1/20/2005	11250	563	12122	606	8112	904	546	43	723	11
AGRI	1/21/2005	17148	857	18632	932	10252	1142	373	30	1172	15
AGRI	1/28/2005	212913	10646							7489	75
AGRI	1/29/2005	137659	6883	135487	6774	67158	7480	18108	1440	7603	77
AGRI	1/30/2005	71973	3599	73357	3668	46300	5157	2149	171	5824	59
AGRI	1/31/2005	33122	1656	34936	1747	14375	1601	3370	268	3023	31
AGRI	2/1/2005	43557	2178	44775	2239	19193	2138	4615	367	3766	39
AGRI	2/2/2005	73788	3689	76993	3850	36875	4107	10690	850	7636	77
AGRI	2/3/2005	64519	3226	72046	3602	38494	4288	1102	88	5383	55
AGRI	2/4/2005	46997	2350	55781	2789	19407	2162	2667	212	3081	32
INDU	1/15/2005	45067	2253	35849	1792	17715	1973	691	55	4371	45
INDU	1/16/2005	188385	9419	148278	7414	56817	6329	19460	1547	7843	79
INDU	1/17/2005	279583	13979	244988	12249	85535	9527	55630	4424	6914	70
INDU	1/18/2005	111615	5581	96848	4842	40520	4513	7658	609	6610	67
INDU	1/19/2005	62886	3144	56432	2822	32280	3595	1006	80	4761	48
INDU	1/20/2005	13425	671	12332	617	8636	962	289	23	854	12
INDU	1/21/2005	17972	899							1218	21
INDU	1/28/2005	256575	12829							8521	86
INDU	1/29/2005	90200	4510			40956	4562	3756	299	6139	62
INDU	1/30/2005	64519	3226	54923	2746	34328	3824	981	78	6008	61
INDU	1/31/2005	35753	1788	28060	1403	17400	1938	691	55	3517	36
INDU	2/1/2005	51440	2572	42148	2107	17546	1954	691	55	4871	50
INDU	2/2/2005	97608	4880							9817	102
INDU	2/3/2005	79129	3956	59067	2953	26306	2930	957	76	6654	67
INDU	2/4/2005	73476	3674	67076	3354	22914	2552	1418	113	5466	55
POLI	1/15/2005	65016	3251	71017	3551	33799	3765	5620	447	5015	51
POLI	1/16/2005	186751	9338	215008	10750	101921	11352	18632	1482	6310	64
POLI	1/17/2005	340565	17028	482455	24123	197859	22038	108583	8635	8183	82
POLI	1/18/2005	143920	7196	191123	9556	108352	12069	4090	325	6737	68
POLI	1/19/2005	71338	3567	80962	4048	48054	5352	2204	175	4602	47
POLI	1/20/2005	15424	771	19260	963	10842	1208	484	39	750	12
POLI	1/21/2005	22232	1112	22428	1121	12517	1394	367	29	1526	18
POLI	1/28/2005	222837	11142	337426	16871	190198	21185	61500	4890	7779	78
POLI	1/29/2005	136751	6838	140022	7001	73921	8234	13904	1106	7946	80
POLI	1/30/2005	80762	4038	89921	4496	39431	4392	15995	1272	7039	71
POLI	1/31/2005	41296	2065	47440	2372	19620	2185	2790	222	3513	36
POLI	2/1/2005	58450	2922	66231	3312	29337	3268	6877	547	5129	52
POLI	2/2/2005	90472	4524	95360	4768	51397	5725	1587	126	9481	95
POLI	2/3/2005	77677	3884	89582	4479	35651	3971	8034	639	7166	72
POLI	2/4/2005	57703	2885	69714	3486					4414	45
TRAF	1/15/2005	77363	3868	73622	3681	34570	3851	1022	81	5069	51
TRAF	1/16/2005	172082	8604	160296	8015	56091	6248	17447	1387	6196	63
TRAF	1/17/2005	276869	13843	278135	13907	85341	9506	50671	4029	7584	76
TRAF	1/18/2005	164973	8249	174647	8732	47122	5249	33895	2695	6881	69
TRAF	1/19/2005	92270	4614	101282	5064	42783	4765	8731	694	5082	52
TRAF	1/20/2005	25408	1270	28378	1419	16543	1843	430	34	881	12
TRAF	1/21/2005	32668	1633	35199	1760	19150	2133	691	55	1474	17
TRAF	1/28/2005	234718	11736							8636	87
TRAF	1/29/2005	158348	7917	151693	7585	61795	6883	12068	960	9286	93
TRAF	1/30/2005	95134	4757	93617	4681	30515	3399	14642	1164	7475	75
TRAF	1/31/2005	57996	2900	63360	3168	29121	3244	845	67	3704	38
TRAF	2/1/2005	66878	3344	70726	3536	31418	3499	2681	213	4674	48
TRAF	2/2/2005	112725	5636	107533	5377	46003	5124	4761	379	9378	94
TRAF	2/3/2005	89036	4452	88421	4421	39475	4397	1029	82	7923	80
TRAF	2/4/2005	86373	4319							5747	58
ZAKO	1/15/2005	115720	5786	126254	6313	107874	12015	3266	260	2299	25
ZAKO	1/16/2005	144828	7241	151493	7575	107452	11968	33593	2671	2494	26
ZAKO	1/17/2005	167241	8362	181790	9089	119748	13338	24216	1926	3123	32
ZAKO	1/18/2005	161858	8093	104446	5222	84884	9455	6501	517	4083	42
ZAKO	1/19/2005	35740	1787	31534	1577	26708	2975	973	77	1627	19
ZAKO	1/20/2005	17873	894	17901	895	14171	1578	404	32	368	10
ZAKO	1/21/2005	21956	1098	100405	5020	84476	9409	9044	719	559	10
ZAKO	1/22/2005	26492	1325	22518	1126					1037	14
ZAKO	1/23/2005	105072	5254	45081	2254					1981	22
ZAKO	2/1/2005	37255	1863	31192	1560					1128	30
ZAKO	2/2/2005	45636	2282	32907	1645					2114	23
ZAKO	2/3/2005	58701	2935	47951	2398					2347	25
ZAKO	2/4/2005	107331	5367	84238	4212					2507	27
ZAKO	2/5/2005	146098	7305							2461	26
ZAKO	2/6/2005	159001	7950							2357	26
HOUSE10	1/18/2005	45486	2274	73624	3681	37720	4201	16050	1276	1129	14
HOUSE10	1/20/2005	11663	583	20187	1009	15963	1778	511	41	211	9
HOUSE10	1/21/2005	30461	1523							316	12
HOUSE15	2/1/2005	52574	2629	63366	3168	37836	4214	16794	1335	1510	17
HOUSE15	2/2/2005	76206	3810	104809	5240	63032	7021	24202	1925	2452	26
HOUSE15	2/3/2005	76232	3812	96914	4846	60321	6719	15345	1220	4331	44
HOUSE17	2/1/2005	18536	927	25691	1285	21487	2393	835	66	431	10
HOUSE17	2/2/2005	26407	1320	47794	2390	30233	3367	7992	636	704	11
HOUSE17	2/3/2005	36715	1836	140857	7043	78254	8716	31250	2485	868	13
HOUSE3	1/18/2005	83625	4181	98769	4938	55334	6163	15954	1269	1918	21
HOUSE3	1/19/2005	60563	3028	107530	5377	65745	7323	21840	1737	1284	16
HOUSE3	1/20/2005	34730	1737	28953	1448	23049	2567	874	70	243	9

	DATE	SO4	USO4	CL	UCL	BR	UBR	NH4	UNH4	NA	UNA
AGRI	1/15/2005	6254	79	1546	65	11	1	3560	37	617	26
AGRI	1/17/2005	8159	103	10216	379	47	3	6465	65	1147	35
AGRI	1/18/2005	7706	97	6055	226	30	2	5063	51	809	29
AGRI	1/19/2005	4459	57	3126	120	15	1	4126	42	577	25
AGRI	1/20/2005	682	16	638	39	3	0	520	10	340	22
AGRI	1/21/2005	1530	23	852	44	6	0	1014	13	448	23
AGRI	1/28/2005	13276	166	9638	358	53	3	9838	99	1794	49
AGRI	1/29/2005	14239	178	3112	119	30	2	8041	81	1051	33
AGRI	1/30/2005	6590	83	1329	58	21	1	4181	43	524	24
AGRI	1/31/2005	3323	44	1460	62	11	1	1919	21	1009	32
AGRI	2/1/2005	3771	49	2246	89	14	1	2759	29	908	30
AGRI	2/2/2005	6756	85	2602	101	24	1	5477	55	745	28
AGRI	2/3/2005	9251	116	624	39	15	1	4917	50	441	23
AGRI	2/4/2005	9183	116	234	32	9	0	3097	32	430	23
INDU	1/15/2005	6148	78	1635	68	12	1	3342	35	666	26
INDU	1/16/2005	10314	130	9807	364	46	3	6558	66	1253	37
INDU	1/17/2005	8962	113	16034	594	93	7	9415	95	1463	42
INDU	1/18/2005	8552	108	5234	196	30	2	4323	44	798	28
INDU	1/19/2005	4314	55	3315	126	15	1	3866	40	908	30
INDU	1/20/2005	833	17	918	46	4	0	600	11	473	24
INDU	1/21/2005	1331	31	1442	81	5	0	918	20	850	45
INDU	1/28/2005	14707	184	12661	469	77	5	11848	119	1764	49
INDU	1/29/2005	11979	150	776	42	20	1	5952	60	724	27
INDU	1/30/2005	6045	77	1422	61	15	1	4057	42	591	25
INDU	1/31/2005	3059	40	2641	102	9	1	2138	23	1478	42
INDU	2/1/2005	3725	50	3730	145	18	1	3525	38	1260	43
INDU	2/2/2005	10671	139	2121	123	21	1	6387	69	1612	74
INDU	2/3/2005	11022	138	3340	127	19	1	5467	55	871	30
INDU	2/4/2005	11668	146	3132	120	16	1	3781	39	776	28
POLI	1/15/2005	6632	84	2759	107	13	1	4221	43	778	28
POLI	1/16/2005	9010	113	7799	290	36	2	6642	67	1045	33
POLI	1/17/2005	10056	126	15978	592	92	7	9711	98	1668	47
POLI	1/18/2005	8015	101	6673	249	32	2	4548	46	843	29
POLI	1/19/2005	4498	58	3636	138	16	1	4028	41	867	30
POLI	1/20/2005	734	16	1073	50	3	0	550	10	507	24
POLI	1/21/2005	1619	24	1466	62	5	0	1278	16	628	26
POLI	1/28/2005	12592	158	11166	414	55	4	11130	112	1816	50
POLI	1/29/2005	14316	179	2924	113	30	2	8495	85	1039	33
POLI	1/30/2005	6791	86	2465	96	16	1	5061	51	606	25
POLI	1/31/2005	3296	43	3209	123	9	0	2588	27	1370	40
POLI	2/1/2005	4521	58	4162	157	18	1	3994	41	1136	35
POLI	2/2/2005	7212	91	5338	200	21	1	7505	76	1109	34
POLI	2/3/2005	9831	124	2396	94	16	1	6614	67	701	27
POLI	2/4/2005	9527	120	1524	64	13	1	3760	39	694	27
TRAF	1/15/2005	7133	90	2995	115	16	1	3774	39	808	29
TRAF	1/16/2005	9355	118	8096	301	42	2	7125	72	1095	34
TRAF	1/17/2005	9409	118	13876	514	73	5	9378	94	1587	45
TRAF	1/18/2005	8275	104	7045	262	38	2	5212	53	985	32
TRAF	1/19/2005	5096	65	6319	236	20	1	4944	50	1820	50
TRAF	1/20/2005	1127	19	1610	67	4	0	847	12	723	27
TRAF	1/21/2005	1892	27	2811	108	7	0	1338	16	1396	40
TRAF	1/28/2005	13295	167	13960	517	63	4	11760	118	2097	56
TRAF	1/29/2005	14904	187	6901	257	35	2	10342	104	1312	39
TRAF	1/30/2005	6930	88	4780	180	20	1	5979	60	1186	36
TRAF	1/31/2005	3743	49	7245	270	13	1	2559	27	3993	102
TRAF	2/1/2005	4473	57	6280	234	15	1	3877	40	2406	64
TRAF	2/2/2005	7416	94	8561	318	33	2	6929	70	3006	78
TRAF	2/3/2005	10540	132	4288	162	18	1	6549	66	1152	35
TRAF	2/4/2005	10409	131	9434	350	16	1	4811	49	4721	120
ZAKO	1/15/2005	3934	51	5238	196	50	3	3604	37	1033	33
ZAKO	1/16/2005	3583	47	6358	237	54	3	3869	40	1092	34
ZAKO	1/17/2005	4058	52	8319	309	62	4	4770	49	1269	38
ZAKO	1/18/2005	6379	81	8075	300	58	3	6252	63	1179	36
ZAKO	1/19/2005	2074	29	1003	48	9	0	1356	16	474	24
ZAKO	1/20/2005	603	15	587	38	4	0	405	10	271	21
ZAKO	1/21/2005	1024	18	687	40	5	0	579	11	381	22
ZAKO	1/22/2005	1650	24	807	43	7	0	926	13	424	23
ZAKO	1/23/2005	3243	43	4774	180	35	2	3063	32	920	31
ZAKO	2/1/2005	2778	53	747	99	12	1	1452	31	344	63
ZAKO	2/2/2005	3776	49	876	45	19	1	2235	24	321	22
ZAKO	2/3/2005	6198	79	507	36	22	1	2942	31	438	23
ZAKO	2/4/2005	7171	91	2819	109	43	2	3804	39	821	29
ZAKO	2/5/2005	4648	60	6869	256	49	3	4555	46	1104	34
ZAKO	2/6/2005	4765	62	7435	278	65	4	4561	47	1372	44
HOUSE10	1/18/2005	3721	48	644	39	10	1	1654	19	343	22
HOUSE10	1/20/2005	527	15	324	33	2	0	170	9	268	21
HOUSE10	1/21/2005	818	20	241	40	2	0	181	11	312	27
HOUSE15	2/1/2005	2566	35	1028	49	14	1	786	12	661	26
HOUSE15	2/2/2005	3528	46	1244	55	8	0	1620	18	565	25
HOUSE15	2/3/2005	5900	75	924	46	12	1	2663	28	581	25
HOUSE17	2/1/2005	1412	22	406	34	5	0	471	10	333	22
HOUSE17	2/2/2005	2329	32	408	35	8	0	912	13	354	23
HOUSE17	2/3/2005	4577	59	251	33	7	0	1742	20	287	22
HOUSE3	1/18/2005	4781	61	1904	77	23	1	1893	21	701	27
HOUSE3	1/19/2005	3425	45	1016	49	14	1	1156	15	688	27
HOUSE3	1/20/2005	839	17	582	38	4	0	54	9	421	23

	DATE	K	UK	CACO3	UCACO3	MGO	UMGO	SIO2	USIO2	FE2O3	UFE2O3
AGRI	1/15/2005	327	26	741.0	51.4	240.2	70.7	584	131	541	31
AGRI	1/17/2005	1583	302	9067.5	1425.7	766.0	73.1	5313	2556	4487	470
AGRI	1/18/2005	1144	172	4697.5	565.4	532.5	71.8	2662	1092	4256	350
AGRI	1/19/2005	447	39	218.5	19.1	93.7	70.6	291	87	371	22
AGRI	1/20/2005	96	7	89.7	9.3	85.5	70.5	138	30	99	5
AGRI	1/21/2005	165	10	146.2	11.2	111.3	70.5	102	23	183	9
AGRI	1/28/2005	1720	341	1070.3	177.8	257.2	70.7	1565	813	839	92
AGRI	1/29/2005	751	107	336.2	41.7	93.7	70.5	778	325	593	49
AGRI	1/30/2005	536	49	174.9	16.8	61.0	70.5	260	83	357	22
AGRI	1/31/2005	214	15	272.3	19.0	297.7	70.9	208	50	203	11
AGRI	2/1/2005	292	22	388.2	27.4	247.3	70.8	393	90	289	16
AGRI	2/2/2005	315	30	346.9	29.4	174.3	70.7	272	88	254	16
AGRI	2/3/2005	395	35	543.1	42.1	161.7	70.6	440	119	698	42
AGRI	2/4/2005	507	39	2517.7	165.1	404.0	71.2	1577	307	808	45
INDU	1/15/2005	315	24	1381.2	89.9	320.1	70.9	841	163	705	39
INDU	1/16/2005	1533	281	11591.0	1741.0	1145.6	76.1	6891	3210	6351	638
INDU	1/17/2005	2031	494	8560.2	1734.0	1027.3	75.0	7814	4402	5471	730
INDU	1/18/2005	1391	180	6103.8	636.4	1202.9	76.7	2975	1058	5802	428
INDU	1/19/2005	451	42	283.5	25.4	158.6	70.6	418	145	321	19
INDU	1/20/2005	193	12	227.0	15.4	130.2	70.6	321	42	231	12
INDU	1/21/2005	223	14	208.5	18.5	249.2	138.4	252	42	181	9
INDU	1/28/2005	1799	410	948.9	181.6	201.9	70.6	1737	990	1533	192
INDU	1/29/2005	510	54	366.9	34.6	106.3	70.6	603	194	616	41
INDU	1/30/2005	458	40	243.9	20.7	93.7	70.5	472	122	377	23
INDU	1/31/2005	205	15	491.2	31.3	356.9	71.1	296	62	319	17
INDU	2/1/2005	343	24	530.1	34.9	346.7	102.1	535	100	486	26
INDU	2/2/2005	725	52	1530.4	98.0	1882.6	221.1	1714	297	2253	120
INDU	2/3/2005	858	87	3192.2	267.9	933.5	74.3	927	286	2867	182
INDU	2/4/2005	1472	145	7275.4	585.6	910.5	74.1	2231	609	5394	335
POLI	1/15/2005	422	39	2053.7	155.9	405.0	71.2	1282	321	929	56
POLI	1/16/2005	1269	232	13846.0	2065.2	677.3	72.5	10343	4768	4600	459
POLI	1/17/2005	2441	649	25112.2	5555.8	1141.4	81.4	18772	11071	7901	1154
POLI	1/18/2005	1327	199	10405.0	1278.2	804.4	73.3	6399	2552	3985	337
POLI	1/19/2005	542	52	376.2	32.9	149.8	70.6	669	196	365	23
POLI	1/20/2005	234	14	280.6	17.6	122.0	70.6	388	43	207	11
POLI	1/21/2005	189	13	211.8	15.6	135.9	70.6	186	42	241	13
POLI	1/28/2005	1922	394	813.6	140.5	224.5	70.7	2642	1359	1674	189
POLI	1/29/2005	984	140	439.8	53.7	109.5	70.6	1058	424	848	70
POLI	1/30/2005	561	55	309.5	28.0	76.7	70.5	420	129	367	24
POLI	1/31/2005	260	19	397.1	26.7	309.7	70.9	264	61	274	15
POLI	2/1/2005	329	28	432.9	33.3	270.0	70.8	431	120	324	19
POLI	2/2/2005	478	51	521.1	48.2	210.8	70.7	457	155	559	37
POLI	2/3/2005	560	54	779.2	65.2	167.4	70.6	532	157	789	50
POLI	2/4/2005	595	53	3327.7	239.2	531.1	71.7	1683	393	1273	74
TRAF	1/15/2005	459	48	3666.3	303.2	694.5	72.6	2464	672	2389	151
TRAF	1/16/2005	1094	187	8455.4	1186.1	837.3	73.6	6438	2844	5044	477
TRAF	1/17/2005	1946	467	13977.1	2784.2	893.4	74.8	10912	6067	7068	928
TRAF	1/18/2005	1457	243	7981.2	1088.7	886.3	73.9	5324	2313	5874	541
TRAF	1/19/2005	602	66	635.6	59.9	207.0	70.7	1482	464	873	59
TRAF	1/20/2005	156	10	375.4	23.1	146.0	70.6	460	63	691	36
TRAF	1/21/2005	196	14	492.8	30.8	184.4	70.7	264	51	765	41
TRAF	1/28/2005	2059	439	1106.8	198.0	231.5	70.7	2265	1205	2120	249
TRAF	1/29/2005	958	152	484.8	65.4	129.0	70.6	1005	445	1437	129
TRAF	1/30/2005	545	60	524.1	49.9	141.0	70.6	441	153	954	65
TRAF	1/31/2005	242	23	1073.8	79.6	480.3	71.5	509	153	744	43
TRAF	2/1/2005	353	33	878.7	68.6	351.8	71.1	565	158	934	56
TRAF	2/2/2005	414	52	1394.8	144.9	320.4	71.0	628	235	1163	86
TRAF	2/3/2005	683	80	1695.8	159.4	306.6	70.9	777	309	1984	133
TRAF	2/4/2005	860	92	4809.8	420.4	673.4	72.5	2546	757	2715	178
ZAKO	1/15/2005	665	84	338.5	37.3	134.0	70.6	240	107	266	20
ZAKO	1/16/2005	755	112	650.1	81.3	93.7	70.5	260	130	435	37
ZAKO	1/17/2005	950	159	1407.7	195.8	123.3	70.6	527	294	558	52
ZAKO	1/18/2005	1000	162	1620.7	217.8	145.9	70.6	690	316	474	43
ZAKO	1/19/2005	212	15	206.2	15.0	83.6	70.5	66	23	96	5
ZAKO	1/20/2005	120	8	123.6	10.1	33.3	70.5	39	15	43	2
ZAKO	1/21/2005	135	9	74.9	8.4	59.1	70.5	31	16	43	2
ZAKO	1/22/2005	208	13	84.6	9.0	69.8	70.5	44	19	98	5
ZAKO	1/23/2005	526	60	425.9	42.3	97.2	74.1	153	78	226	16
ZAKO	2/1/2005	252	18	191.1	25.5	48.3	217.6	17	55	83	5
ZAKO	2/2/2005	252	19	117.8	11.2	38.3	70.5	70	32	99	6
ZAKO	2/3/2005	363	30	137.8	13.1	41.5	70.5	62	41	123	7
ZAKO	2/4/2005	642	77	425.8	44.2	62.9	70.5	215	100	234	17
ZAKO	2/5/2005	759	114	533.5	67.6	78.0	70.5	443	207	404	34
ZAKO	2/6/2005	984	125	740.5	80.5	95.1	96.1	616	249	481	36
HOUSE10	1/18/2005	566	41	907.5	59.8	82.1	70.3	453	92	516	29
HOUSE10	1/20/2005	90	6	344.6	20.1	75.2	70.3	242	28	92	5
HOUSE10	1/21/2005	99	7	787.0	45.4	102.7	90.0	986	118	107	6
HOUSE15	2/1/2005	403	35	2095.2	147.1	313.2	70.7	1594	345	474	27
HOUSE15	2/2/2005	446	44	1401.5	115.1	183.9	71.0	1507	406	329	21
HOUSE15	2/3/2005	623	60	1897.2	154.6	271.3	70.7	1772	474	615	39
HOUSE17	2/1/2005	163	11	323.5	20.7	68.3	70.3	122	32	128	7
HOUSE17	2/2/2005	161	12	518.2	32.3	59.9	72.3	208	48	142	8
HOUSE17	2/3/2005	261	18	418.2	26.9	49.2	73.5	128	36	202	11
HOUSE3	1/18/2005	951	98	2090.0	180.9	201.3	70.7	1448	423	1442	94
HOUSE3	1/19/2005	457	40	1329.8	98.1	128.5	70.3	1167	273	378	22
HOUSE3	1/20/2005	271	21	2400.7	145.7	207.9	71.2	1777	275	603	32

	DATE	AL2O3	UAL2O3	ZNO	UZNO	TIO2	UTIO2	CUO	UCUO	V2O5	UV2O5
AGRI	1/15/2005	398	153	295.2	15.6	20.6	2.0	11.9	0.8	5.4	0.9
AGRI	1/17/2005	2215	1438	657.7	42.2	122.1	17.6	85.7	5.8	13.1	2.7
AGRI	1/18/2005	1289	868	511.7	29.4	87.2	10.4	127.0	7.5	7.0	3.5
AGRI	1/19/2005	225	107	192.7	10.8	15.0	1.7	34.4	1.9	2.7	0.7
AGRI	1/20/2005	94	42	50.4	4.7	5.5	1.2	3.3	0.3	1.4	0.6
AGRI	1/21/2005	84	38	99.0	6.4	6.5	1.2	5.0	0.4	1.7	0.6
AGRI	1/28/2005	1611	1117	624.1	41.1	48.2	7.4	46.6	3.3	7.0	1.2
AGRI	1/29/2005	774	458	403.7	23.4	28.3	3.5	16.0	1.1	5.0	0.9
AGRI	1/30/2005	311	140	214.8	11.9	13.3	1.7	12.0	0.8	3.0	0.8
AGRI	1/31/2005	134	64	162.4	9.2	8.8	1.4	8.9	0.7	2.5	0.7
AGRI	2/1/2005	293	116	172.3	9.6	18.7	1.8	11.4	0.7	5.0	0.8
AGRI	2/2/2005	314	143	224.5	12.4	17.3	1.9	15.2	0.9	5.0	0.8
AGRI	2/3/2005	378	184	270.2	14.5	23.1	2.2	17.7	1.1	2.7	0.8
AGRI	2/4/2005	866	286	120.9	7.3	49.7	3.6	9.1	0.6	6.2	1.0
INDU	1/15/2005	448	153	161.4	9.2	30.9	2.5	18.3	1.1	5.4	0.9
INDU	1/16/2005	2457	1592	621.4	39.0	137.2	19.0	162.6	10.6	7.8	3.0
INDU	1/17/2005	2814	2059	1059.9	79.0	147.4	27.1	256.6	20.1	15.4	3.3
INDU	1/18/2005	1307	750	582.6	32.1	62.9	7.1	63.1	3.7	5.6	3.0
INDU	1/19/2005	293	190	185.0	10.4	14.6	1.8	28.4	1.6	2.3	0.8
INDU	1/20/2005	176	54	74.3	5.4	10.9	1.4	8.5	0.6	1.1	0.7
INDU	1/21/2005	183	66	57.5	8.2	10.8	2.4	32.1	1.8	2.2	1.2
INDU	1/28/2005	1513	1155	921.9	65.8	56.9	10.0	93.2	7.1	9.0	1.5
INDU	1/29/2005	545	268	357.9	19.4	25.9	2.7	23.2	1.4	4.6	0.9
INDU	1/30/2005	363	153	171.8	9.7	17.9	1.9	12.5	0.8	3.8	0.8
INDU	1/31/2005	160	76	172.8	9.6	13.8	1.5	26.6	1.5	3.5	0.7
INDU	2/1/2005	342	115	277.9	15.2	24.7	2.4	21.7	1.3	4.4	1.0
INDU	2/2/2005	883	358	513.2	28.7	76.4	6.4	30.3	2.0	7.7	2.6
INDU	2/3/2005	588	335	286.7	15.6	29.0	3.0	110.4	5.9	5.3	1.4
INDU	2/4/2005	1099	527	222.5	12.3	57.8	5.4	58.0	3.2	6.3	2.4
POLI	1/15/2005	607	298	251.9	13.7	41.2	3.4	25.3	1.6	5.8	1.1
POLI	1/16/2005	3165	1961	618.5	38.7	221.1	29.9	120.9	7.9	13.2	3.3
POLI	1/17/2005	5527	4083	1625.7	129.4	316.0	63.0	220.8	18.6	19.3	5.3
POLI	1/18/2005	1955	1101	631.5	36.6	146.9	16.7	69.9	4.3	9.5	2.5
POLI	1/19/2005	382	196	330.5	17.7	22.6	2.3	32.6	1.8	2.8	0.8
POLI	1/20/2005	188	48	133.4	7.8	12.8	1.4	6.2	0.5	0.8	0.6
POLI	1/21/2005	124	67	82.9	5.8	9.8	1.4	13.0	0.8	1.4	0.7
POLI	1/28/2005	1902	1288	1030.9	68.9	80.1	12.5	63.3	4.6	5.8	1.6
POLI	1/29/2005	911	510	635.8	36.4	39.1	4.5	22.3	1.7	6.1	1.1
POLI	1/30/2005	372	170	191.7	10.8	18.4	2.1	12.9	0.8	3.1	0.8
POLI	1/31/2005	123	67	148.2	8.5	13.1	1.5	27.2	1.5	2.5	0.7
POLI	2/1/2005	367	175	558.0	29.0	20.8	2.0	19.3	1.3	4.3	0.8
POLI	2/2/2005	365	204	266.5	14.7	20.4	2.2	19.5	1.2	3.2	0.8
POLI	2/3/2005	425	205	304.9	16.5	19.4	2.1	21.1	1.3	3.7	0.8
POLI	2/4/2005	797	368	282.7	15.1	44.3	3.6	15.1	1.0	5.2	1.2
TRAF	1/15/2005	785	387	437.4	23.4	82.3	7.0	123.9	6.8	8.2	2.0
TRAF	1/16/2005	2101	1272	632.7	38.6	159.5	20.6	219.7	13.8	9.8	2.9
TRAF	1/17/2005	3568	2535	1173.2	86.4	230.0	41.4	260.5	20.2	19.0	4.4
TRAF	1/18/2005	1833	1133	740.4	44.5	128.4	16.5	193.6	12.0	7.7	3.4
TRAF	1/19/2005	943	447	297.9	16.4	45.5	4.2	132.3	7.3	4.9	1.1
TRAF	1/20/2005	239	65	79.4	5.6	17.1	1.7	73.2	3.8	1.6	0.8
TRAF	1/21/2005	167	65	139.4	8.1	14.5	1.6	50.8	2.7	2.2	0.8
TRAF	1/28/2005	2006	1384	936.6	64.1	71.8	11.7	106.4	7.8	9.4	1.8
TRAF	1/29/2005	883	533	500.9	29.9	37.6	4.9	107.0	6.6	3.9	1.2
TRAF	1/30/2005	355	183	256.4	14.3	25.1	2.7	85.0	4.7	3.7	0.9
TRAF	1/31/2005	256	159	238.8	12.9	30.8	2.7	62.6	3.3	3.8	1.1
TRAF	2/1/2005	311	157	217.6	12.0	28.0	2.6	68.4	3.7	3.4	1.0
TRAF	2/2/2005	509	276	467.3	25.9	32.0	3.5	130.5	7.4	6.0	1.1
TRAF	2/3/2005	491	380	258.6	14.4	24.3	3.1	54.6	3.1	4.2	1.7
TRAF	2/4/2005	1207	567	263.6	14.6	70.5	6.3	59.0	3.4	6.0	1.7
ZAKO	1/15/2005	231	147	233.6	13.5	11.8	1.7	14.9	1.0	1.8	0.7
ZAKO	1/16/2005	274	187	343.6	20.2	14.5	2.1	22.3	1.5	1.2	0.7
ZAKO	1/17/2005	576	427	430.2	26.1	21.6	3.1	27.7	1.9	2.7	0.9
ZAKO	1/18/2005	463	308	416.3	25.1	18.8	2.7	21.6	1.5	2.7	0.8
ZAKO	1/19/2005	68	35	85.7	5.9	4.9	1.2	4.1	0.4	0.7	0.6
ZAKO	1/20/2005	11	23	26.0	4.1	1.6	1.1	1.9	0.3	0.8	0.6
ZAKO	1/21/2005	3	26	28.9	4.2	1.3	1.1	2.1	0.3	1.1	0.6
ZAKO	1/22/2005	10	31	103.9	6.6	2.3	1.1	2.9	0.3	0.7	0.6
ZAKO	1/23/2005	162	119	324.6	18.0	11.0	1.6	12.0	1.0	1.1	0.7
ZAKO	2/1/2005	118	95	144.5	14.2	2.0	3.5	4.7	0.8	1.5	1.7
ZAKO	2/2/2005	99	66	111.3	6.9	4.8	1.3	6.4	0.5	1.6	0.6
ZAKO	2/3/2005	108	87	144.3	8.4	6.2	1.3	7.7	0.5	2.2	0.6
ZAKO	2/4/2005	248	173	280.5	15.8	10.1	1.6	15.3	1.0	2.0	0.7
ZAKO	2/5/2005	445	297	298.7	17.7	16.3	2.3	36.4	2.3	1.7	0.7
ZAKO	2/6/2005	603	357	390.2	22.2	29.2	3.4	26.5	1.7	1.9	1.0
HOUSE10	1/18/2005	253	102	220.3	11.9	12.7	1.6	11.1	0.8	1.4	0.7
HOUSE10	1/20/2005	89	35	45.4	4.5	7.0	1.2	4.6	0.4	0.3	0.6
HOUSE10	1/21/2005	162	70	52.2	5.7	11.6	1.6	12.2	0.8	1.6	0.8
HOUSE15	2/1/2005	1179	419	190.7	10.5	59.3	4.5	17.1	1.0	4.0	1.2
HOUSE15	2/2/2005	777	349	104.8	6.8	36.1	3.2	16.9	1.0	3.6	0.9
HOUSE15	2/3/2005	1127	472	186.3	10.5	60.1	4.9	38.4	2.1	3.8	1.0
HOUSE17	2/1/2005	117	56	83.5	5.8	5.8	1.2	5.8	0.4	1.8	0.6
HOUSE17	2/2/2005	127	72	115.6	7.1	8.4	1.4	6.6	0.5	2.3	0.7
HOUSE17	2/3/2005	102	58	116.4	7.2	7.6	1.4	8.7	0.6	0.8	0.6
HOUSE3	1/18/2005	850	429	450.7	24.1	48.0	4.3	33.9	2.1	4.0	1.1
HOUSE3	1/19/2005	613	240	213.2	11.7	34.0	2.8	17.6	1.0	2.4	0.8
HOUSE3	1/20/2005	1059	281	103.8	6.6	84.5	5.4	35.8	1.9	4.4	1.2

	DATE	MNO2	UMNO2	PBO	UPBO	NI2O	UNI2O	BAO	UBAO	SRO	USRO
AGRI	1/15/2005	11.6	1.2	88.7	4.6	2.3	0.3	6.0	4.7	2.6	0.2
AGRI	1/17/2005	96.7	12.0	197.9	12.2	6.9	1.1	41.0	6.2	10.5	0.7
AGRI	1/18/2005	72.1	13.0	152.7	8.5	18.3	1.9	39.3	6.0	7.6	0.5
AGRI	1/19/2005	11.0	1.0	79.9	4.2	1.2	0.3	5.4	4.7	1.2	0.1
AGRI	1/20/2005	4.5	0.6	15.7	0.9	0.3	0.2	-0.1	4.7	0.6	0.1
AGRI	1/21/2005	8.7	0.7	39.7	2.0	0.5	0.2	2.2	4.7	1.3	0.1
AGRI	1/28/2005	23.5	3.0	224.8	14.2	3.2	0.6	12.1	5.2	5.2	0.4
AGRI	1/29/2005	23.3	2.3	141.8	7.9	2.3	0.4	8.2	4.9	3.1	0.2
AGRI	1/30/2005	11.2	1.2	79.3	4.1	1.5	0.3	1.1	4.7	2.2	0.2
AGRI	1/31/2005	8.9	0.9	52.1	2.7	0.9	0.2	1.6	4.7	2.3	0.2
AGRI	2/1/2005	13.3	1.1	77.3	4.0	2.4	0.3	4.2	4.7	2.6	0.2
AGRI	2/2/2005	12.1	1.0	85.8	4.5	2.0	0.3	4.7	4.8	2.5	0.2
AGRI	2/3/2005	17.9	1.6	82.1	4.3	1.9	0.3	7.1	4.8	2.5	0.2
AGRI	2/4/2005	19.3	1.7	40.8	2.1	2.3	0.3	7.5	4.8	25.9	1.4
INDU	1/15/2005	23.9	1.8	45.7	2.4	2.1	0.3	4.1	4.7	3.4	0.2
INDU	1/16/2005	131.2	15.8	206.2	12.5	5.4	1.2	43.4	6.2	12.6	0.8
INDU	1/17/2005	163.5	23.4	322.8	22.9	10.7	2.0	51.4	7.4	12.4	0.9
INDU	1/18/2005	93.2	14.3	159.0	8.6	5.4	0.8	22.6	5.3	7.3	0.4
INDU	1/19/2005	27.7	2.1	68.3	3.6	1.0	0.3	3.9	4.7	1.6	0.1
INDU	1/20/2005	7.4	0.7	19.8	1.1	0.5	0.2	5.4	4.7	1.3	0.1
INDU	1/21/2005	12.0	1.1	24.7	1.4	0.4	0.4	16.4	9.3	6.3	0.4
INDU	1/28/2005	34.6	4.9	232.8	15.9	4.5	0.8	11.0	5.1	6.1	0.5
INDU	1/29/2005	25.6	2.1	105.7	5.6	2.7	0.4	8.7	4.9	2.7	0.2
INDU	1/30/2005	12.1	1.1	55.1	2.9	1.7	0.3	6.0	4.7	2.0	0.2
INDU	1/31/2005	11.8	1.0	43.4	2.2	1.2	0.3	2.7	4.7	2.4	0.2
INDU	2/1/2005	19.0	1.5	98.4	5.0	2.3	0.4	6.7	6.9	4.1	0.3
INDU	2/2/2005	83.1	6.6	137.7	7.1	3.6	0.8	15.6	14.5	4.9	0.4
INDU	2/3/2005	48.7	5.9	105.7	5.5	2.9	0.5	8.1	4.9	3.7	0.2
INDU	2/4/2005	48.9	9.4	110.1	5.7	3.7	0.7	5.4	4.8	27.0	1.4
POLI	1/15/2005	22.8	2.3	71.9	3.8	2.0	0.3	14.6	5.0	4.1	0.3
POLI	1/16/2005	131.5	14.8	115.3	7.0	6.4	1.1	61.5	7.1	15.2	1.0
POLI	1/17/2005	386.3	58.2	308.2	23.3	10.9	2.4	91.5	11.1	26.2	2.0
POLI	1/18/2005	111.4	11.1	152.9	8.6	4.0	0.8	33.4	5.7	11.2	0.7
POLI	1/19/2005	15.2	1.4	83.3	4.3	1.5	0.3	5.6	4.8	2.7	0.2
POLI	1/20/2005	5.4	0.6	17.4	0.9	0.3	0.2	3.0	4.6	1.3	0.1
POLI	1/21/2005	10.0	1.0	34.4	1.8	0.8	0.2	0.6	4.6	1.0	0.1
POLI	1/28/2005	113.9	13.4	209.1	13.5	4.7	0.8	26.4	5.6	5.6	0.4
POLI	1/29/2005	28.7	2.8	211.4	11.8	2.7	0.4	11.7	4.9	3.9	0.3
POLI	1/30/2005	9.7	1.0	64.5	3.4	1.3	0.3	4.9	4.7	2.4	0.2
POLI	1/31/2005	10.5	0.9	102.7	5.2	1.2	0.3	3.4	4.6	1.9	0.2
POLI	2/1/2005	14.2	1.2	88.7	4.6	2.5	0.4	3.4	4.8	3.5	0.2
POLI	2/2/2005	20.9	1.7	84.1	4.5	2.8	0.4	3.8	4.7	2.4	0.2
POLI	2/3/2005	22.5	1.9	66.1	3.5	1.8	0.3	2.9	4.7	2.2	0.2
POLI	2/4/2005	24.1	2.7	69.2	3.6	2.4	0.4	8.4	4.8	29.9	1.6
TRAF	1/15/2005	39.7	4.9	89.0	4.7	3.3	0.6	44.0	6.0	6.3	0.4
TRAF	1/16/2005	90.6	10.9	139.8	8.3	5.3	1.0	76.9	7.9	15.1	0.9
TRAF	1/17/2005	155.0	22.7	262.5	18.5	10.6	2.0	116.8	11.9	19.5	1.4
TRAF	1/18/2005	101.9	13.9	157.9	9.2	6.4	1.1	61.2	7.0	10.4	0.6
TRAF	1/19/2005	18.6	2.1	86.3	4.6	1.8	0.4	20.0	5.3	5.2	0.3
TRAF	1/20/2005	9.2	1.1	25.3	1.3	0.7	0.3	9.4	4.8	1.9	0.1
TRAF	1/21/2005	15.6	1.5	41.2	2.1	1.4	0.3	9.8	4.9	2.0	0.2
TRAF	1/28/2005	35.7	5.1	255.0	16.8	4.0	0.8	45.0	6.5	8.9	0.6
TRAF	1/29/2005	32.1	3.6	157.4	9.1	3.1	0.5	28.4	5.5	4.3	0.3
TRAF	1/30/2005	16.2	1.8	72.9	3.9	2.0	0.4	17.6	5.1	2.8	0.2
TRAF	1/31/2005	15.8	2.0	55.1	2.9	2.0	0.4	17.4	5.3	3.9	0.3
TRAF	2/1/2005	19.3	2.1	74.2	3.9	2.4	0.4	13.4	5.1	3.1	0.2
TRAF	2/2/2005	25.5	2.5	126.4	6.9	3.4	0.5	26.6	5.6	5.9	0.4
TRAF	2/3/2005	32.8	6.3	66.7	3.6	3.2	0.6	19.2	5.2	3.4	0.2
TRAF	2/4/2005	36.9	4.4	105.8	5.6	3.3	0.6	28.3	5.6	28.6	1.5
ZAKO	1/15/2005	8.1	0.9	71.6	4.0	1.8	0.3	7.1	4.9	3.5	0.2
ZAKO	1/16/2005	10.3	1.2	85.9	4.9	1.5	0.3	13.7	5.1	4.6	0.3
ZAKO	1/17/2005	14.5	2.0	96.8	5.7	2.1	0.4	12.5	5.0	5.5	0.4
ZAKO	1/18/2005	85.7	8.0	105.8	6.2	2.0	0.4	9.0	4.9	4.8	0.3
ZAKO	1/19/2005	8.6	0.7	22.0	1.2	0.4	0.2	-0.3	4.5	1.1	0.1
ZAKO	1/20/2005	4.3	0.5	9.3	0.5	0.1	0.2	1.3	4.6	0.4	0.1
ZAKO	1/21/2005	4.7	0.5	10.4	0.6	0.2	0.2	1.2	4.6	0.5	0.1
ZAKO	1/22/2005	9.2	0.7	17.7	1.0	0.6	0.2	2.2	4.6	0.6	0.1
ZAKO	1/23/2005	8.5	0.9	67.3	3.7	1.3	0.3	7.3	5.0	3.4	0.2
ZAKO	2/1/2005	6.2	1.2	26.5	1.6	0.8	0.6	2.1	14.2	0.7	0.2
ZAKO	2/2/2005	5.5	0.6	36.6	1.9	1.1	0.2	0.2	4.7	1.1	0.1
ZAKO	2/3/2005	4.7	0.5	50.1	2.6	1.2	0.3	-1.1	4.6	1.7	0.1
ZAKO	2/4/2005	7.2	0.8	69.4	3.8	1.6	0.3	7.5	4.8	4.0	0.3
ZAKO	2/5/2005	7.7	1.0	81.3	4.7	2.3	0.4	4.6	4.8	4.3	0.3
ZAKO	2/6/2005	13.4	1.4	138.0	7.6	3.0	0.5	11.4	6.7	7.5	0.5
HOUSE10	1/18/2005	15.6	1.3	60.1	3.1	1.4	0.3	6.0	4.7	1.2	0.1
HOUSE10	1/20/2005	3.8	0.5	12.0	0.7	0.4	0.2	-1.1	4.6	0.9	0.1
HOUSE10	1/21/2005	5.9	0.6	16.5	0.9	0.6	0.3	2.6	5.9	2.0	0.2
HOUSE15	2/1/2005	19.3	1.7	58.3	3.0	6.3	0.5	47.9	6.0	32.5	1.7
HOUSE15	2/2/2005	15.6	1.3	29.9	1.6	3.0	0.4	23.3	4.3	16.5	0.9
HOUSE15	2/3/2005	19.6	1.6	38.9	2.1	4.5	0.5	28.5	5.3	21.3	1.1
HOUSE17	2/1/2005	5.9	0.6	29.1	1.5	1.0	0.2	1.9	4.6	0.7	0.1
HOUSE17	2/2/2005	8.0	0.7	37.3	1.9	1.2	0.3	-0.7	4.7	1.2	0.1
HOUSE17	2/3/2005	7.3	0.7	28.0	1.5	1.0	0.3	0.8	4.8	0.7	0.1
HOUSE3	1/18/2005	36.7	3.4	94.7	5.0	3.4	0.4	14.3	4.9	7.0	0.4
HOUSE3	1/19/2005	12.8	1.1	56.6	2.9	1.8	0.3	10.7	4.9	8.5	0.5
HOUSE3	1/20/2005	16.2	1.5	21.6	1.1	3.7	0.4	15.2	5.0	13.9	0.7

	DATE	CR2O3	UCR2O3	SB2O3	USB2O3	SNO2	USNO2	RB2O	URB2O	ZRO2	UZRO2
AGRI	1/15/2005	26.0	1.8	4.2	1.4	3.9	1.2	2.07	0.18	1.3	0.2
AGRI	1/17/2005	39.1	5.0	16.7	2.0	15.8	1.7	10.46	0.75	13.1	0.9
AGRI	1/18/2005	69.8	7.4	9.3	1.6	10.5	1.4	7.85	0.52	7.8	0.5
AGRI	1/19/2005	11.9	1.1	6.1	1.5	3.0	1.1	2.50	0.21	0.9	0.1
AGRI	1/20/2005	2.2	0.8	1.5	1.3	1.0	1.1	0.84	0.10	0.5	0.1
AGRI	1/21/2005	6.3	0.9	3.6	1.4	2.0	1.1	1.58	0.14	0.6	0.1
AGRI	1/28/2005	7.7	1.4	16.8	2.0	10.8	1.5	7.70	0.60	6.9	0.5
AGRI	1/29/2005	30.8	2.9	11.7	1.7	6.9	1.3	4.26	0.33	1.6	0.2
AGRI	1/30/2005	45.4	3.1	3.7	1.4	6.1	1.2	5.32	0.34	0.9	0.1
AGRI	1/31/2005	23.3	1.6	2.3	1.3	3.0	1.1	1.72	0.17	1.2	0.2
AGRI	2/1/2005	7.1	0.9	5.7	1.4	2.5	1.1	2.28	0.19	0.9	0.1
AGRI	2/2/2005	2.1	0.8	9.2	1.6	4.5	1.2	2.87	0.24	1.0	0.2
AGRI	2/3/2005	3.1	0.9	5.9	1.4	3.8	1.2	3.23	0.24	3.4	0.3
AGRI	2/4/2005	3.7	0.9	2.9	1.3	2.6	1.1	3.58	0.24	2.3	0.3
INDU	1/15/2005	13.7	1.2	2.9	1.4	1.4	1.1	2.18	0.19	1.5	0.2
INDU	1/16/2005	21.9	3.8	17.5	2.0	8.3	1.4	10.12	0.71	16.5	1.1
INDU	1/17/2005	38.0	6.2	39.3	3.7	20.8	2.2	10.61	0.92	18.8	1.4
INDU	1/18/2005	28.9	4.4	10.4	1.7	10.0	1.4	11.29	0.68	16.9	1.0
INDU	1/19/2005	3.3	0.9	4.6	1.4	4.6	1.2	1.83	0.18	1.0	0.1
INDU	1/20/2005	0.8	0.8	2.7	1.3	1.7	1.1	0.89	0.11	0.7	0.1
INDU	1/21/2005	3.5	1.5	9.2	2.7	1.6	2.1	0.78	0.16	0.4	0.2
INDU	1/28/2005	8.4	1.7	17.9	2.1	17.5	1.9	11.31	0.91	4.6	0.4
INDU	1/29/2005	13.5	1.3	11.5	1.6	4.9	1.2	3.55	0.26	1.9	0.2
INDU	1/30/2005	2.7	0.8	4.6	1.4	4.0	1.2	3.12	0.23	1.1	0.2
INDU	1/31/2005	10.3	1.0	3.5	1.4	2.2	1.1	1.50	0.15	1.1	0.2
INDU	2/1/2005	3.1	1.2	8.0	2.1	6.3	1.7	3.32	0.27	1.5	0.2
INDU	2/2/2005	25.9	3.3	10.8	4.2	7.7	3.5	5.29	0.46	12.2	0.8
INDU	2/3/2005	11.4	1.9	3.4	1.4	5.0	1.2	9.52	0.55	24.3	1.3
INDU	2/4/2005	6.8	2.8	2.2	1.3	4.9	1.2	14.70	0.82	2.3	0.3
POLI	1/15/2005	26.4	2.0	6.7	1.5	5.0	1.2	2.32	0.21	2.5	0.2
POLI	1/16/2005	24.1	3.6	22.6	2.3	14.3	1.6	7.33	0.53	15.5	1.0
POLI	1/17/2005	66.2	11.3	43.7	4.4	29.3	3.1	13.28	1.19	45.0	3.4
POLI	1/18/2005	30.2	3.5	16.6	1.9	11.4	1.5	7.94	0.53	13.2	0.8
POLI	1/19/2005	3.4	0.9	9.1	1.6	3.9	1.2	2.44	0.20	1.9	0.2
POLI	1/20/2005	1.5	0.8	1.3	1.3	0.6	1.0	0.70	0.09	0.8	0.1
POLI	1/21/2005	4.2	0.9	5.4	1.4	2.0	1.1	1.30	0.12	0.6	0.1
POLI	1/28/2005	16.2	2.4	16.5	2.0	10.5	1.5	8.14	0.63	6.3	0.5
POLI	1/29/2005	25.2	2.4	15.5	1.8	5.8	1.2	5.14	0.39	2.5	0.2
POLI	1/30/2005	2.6	0.8	4.3	1.4	3.5	1.1	3.68	0.26	1.0	0.1
POLI	1/31/2005	12.2	1.1	3.3	1.3	3.2	1.1	1.64	0.16	1.0	0.1
POLI	2/1/2005	9.5	1.1	8.6	1.5	5.1	1.2	2.43	0.21	1.5	0.2
POLI	2/2/2005	2.7	0.9	6.3	1.5	4.1	1.2	3.32	0.25	1.7	0.2
POLI	2/3/2005	4.3	0.9	5.8	1.4	2.4	1.1	4.25	0.28	3.2	0.2
POLI	2/4/2005	4.0	1.1	3.3	1.4	3.1	1.1	4.89	0.31	3.0	0.3
TRAF	1/15/2005	33.8	2.9	20.0	2.0	10.6	1.4	2.85	0.24	9.7	0.6
TRAF	1/16/2005	25.5	3.6	38.7	3.1	21.4	2.0	7.94	0.57	22.2	1.4
TRAF	1/17/2005	51.6	8.1	58.8	5.0	37.0	3.4	12.73	1.05	32.3	2.3
TRAF	1/18/2005	34.5	4.8	34.8	2.8	20.3	1.9	9.09	0.62	20.2	1.2
TRAF	1/19/2005	5.0	1.0	12.8	1.7	12.3	1.5	3.48	0.27	5.0	0.3
TRAF	1/20/2005	3.0	0.9	6.2	1.4	3.4	1.1	0.91	0.11	3.1	0.2
TRAF	1/21/2005	9.2	1.0	6.8	1.5	4.0	1.2	1.55	0.14	2.6	0.2
TRAF	1/28/2005	12.8	2.2	24.8	2.5	20.0	2.0	10.01	0.80	10.3	0.7
TRAF	1/29/2005	33.1	3.4	17.7	2.0	10.6	1.4	5.61	0.41	5.3	0.4
TRAF	1/30/2005	6.5	1.0	8.7	1.5	6.8	1.3	3.94	0.28	3.9	0.3
TRAF	1/31/2005	12.7	1.3	8.5	1.6	5.6	1.3	2.08	0.18	3.8	0.3
TRAF	2/1/2005	7.0	1.1	11.8	1.7	4.6	1.2	2.43	0.21	3.5	0.3
TRAF	2/2/2005	7.5	1.1	20.0	2.1	12.8	1.5	4.24	0.33	7.0	0.4
TRAF	2/3/2005	10.1	2.1	9.5	1.6	7.4	1.3	6.44	0.41	6.7	0.4
TRAF	2/4/2005	9.6	1.7	13.7	1.8	8.9	1.4	7.86	0.49	11.3	0.7
ZAKO	1/15/2005	2.7	0.8	4.2	1.4	4.3	1.2	5.53	0.42	1.1	0.2
ZAKO	1/16/2005	1.8	0.8	3.5	1.4	6.5	1.3	5.80	0.43	1.8	0.2
ZAKO	1/17/2005	3.7	1.0	6.7	1.5	8.4	1.3	6.11	0.47	2.0	0.2
ZAKO	1/18/2005	3.0	0.9	11.4	1.7	7.2	1.3	5.70	0.46	1.3	0.2
ZAKO	1/19/2005	0.7	0.8	1.5	1.3	2.2	1.1	1.14	0.13	0.4	0.1
ZAKO	1/20/2005	0.4	0.7	1.4	1.3	0.8	1.1	0.64	0.09	0.1	0.1
ZAKO	1/21/2005	0.1	0.7	0.5	1.3	0.7	1.0	0.61	0.10	0.2	0.1
ZAKO	1/22/2005	0.0	0.7	1.3	1.3	1.4	1.1	1.18	0.12	0.1	0.1
ZAKO	1/23/2005	0.8	0.8	6.2	1.5	4.1	1.2	3.76	0.32	0.5	0.1
ZAKO	2/1/2005	3.0	2.3	2.3	3.9	-0.5	3.2	1.25	0.27	0.5	0.3
ZAKO	2/2/2005	1.1	0.8	2.8	1.3	1.4	1.1	1.98	0.18	0.3	0.1
ZAKO	2/3/2005	1.6	0.8	2.6	1.3	1.6	1.1	2.68	0.22	0.5	0.1
ZAKO	2/4/2005	1.3	0.8	4.7	1.4	4.8	1.2	4.97	0.36	0.9	0.2
ZAKO	2/5/2005	2.1	0.8	4.5	1.4	3.9	1.2	6.20	0.45	1.5	0.2
ZAKO	2/6/2005	2.9	1.1	5.6	1.9	6.2	1.6	9.99	0.69	2.2	0.3
HOUSE10	1/18/2005	17.1	1.3	2.9	1.3	1.7	1.1	3.03	0.21	2.5	0.2
HOUSE10	1/20/2005	1.5	0.8	1.4	1.3	0.8	1.1	0.40	0.08	2.0	0.2
HOUSE10	1/21/2005	2.1	1.0	2.4	1.7	0.5	1.4	0.60	0.10	12.9	0.7
HOUSE15	2/1/2005	3.5	0.9	5.3	1.4	1.8	1.1	1.78	0.18	1.7	0.3
HOUSE15	2/2/2005	4.2	0.9	2.5	1.1	1.3	0.9	1.68	0.14	1.1	0.2
HOUSE15	2/3/2005	3.7	0.9	2.7	1.3	3.4	1.1	3.73	0.25	1.8	0.2
HOUSE17	2/1/2005	1.7	0.8	2.2	1.3	0.1	1.1	0.89	0.10	0.2	0.1
HOUSE17	2/2/2005	1.9	0.8	3.6	1.4	0.8	1.1	1.17	0.13	0.6	0.1
HOUSE17	2/3/2005	2.3	0.8	3.4	1.4	0.9	1.1	1.55	0.14	0.7	0.1
HOUSE3	1/18/2005	9.9	1.3	9.9	1.6	7.2	1.2	5.17	0.35	5.8	0.4
HOUSE3	1/19/2005	2.5	0.8	3.0	1.4	4.8	1.2	2.27	0.19	4.3	0.3
HOUSE3	1/20/2005	6.2	1.0	2.2	1.3	3.5	1.2	1.23	0.12	7.0	0.4

	DATE	MOO3	UMOO3	AS2O3	UAS2O3	SEO2	USEO2	CDO	UCDO	GA2O3	UGA2O3
AGRI	1/15/2005	1.0	0.21	0.7	0.4	4.01	0.25	3.50	0.64	1.53	0.50
AGRI	1/17/2005	5.2	0.45	2.2	0.8	4.61	0.35	5.99	0.79	4.70	0.97
AGRI	1/18/2005	4.0	0.37	3.5	0.7	3.39	0.25	4.85	0.72	1.49	0.75
AGRI	1/19/2005	1.6	0.23	1.1	0.4	2.00	0.16	1.61	0.58	1.30	0.49
AGRI	1/20/2005	0.4	0.19	0.5	0.2	0.55	0.08	0.47	0.55	0.52	0.20
AGRI	1/21/2005	0.3	0.19	0.6	0.3	0.85	0.10	1.12	0.57	0.90	0.28
AGRI	1/28/2005	2.3	0.30	1.5	0.9	8.90	0.62	6.60	0.83	5.37	0.99
AGRI	1/29/2005	1.3	0.23	3.0	0.6	4.52	0.31	5.09	0.72	3.44	0.69
AGRI	1/30/2005	2.7	0.28	3.3	0.5	2.97	0.21	1.98	0.60	3.34	0.49
AGRI	1/31/2005	0.6	0.20	2.2	0.4	1.50	0.14	1.95	0.60	2.01	0.49
AGRI	2/1/2005	0.6	0.20	2.3	0.4	1.93	0.15	1.44	0.57	2.44	0.42
AGRI	2/2/2005	1.2	0.22	5.1	0.5	3.03	0.21	2.78	0.63	3.65	0.52
AGRI	2/3/2005	0.8	0.22	0.7	0.4	3.32	0.22	1.98	0.59	1.40	0.48
AGRI	2/4/2005	0.5	0.20	2.3	0.3	1.97	0.15	1.19	0.56	1.14	0.36
INDU	1/15/2005	0.8	0.21	0.9	0.3	3.80	0.24	1.60	0.57	0.98	0.46
INDU	1/16/2005	6.6	0.53	0.3	0.8	8.93	0.59	4.39	0.71	2.42	0.90
INDU	1/17/2005	8.5	0.73	1.1	1.2	6.12	0.51	10.28	1.13	2.90	1.27
INDU	1/18/2005	3.6	0.36	1.4	0.7	3.70	0.27	6.17	0.77	1.72	0.79
INDU	1/19/2005	1.1	0.22	1.3	0.4	3.72	0.24	2.56	0.61	1.10	0.46
INDU	1/20/2005	0.9	0.21	0.3	0.2	2.42	0.16	0.84	0.56	0.32	0.23
INDU	1/21/2005	0.6	0.37	0.0	0.3	0.94	0.15	0.01	1.04	0.46	0.38
INDU	1/28/2005	2.7	0.32	0.9	0.9	7.85	0.59	7.55	0.90	1.90	1.04
INDU	1/29/2005	1.3	0.23	2.4	0.5	3.66	0.24	3.56	0.64	2.31	0.58
INDU	1/30/2005	1.7	0.24	2.2	0.4	2.11	0.16	1.16	0.56	2.25	0.40
INDU	1/31/2005	0.9	0.21	2.1	0.3	1.43	0.13	2.09	0.60	1.08	0.36
INDU	2/1/2005	1.7	0.32	2.8	0.6	2.73	0.22	3.29	0.88	3.33	0.62
INDU	2/2/2005	2.4	0.67	4.1	0.9	4.10	0.37	2.48	1.71	1.93	1.05
INDU	2/3/2005	0.8	0.27	2.4	0.5	2.37	0.19	3.28	0.64	0.18	0.54
INDU	2/4/2005	0.4	0.21	5.3	0.6	2.11	0.18	2.56	0.61	0.23	0.49
POLI	1/15/2005	2.1	0.26	1.1	0.4	2.77	0.20	2.68	0.61	1.17	0.64
POLI	1/16/2005	10.0	0.72	1.9	0.6	4.18	0.31	3.38	0.68	2.79	0.77
POLI	1/17/2005	46.5	3.64	0.5	1.2	10.70	0.89	10.61	1.30	5.49	1.55
POLI	1/18/2005	6.7	0.51	1.5	0.6	5.93	0.39	5.12	0.74	2.16	0.78
POLI	1/19/2005	1.5	0.24	2.1	0.4	2.40	0.18	3.38	0.65	1.34	0.52
POLI	1/20/2005	0.5	0.20	0.2	0.2	0.40	0.07	0.26	0.52	0.69	0.26
POLI	1/21/2005	0.7	0.20	0.6	0.2	0.93	0.10	1.29	0.56	0.56	0.25
POLI	1/28/2005	6.1	0.51	2.1	0.8	5.99	0.44	5.53	0.77	2.83	1.02
POLI	1/29/2005	1.9	0.26	2.6	0.8	4.58	0.32	4.83	0.71	3.30	1.04
POLI	1/30/2005	1.7	0.24	3.1	0.4	2.26	0.17	1.93	0.58	2.23	0.43
POLI	1/31/2005	0.4	0.19	1.2	0.4	1.19	0.12	1.61	0.57	1.67	0.45
POLI	2/1/2005	1.4	0.24	2.9	0.5	2.58	0.19	2.24	0.61	2.66	0.64
POLI	2/2/2005	0.9	0.22	3.6	0.5	3.92	0.26	2.08	0.60	2.44	0.52
POLI	2/3/2005	1.1	0.23	0.8	0.4	4.47	0.28	1.96	0.59	1.40	0.48
POLI	2/4/2005	0.9	0.22	1.8	0.4	4.98	0.30	1.94	0.59	1.04	0.47
TRAF	1/15/2005	8.3	0.56	1.3	0.5	4.11	0.27	3.02	0.63	1.62	0.72
TRAF	1/16/2005	16.8	1.10	2.8	0.7	12.67	0.80	4.20	0.71	3.58	0.87
TRAF	1/17/2005	22.5	1.70	2.6	1.1	5.82	0.49	7.22	0.98	4.88	1.34
TRAF	1/18/2005	13.7	0.91	1.8	0.7	4.40	0.32	5.71	0.76	1.41	0.83
TRAF	1/19/2005	3.9	0.35	1.5	0.5	2.78	0.21	3.49	0.66	0.62	0.61
TRAF	1/20/2005	2.4	0.27	0.2	0.2	0.62	0.09	0.17	0.54	0.19	0.25
TRAF	1/21/2005	2.7	0.28	0.0	0.3	1.14	0.11	0.96	0.56	0.50	0.33
TRAF	1/28/2005	7.5	0.60	0.2	1.0	9.40	0.68	7.84	0.91	3.36	1.32
TRAF	1/29/2005	4.7	0.40	2.3	0.7	5.02	0.35	5.55	0.75	2.67	0.77
TRAF	1/30/2005	3.9	0.34	2.5	0.4	2.53	0.19	1.43	0.57	1.77	0.50
TRAF	1/31/2005	3.0	0.31	1.7	0.4	1.66	0.15	1.47	0.61	1.04	0.45
TRAF	2/1/2005	2.8	0.29	2.0	0.4	1.84	0.16	1.94	0.60	1.60	0.53
TRAF	2/2/2005	6.9	0.50	4.6	0.7	4.15	0.29	4.25	0.71	3.76	0.76
TRAF	2/3/2005	4.4	0.37	0.9	0.4	4.60	0.29	1.35	0.58	0.33	0.58
TRAF	2/4/2005	4.5	0.40	1.3	0.6	3.62	0.25	2.05	0.62	1.06	0.68
ZAKO	1/15/2005	1.1	0.22	2.0	0.5	4.53	0.30	1.99	0.60	0.71	0.56
ZAKO	1/16/2005	2.1	0.26	3.4	0.6	4.41	0.30	1.91	0.60	1.15	0.57
ZAKO	1/17/2005	2.0	0.26	2.5	0.6	4.73	0.33	1.83	0.60	0.48	0.61
ZAKO	1/18/2005	1.4	0.24	2.4	0.6	5.32	0.37	3.03	0.65	0.71	0.71
ZAKO	1/19/2005	0.3	0.19	1.1	0.2	1.18	0.11	0.39	0.54	0.28	0.24
ZAKO	1/20/2005	0.2	0.18	0.6	0.2	0.47	0.08	0.46	0.54	0.16	0.16
ZAKO	1/21/2005	0.2	0.18	0.5	0.2	0.62	0.08	0.12	0.52	0.15	0.17
ZAKO	1/22/2005	0.2	0.18	0.9	0.2	0.91	0.10	0.35	0.53	0.13	0.25
ZAKO	1/23/2005	0.8	0.22	2.8	0.5	4.16	0.28	1.77	0.61	0.49	0.64
ZAKO	2/1/2005	0.1	0.56	2.1	0.5	1.47	0.24	1.05	1.66	0.62	0.57
ZAKO	2/2/2005	0.9	0.21	2.3	0.3	2.72	0.18	0.58	0.55	0.73	0.30
ZAKO	2/3/2005	0.6	0.20	2.1	0.4	2.41	0.17	1.93	0.59	0.88	0.35
ZAKO	2/4/2005	1.9	0.25	2.9	0.5	4.20	0.28	1.48	0.59	0.17	0.48
ZAKO	2/5/2005	3.6	0.33	3.1	0.5	4.59	0.31	2.58	0.62	0.08	0.51
ZAKO	2/6/2005	3.6	0.39	6.1	0.9	6.26	0.42	2.14	0.81	1.95	0.88
HOUSE10	1/18/2005	0.8	0.21	1.5	0.3	1.62	0.14	1.85	0.58	1.08	0.48
HOUSE10	1/20/2005	0.2	0.19	0.3	0.2	0.41	0.08	0.56	0.55	0.24	0.21
HOUSE10	1/21/2005	0.2	0.27	0.2	0.2	0.51	0.10	0.36	0.69	0.42	0.29
HOUSE15	2/1/2005	0.7	0.21	1.4	0.4	1.15	0.12	1.79	0.58	1.66	0.43
HOUSE15	2/2/2005	0.5	0.16	0.7	0.2	1.21	0.10	0.88	0.46	0.67	0.26
HOUSE15	2/3/2005	1.0	0.22	0.8	0.3	2.75	0.19	1.00	0.55	0.49	0.40
HOUSE17	2/1/2005	0.1	0.18	0.8	0.2	0.56	0.08	1.41	0.56	0.74	0.24
HOUSE17	2/2/2005	0.4	0.20	1.5	0.3	0.85	0.10	1.27	0.58	1.48	0.35
HOUSE17	2/3/2005	0.5	0.20	1.1	0.2	1.19	0.11	1.18	0.59	0.76	0.35
HOUSE3	1/18/2005	2.5	0.28	0.8	0.5	2.88	0.21	3.11	0.63	1.54	0.69
HOUSE3	1/19/2005	0.9	0.22	1.2	0.3	1.52	0.13	2.23	0.60	1.67	0.39
HOUSE3	1/20/2005	0.4	0.22	0.1	0.2	0.41	0.08	0.48	0.56	0.41	0.26

	DATE	FLUO	UFLUO	DMPHE	UDMPHE	PYR	UPYR	CPCDP	UCPCDP	BAANT	UBAANT	CHRYS	UCHRYS
AGRI	1/15/2005	8.9	1.1	0.7	0.7	7.5	0.8	5.6	0.2	5.7	0.4	6.1	0.5
AGRI	1/17/2005	54.7	6.5	0.7	0.7	56.7	6.3	99.4	4.3	85.1	5.7	89.6	7.4
AGRI	1/18/2005	19.8	2.4	0.7	0.7	20.6	2.3	10.8	0.5	40.3	2.7	33.2	2.8
AGRI	1/19/2005	8.2	1.0	0.7	0.7	7.8	0.9	10.8	0.5	14.5	1.0	14.9	1.2
AGRI	1/20/2005	10.6	1.3	0.7	0.7	7.1	0.8	3.5	0.2	2.7	0.2	2.8	0.2
AGRI	1/21/2005	10.4	1.2	0.7	0.7	8.7	1.0	5.3	0.2	4.7	0.3	4.3	0.4
AGRI	1/28/2005	34.6	4.1	0.7	0.7	33.1	3.7	18.0	0.8	47.8	3.2	44.2	3.7
AGRI	1/29/2005	15.3	1.8	0.7	0.7	13.7	1.5	17.1	0.7	24.0	1.6	22.2	1.8
AGRI	1/30/2005	14.0	1.7	0.7	0.7	12.1	1.4	8.9	0.4	8.7	0.6	8.2	0.7
AGRI	1/31/2005	15.8	1.9	0.7	0.7	12.2	1.4	11.1	0.5	10.0	0.7	10.6	0.9
AGRI	2/1/2005	20.0	2.4	0.7	0.7	14.6	1.6	15.4	0.7	20.4	1.4	19.0	1.6
AGRI	2/2/2005	11.3	1.3	0.7	0.7	9.4	1.1	8.4	0.4	7.9	0.5	9.7	0.8
AGRI	2/3/2005	12.0	1.4	0.7	0.7	9.1	1.0	5.9	0.3	5.7	0.4	5.6	0.5
AGRI	2/4/2005												
INDU	1/15/2005	10.3	1.2	1.0	0.2	7.2	0.8	3.3	0.1	3.6	0.2	3.4	0.3
INDU	1/16/2005	68.3	8.1	4.1	1.0	86.2	9.7	28.2	1.2	50.8	3.4	43.9	3.6
INDU	1/17/2005	157.0	18.7	4.0	1.0	207.9	23.3	58.8	2.5	105.3	7.0	82.9	6.9
INDU	1/18/2005	28.7	3.4	1.8	0.4	41.2	4.6	11.5	0.5	27.1	1.8	23.6	2.0
INDU	1/19/2005	14.4	1.7	1.8	0.4	15.3	1.7	11.8	0.5	9.9	0.7	10.7	0.9
INDU	1/20/2005	6.7	0.8	2.1	0.5	6.8	0.8	2.7	0.1	0.5	0.0	2.5	0.2
INDU	1/21/2005												
INDU	1/28/2005												
INDU	1/29/2005	27.7	3.3	0.7	0.7	32.4	3.6	14.0	0.6	16.6	1.1	16.4	1.4
INDU	1/30/2005	22.9	2.7	2.2	0.5	27.2	3.0	12.8	0.6	12.8	0.8	13.0	1.1
INDU	1/31/2005	10.2	1.2	2.1	0.5	11.2	1.3	6.8	0.3	3.8	0.3	5.6	0.5
INDU	2/1/2005	14.5	1.7	3.1	0.7	17.4	1.9	11.5	0.5	7.3	0.5	8.9	0.7
INDU	2/2/2005												
INDU	2/3/2005	12.8	1.5	1.7	0.4	14.9	1.7	10.2	0.4	7.0	0.5	8.8	0.7
INDU	2/4/2005	15.6	1.9	5.1	1.2	17.9	2.0	10.8	0.5	9.0	0.6	10.8	0.9
POLI	1/15/2005	10.7	1.3	0.7	0.7	9.1	1.0	10.5	0.5	11.4	0.8	11.7	1.0
POLI	1/16/2005	21.5	2.6	0.7	0.7	22.2	2.5	45.2	2.0	46.6	3.1	40.9	3.4
POLI	1/17/2005	92.6	11.0	0.7	0.7	96.2	10.8	177.2	7.7	193.1	12.8	152.2	12.6
POLI	1/18/2005	31.3	3.7	0.7	0.7	27.1	3.0	37.2	1.6	39.1	2.6	35.7	3.0
POLI	1/19/2005	9.8	1.2	0.7	0.7	8.9	1.0	16.0	0.7	21.2	1.4	21.3	1.8
POLI	1/20/2005	11.5	1.4	0.7	0.7	8.0	0.9	4.7	0.2	2.9	0.2	3.3	0.3
POLI	1/21/2005	11.3	1.4	0.7	0.7	8.5	1.0	4.4	0.2	3.2	0.2	3.4	0.3
POLI	1/28/2005	102.1	12.2	0.7	0.7	105.1	11.8	201.8	8.7	185.7	12.3	143.2	11.9
POLI	1/29/2005	36.7	4.4	0.7	0.7	38.2	4.3	36.4	1.6	57.1	3.8	49.7	4.1
POLI	1/30/2005	20.5	2.4	0.7	0.7	17.7	2.0	18.1	0.8	25.9	1.7	23.9	2.0
POLI	1/31/2005	13.4	1.6	0.7	0.7	11.5	1.3	9.3	0.4	10.3	0.7	10.4	0.9
POLI	2/1/2005	12.9	1.5	0.7	0.7	11.3	1.3	12.3	0.5	12.5	0.8	12.5	1.0
POLI	2/2/2005	16.3	1.9	0.7	0.7	14.7	1.6	16.0	0.7	20.1	1.3	19.1	1.6
POLI	2/3/2005	8.1	1.0	0.7	0.7	6.9	0.8	7.0	0.3	7.6	0.5	8.3	0.7
POLI	2/4/2005												
TRAF	1/15/2005	11.5	1.4	1.2	0.3	10.2	1.1	5.9	0.3	6.0	0.4	7.1	0.6
TRAF	1/16/2005	44.1	5.3	0.7	0.7	45.2	5.1	22.6	1.0	27.8	1.8	23.6	2.0
TRAF	1/17/2005	123.3	14.7	1.3	0.3	127.4	14.3	57.4	2.5	68.3	4.5	56.2	4.7
TRAF	1/18/2005	47.8	5.7	1.5	0.4	47.3	5.3	8.5	0.4	29.7	2.0	26.7	2.2
TRAF	1/19/2005	18.9	2.3	1.5	0.4	20.9	2.3	8.6	0.4	12.0	0.8	12.4	1.0
TRAF	1/20/2005	6.4	0.8	1.6	0.4	4.6	0.5	1.8	0.1	1.4	0.1	1.9	0.2
TRAF	1/21/2005	9.1	1.1	0.7	0.7	7.2	0.8	2.6	0.1	3.4	0.2	3.9	0.3
TRAF	1/28/2005			0.7	0.7								
TRAF	1/29/2005	62.1	7.4	0.7	0.7	61.8	6.9	20.5	0.9	28.4	1.9	26.8	2.2
TRAF	1/30/2005	28.9	3.4	0.7	0.7	31.6	3.5	10.2	0.4	16.6	1.1	15.1	1.2
TRAF	1/31/2005	12.3	1.5	0.7	0.7	10.5	1.2	3.6	0.2	4.1	0.3	5.6	0.5
TRAF	2/1/2005	19.9	2.4	4.3	1.0	17.4	1.9	7.2	0.3	9.5	0.6	10.1	0.8
TRAF	2/2/2005	28.9	3.5	0.7	0.7	33.9	3.8	13.8	0.6	17.4	1.2	17.1	1.4
TRAF	2/3/2005	12.3	1.5	0.7	0.7	14.7	1.6	6.0	0.3	7.8	0.5	7.6	0.6
TRAF	2/4/2005												
ZAKO	1/15/2005	197.2	23.5	1.2	0.3	188.5	21.1	8.5	0.4	91.1	6.1	71.3	5.9
ZAKO	1/16/2005	235.5	28.1	1.4	0.3	228.8	25.6	101.3	4.4	103.0	6.8	84.1	7.0
ZAKO	1/17/2005	293.9	35.1	3.1	0.7	283.4	31.7	107.1	4.6	122.8	8.2	100.5	8.3
ZAKO	1/18/2005	138.7	16.5	1.8	0.4	142.4	15.9	12.7	0.5	63.0	4.2	53.3	4.4
ZAKO	1/19/2005	45.0	5.4	1.8	0.4	40.8	4.6	12.7	0.5	18.0	1.2	14.9	1.2
ZAKO	1/20/2005	25.8	3.1	1.3	0.3	23.1	2.6	9.7	0.4	9.3	0.6	8.1	0.7
ZAKO	1/21/2005	101.9	12.2	1.3	0.3	97.8	10.9	56.2	2.4	64.4	4.3	54.5	4.5
ZAKO	1/22/2005	31.0	3.7	1.3	0.3	25.8	2.9	11.5	0.5	10.4	0.7	9.7	0.8
ZAKO	1/23/2005	59.3	7.1	1.9	0.5	53.6	6.0	22.8	1.0	26.0	1.7	21.3	1.8
ZAKO	2/1/2005												
ZAKO	2/2/2005												
ZAKO	2/3/2005												
ZAKO	2/4/2005												
ZAKO	2/5/2005												
ZAKO	2/6/2005												
HOUSE10	1/18/2005	18.27	2.18	0.7	0.7	16.28	1.82	17.08	0.74	16.09	1.07	16.19	1.34
HOUSE10	1/20/2005	4.03	0.48	0.7	0.7	4.08	0.46	2.80	0.12	1.93	0.13	2.57	0.21
HOUSE10	1/21/2005												
HOUSE15	2/1/2005	11.72	1.40	0.7	0.7	12.05	1.35	10.25	0.44	8.89	0.59	7.88	0.65
HOUSE15	2/2/2005	13.03	1.55	0.7	0.7	11.03	1.23	9.96	0.43	12.35	0.82	13.90	1.15
HOUSE15	2/3/2005	10.38	1.24	0.7	0.7	8.10	0.91	4.72	0.20	5.62	0.37	6.82	0.57
HOUSE17	2/1/2005	6.88	0.82	0.7	0.7	7.85	0.88	4.79	0.21	4.34	0.29	4.60	0.38
HOUSE17	2/2/2005	17.47	2.08	0.7	0.7	15.19	1.70	9.26	0.40	9.22	0.61	9.97	0.83
HOUSE17	2/3/2005	12.79	1.53	0.7	0.7	9.18	1.03	4.73	0.20	5.57	0.37	7.37	0.61
HOUSE3	1/18/2005	25.02	2.98	0.7	0.7	25.11	2.81	22.39	0.97	26.42	1.76	25.73	2.13
HOUSE3	1/19/2005	17.77	2.12	0.7	0.7	15.43	1.73	10.59	0.46	16.55	1.10	14.75	1.22
HOUSE3	1/20/2005	5.47	0.65	0.7	0.7	4.86	0.54	2.98	0.13	2.79	0.19	2.58	0.21

	DATE	BBFLU	UBBFLU	BKFLU	UBKFLU	BEPYR	UBEPYR	BAPYR	UBAPYR	PERYL	UPERYL	IN123	UIN123	DBAHA
AGRI	1/15/2005	18.4	0.8	10.8	0.2	8.1	0.4	13.1	0.4	2.4	0.1	13.3	0.4	3.5
AGRI	1/17/2005	92.8	3.9	92.9	2.1	57.0	2.5	126.0	4.1	15.1	0.5	114.7	3.5	14.3
AGRI	1/18/2005	49.8	2.1	44.8	1.0	26.2	1.2	53.9	1.7	6.4	0.2	50.2	1.5	9.1
AGRI	1/19/2005	24.3	1.0	23.6	0.5	14.9	0.7	24.3	0.8	6.4	0.2	21.3	0.6	8.1
AGRI	1/20/2005	6.4	0.3	3.9	0.1	3.1	0.1	5.0	0.2	0.8	0.0	11.7	0.4	2.0
AGRI	1/21/2005	7.1	0.3	5.7	0.1	4.3	0.2	7.7	0.2	1.1	0.0	10.6	0.3	1.7
AGRI	1/28/2005	48.6	2.0	59.0	1.3	33.7	1.5	59.6	1.9	7.4	0.3	51.7	1.6	19.6
AGRI	1/29/2005	28.1	1.2	29.6	0.7	18.2	0.8	30.0	1.0	7.3	0.3	27.1	0.8	11.3
AGRI	1/30/2005	19.4	0.8	13.5	0.3	9.6	0.4	11.0	0.4	2.9	0.1	10.3	0.3	4.6
AGRI	1/31/2005	18.9	0.8	18.8	0.4	13.5	0.6	17.2	0.6	4.5	0.2	16.3	0.5	7.5
AGRI	2/1/2005	34.6	1.5	32.3	0.7	20.2	0.9	32.7	1.1	5.1	0.2	31.5	0.9	14.2
AGRI	2/2/2005	18.2	0.8	17.1	0.4	13.4	0.6	15.5	0.5	4.0	0.1	16.3	0.5	7.3
AGRI	2/3/2005	13.7	0.6	8.7	0.2	6.5	0.3	7.1	0.2	1.9	0.1	7.0	0.2	3.6
AGRI	2/4/2005													
INDU	1/15/2005	4.7	0.2	4.7	0.1	2.8	0.1	5.0	0.2	0.9	0.0	3.1	0.1	0.7
INDU	1/16/2005	39.6	1.7	41.7	0.9	25.9	1.2	46.2	1.5	7.5	0.3	25.5	0.8	5.9
INDU	1/17/2005	84.7	3.6	85.7	1.9	47.8	2.1	87.3	2.8	11.9	0.4	48.2	1.5	10.2
INDU	1/18/2005	34.5	1.4	28.7	0.6	18.8	0.8	29.7	1.0	3.5	0.1	17.5	0.5	4.8
INDU	1/19/2005	16.7	0.7	15.8	0.4	9.6	0.4	12.9	0.4	3.6	0.1	9.6	0.3	3.0
INDU	1/20/2005	5.9	0.2	5.0	0.1	4.3	0.2	3.0	0.1	0.6	0.0	2.4	0.1	1.8
INDU	1/21/2005													
INDU	1/28/2005													
INDU	1/29/2005	20.3	0.9	20.5	0.5	12.0	0.5	18.0	0.6	4.8	0.2	11.7	0.4	3.4
INDU	1/30/2005	19.1	0.8	16.8	0.4	10.6	0.5	13.0	0.4	3.9	0.1	9.6	0.3	3.2
INDU	1/31/2005	8.1	0.3	9.1	0.2	6.7	0.3	6.0	0.2	1.5	0.1	4.5	0.1	2.1
INDU	2/1/2005	16.4	0.7	14.5	0.3	9.7	0.4	11.4	0.4	3.0	0.1	7.6	0.2	2.9
INDU	2/2/2005													
INDU	2/3/2005	12.7	0.5	11.2	0.3	8.6	0.4	9.5	0.3	3.8	0.1	7.0	0.2	3.0
INDU	2/4/2005	17.0	0.7	14.3	0.3	10.3	0.5	12.8	0.4	5.5	0.2	7.9	0.2	2.8
POLI	1/15/2005	23.9	1.0	21.0	0.5	15.0	0.7	24.8	0.8	4.7	0.2	23.4	0.7	6.1
POLI	1/16/2005	56.1	2.4	48.0	1.1	31.4	1.4	57.3	1.8	10.6	0.4	63.8	1.9	10.3
POLI	1/17/2005	169.2	7.1	156.8	3.5	102.0	4.6	235.4	7.6	31.7	1.1	166.8	5.0	25.7
POLI	1/18/2005	66.7	2.8	58.0	1.3	38.2	1.7	73.6	2.4	17.6	0.6	76.1	2.3	24.7
POLI	1/19/2005	39.1	1.6	34.5	0.8	22.9	1.0	41.3	1.3	8.7	0.3	45.3	1.4	13.2
POLI	1/20/2005	7.4	0.3	4.9	0.1	3.8	0.2	6.7	0.2	1.2	0.0	13.3	0.4	2.1
POLI	1/21/2005	8.4	0.4	4.9	0.1	4.1	0.2	6.9	0.2	1.2	0.0	15.4	0.5	2.5
POLI	1/28/2005	176.6	7.4	167.0	3.7	104.2	4.7	266.1	8.6	40.5	1.4	269.6	8.1	36.2
POLI	1/29/2005	76.4	3.2	55.2	1.2	36.8	1.6	79.6	2.6	12.3	0.4	96.2	2.9	12.7
POLI	1/30/2005	41.6	1.7	32.4	0.7	23.0	1.0	45.5	1.5	7.8	0.3	55.5	1.7	16.1
POLI	1/31/2005	17.1	0.7	15.7	0.4	12.5	0.6	16.3	0.5	3.8	0.1	19.9	0.6	7.3
POLI	2/1/2005	24.2	1.0	21.2	0.5	14.5	0.6	24.3	0.8	6.1	0.2	26.4	0.8	12.6
POLI	2/2/2005	38.1	1.6	28.8	0.6	19.9	0.9	35.9	1.2	7.1	0.2	39.9	1.2	17.5
POLI	2/3/2005	18.7	0.8	14.5	0.3	12.2	0.5	15.7	0.5	3.8	0.1	16.2	0.5	7.3
POLI	2/4/2005													
TRAF	1/15/2005	11.5	0.5	8.9	0.2	7.1	0.3	8.8	0.3	11.0	0.4	6.5	0.2	2.8
TRAF	1/16/2005	26.9	1.1	25.3	0.6	15.6	0.7	26.0	0.8	5.7	0.2	17.3	0.5	4.3
TRAF	1/17/2005	50.9	2.1	55.9	1.3	31.0	1.4	65.8	2.1	12.3	0.4	33.0	1.0	7.3
TRAF	1/18/2005	28.9	1.2	32.0	0.7	18.2	0.8	38.0	1.2	2.9	0.1	19.1	0.6	5.0
TRAF	1/19/2005	16.3	0.7	15.8	0.4	9.9	0.4	14.7	0.5	2.9	0.1	9.2	0.3	3.1
TRAF	1/20/2005	2.8	0.1	2.7	0.1	1.9	0.1	2.1	0.1	0.7	0.0	1.9	0.1	0.5
TRAF	1/21/2005	5.3	0.2	4.9	0.1	3.6	0.2	4.3	0.1	0.9	0.0	3.7	0.1	0.7
TRAF	1/28/2005													
TRAF	1/29/2005	28.8	1.2	29.1	0.7	16.1	0.7	27.2	0.9	6.7	0.2	18.9	0.6	4.5
TRAF	1/30/2005	20.0	0.8	17.2	0.4	11.1	0.5	16.7	0.5	3.5	0.1	10.5	0.3	3.8
TRAF	1/31/2005	9.4	0.4	7.8	0.2	5.6	0.2	5.9	0.2	1.4	0.0	4.8	0.1	2.4
TRAF	2/1/2005	14.3	0.6	14.8	0.3	8.6	0.4	12.0	0.4	2.6	0.1	8.5	0.3	3.1
TRAF	2/2/2005	20.0	0.8	20.9	0.5	13.1	0.6	21.0	0.7	4.0	0.1	12.7	0.4	4.0
TRAF	2/3/2005	10.4	0.4	11.5	0.3	7.0	0.3	11.8	0.4	2.2	0.1	8.9	0.3	1.6
TRAF	2/4/2005													
ZAKO	1/15/2005	67.7	2.8	66.1	1.5	40.8	1.8	85.6	2.8	13.9	0.5	49.2	1.5	16.9
ZAKO	1/16/2005	78.6	3.3	71.4	1.6	48.2	2.2	102.0	3.3	16.5	0.6	64.8	2.0	18.2
ZAKO	1/17/2005	91.9	3.9	91.9	2.1	55.7	2.5	123.1	4.0	18.8	0.7	76.9	2.3	19.9
ZAKO	1/18/2005	46.7	2.0	50.4	1.1	28.9	1.3	60.4	1.9	3.2	0.1	39.4	1.2	14.5
ZAKO	1/19/2005	15.1	0.6	11.3	0.3	9.4	0.4	14.6	0.5	3.2	0.1	10.0	0.3	9.5
ZAKO	1/20/2005	9.4	0.4	7.5	0.2	5.6	0.2	7.2	0.2	1.5	0.1	6.0	0.2	8.7
ZAKO	1/21/2005	59.8	2.5	54.6	1.2	35.9	1.6	76.6	2.5	12.0	0.4	44.5	1.3	16.0
ZAKO	1/22/2005	13.0	0.5	9.8	0.2	7.3	0.3	12.2	0.4	2.5	0.1	8.5	0.3	9.3
ZAKO	1/23/2005	25.5	1.1	23.6	0.5	14.6	0.7	27.3	0.9	15.3	0.5	16.0	0.5	10.1
ZAKO	2/1/2005													
ZAKO	2/2/2005													
ZAKO	2/3/2005													
ZAKO	2/4/2005													
ZAKO	2/5/2005													
ZAKO	2/6/2005													
HOUSE10	1/18/2005	2.60	0.11	25.75	0.58	14.84	0.66	35.59	1.15	5.86	0.21	25.43	0.77	3.51
HOUSE10	1/20/2005	3.44	0.14	3.09	0.07	1.96	0.09	3.66	0.12	1.36	0.05	3.72	0.11	1.15
HOUSE10	1/21/2005													
HOUSE15	2/1/2005	12.67	0.53	12.92	0.29	7.80	0.35	17.38	0.56	3.43	0.12	16.44	0.50	2.05
HOUSE15	2/2/2005	27.40	1.15	24.45	0.55	15.80	0.71	29.98	0.97	5.05	0.18	30.54	0.92	2.81
HOUSE15	2/3/2005	13.71	0.58	10.32	0.23	7.18	0.32	11.22	0.36	2.66	0.09	13.02	0.39	1.85
HOUSE17	2/1/2005	7.37	0.31	6.43	0.14	4.41	0.20	9.07	0.29	2.11	0.07	8.67	0.26	1.37
HOUSE17	2/2/2005	15.97	0.67	13.55	0.30	9.32	0.42	13.22	0.43	3.38	0.12	13.46	0.41	2.37
HOUSE17	2/3/2005	14.31	0.60	9.11	0.20	6.84	0.31	12.09	0.39	2.42	0.09	12.38	0.37	1.74
HOUSE3	1/18/2005	41.32	1.73	41.10	0.92	24.20	1.08	55.70	1.80	6.72	0.24	36.25	1.09	3.15
HOUSE3	1/19/2005	22.18	0.93	19.79	0.44	11.97	0.53	23.66	0.76	4.33	0.15	23.16	0.70	2.46
HOUSE3	1/20/2005	3.89	0.16	3.58	0.08	2.41	0.11	4.45	0.14	1.57	0.06	4.52	0.14	1.33

	DATE	UDBAHA	BGPER	UBGPER	COR	UCOR	ACRID	UACRID	PANTR	UPANTR	BCACR	UBCACR	DBAHAC	UDBAHAC
AGRI	1/15/2005	0.0	12.9	0.4	27.9	1.3	1.3	0.1	1.4	0.1	0.9	0.1	0.1	0.1
AGRI	1/17/2005	0.2	63.3	1.9	94.4	4.3	16.9	1.2	13.0	0.6	6.6	0.4	0.1	0.1
AGRI	1/18/2005	0.1	29.7	0.9	54.8	2.5	3.2	0.2	2.3	0.1	1.5	0.1	0.1	0.1
AGRI	1/19/2005	0.1	16.4	0.5	38.3	1.7	2.1	0.1	2.3	0.1	1.5	0.1	0.1	0.1
AGRI	1/20/2005	0.0	5.6	0.2	18.1	0.8	0.6	0.6	0.6	0.0	0.7	0.0	0.1	0.1
AGRI	1/21/2005	0.0	5.9	0.2	15.6	0.7	1.3	0.1	1.5	0.1	0.7	0.0	0.1	0.1
AGRI	1/28/2005	0.3	37.6	1.1	81.7	3.7	6.0	0.4	7.9	0.3	3.5	0.2	0.1	0.1
AGRI	1/29/2005	0.2	20.8	0.6	43.7	2.0	9.3	0.7	8.6	0.4	4.3	0.3	0.1	0.1
AGRI	1/30/2005	0.1	15.8	0.5	33.4	1.5	3.3	0.2	3.3	0.1	1.7	0.1	0.1	0.1
AGRI	1/31/2005	0.1	13.8	0.4	33.4	1.5	4.4	0.3	2.5	0.1	2.2	0.1	0.1	0.1
AGRI	2/1/2005	0.2	22.1	0.7	41.3	1.9	8.6	0.6	6.9	0.3	4.5	0.3	0.1	0.1
AGRI	2/2/2005	0.1	13.0	0.4	34.8	1.6	4.2	0.3	3.1	0.1	2.2	0.1	0.1	0.1
AGRI	2/3/2005	0.1	11.3	0.3	31.8	1.4	0.6	0.6	0.6	0.6	1.2	0.1	0.1	0.1
AGRI	2/4/2005													
INDU	1/15/2005	0.0	3.1	0.1	3.8	0.2	0.6	0.6	0.6	0.0	0.6	0.6	1.9	0.1
INDU	1/16/2005	0.1	25.3	0.8	33.4	1.5	0.6	0.6	1.0	0.0	7.3	0.4	0.1	0.1
INDU	1/17/2005	0.1	49.1	1.5	64.0	2.9	13.0	0.9	18.3	0.8	8.3	0.5	0.1	0.1
INDU	1/18/2005	0.1	18.6	0.6	24.5	1.1	4.8	0.3	3.9	0.2	1.8	0.1	0.1	0.1
INDU	1/19/2005	0.0	9.9	0.3	14.7	0.7	3.5	0.2	4.0	0.2	1.9	0.1	4.1	0.2
INDU	1/20/2005	0.0	2.2	0.1	7.2	0.3	0.6	0.6	0.6	0.6	0.6	0.0	0.1	0.1
INDU	1/21/2005													
INDU	1/28/2005													
INDU	1/29/2005	0.0	12.5	0.4	18.9	0.9	3.4	0.2	4.3	0.2	2.4	0.1	5.6	0.3
INDU	1/30/2005	0.0	10.2	0.3	15.9	0.7	3.0	0.2	5.7	0.3	2.5	0.1	5.9	0.3
INDU	1/31/2005	0.0	4.8	0.1	9.6	0.4	0.6	0.6	0.6	0.6	1.1	0.1	2.5	0.1
INDU	2/1/2005	0.0	7.8	0.2	12.6	0.6	0.6	0.6	0.6	0.6	1.9	0.1	3.0	0.2
INDU	2/2/2005													
INDU	2/3/2005	0.0	8.0	0.2	9.8	0.4	2.9	0.2	3.2	0.1	1.9	0.1	5.3	0.3
INDU	2/4/2005	0.0	8.7	0.3	10.7	0.5	3.4	0.2	3.3	0.1	2.2	0.1	8.0	0.5
POLI	1/15/2005	0.1	16.7	0.5	37.3	1.7	2.5	0.2	3.4	0.1	1.6	0.1	0.1	0.1
POLI	1/16/2005	0.1	39.7	1.2	60.9	2.8	8.2	0.6	7.4	0.3	4.4	0.3	0.1	0.1
POLI	1/17/2005	0.4	114.4	3.4	141.6	6.4	31.7	2.2	29.9	1.3	15.4	0.9	0.1	0.1
POLI	1/18/2005	0.3	48.7	1.5	96.5	4.4	11.7	0.8	5.7	0.3	5.1	0.3	0.1	0.1
POLI	1/19/2005	0.2	29.3	0.9	52.3	2.4	5.9	0.4	6.4	0.3	2.9	0.2	0.1	0.1
POLI	1/20/2005	0.0	7.1	0.2	19.6	0.9	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.1
POLI	1/21/2005	0.0	8.3	0.2	21.3	1.0	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.1
POLI	1/28/2005	0.5	145.8	4.4	246.6	11.2	22.3	1.6	18.3	0.8	16.3	0.9	24.4	1.4
POLI	1/29/2005	0.2	49.1	1.5	89.0	4.0	10.9	0.8	9.5	0.4	6.7	0.4	22.8	1.3
POLI	1/30/2005	0.2	34.3	1.0	69.5	3.2	6.4	0.4	4.8	0.2	4.9	0.3	22.2	1.3
POLI	1/31/2005	0.1	16.0	0.5	36.8	1.7	0.6	0.6	0.6	0.6	1.6	0.1	0.1	0.1
POLI	2/1/2005	0.2	19.3	0.6	42.2	1.9	4.4	0.3	4.9	0.2	3.0	0.2	0.1	0.1
POLI	2/2/2005	0.2	23.6	0.7	44.3	2.0	6.7	0.5	5.9	0.3	4.8	0.3	0.1	0.1
POLI	2/3/2005	0.1	14.5	0.4	36.6	1.7	2.5	0.2	3.1	0.1	1.7	0.1	0.1	0.1
POLI	2/4/2005													
TRAF	1/15/2005	0.0	6.7	0.2	14.4	0.7	1.2	0.1	0.6	0.6	1.0	0.1	2.9	0.2
TRAF	1/16/2005	0.1	17.5	0.5	28.8	1.3	3.5	0.2	0.6	0.6	3.1	0.2	6.5	0.4
TRAF	1/17/2005	0.1	33.2	1.0	58.6	2.7	9.6	0.7	15.9	0.7	3.1	0.2	0.1	0.1
TRAF	1/18/2005	0.1	19.5	0.6	32.1	1.5	5.0	0.4	4.4	0.2	1.7	0.1	5.2	0.3
TRAF	1/19/2005	0.0	9.2	0.3	17.0	0.8	2.8	0.2	4.5	0.2	1.7	0.1	2.9	0.2
TRAF	1/20/2005	0.0	2.1	0.1	2.9	0.1	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.1
TRAF	1/21/2005	0.0	4.1	0.1	5.1	0.2	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.1
TRAF	1/28/2005													
TRAF	1/29/2005	0.1	17.9	0.5	26.5	1.2	7.1	0.5	10.5	0.5	3.6	0.2	5.3	0.3
TRAF	1/30/2005	0.1	11.2	0.3	17.0	0.8	3.0	0.2	4.5	0.2	2.1	0.1	4.7	0.3
TRAF	1/31/2005	0.0	4.9	0.1	9.6	0.4	1.6	0.1	2.6	0.1	1.0	0.1	0.1	0.1
TRAF	2/1/2005	0.0	8.9	0.3	14.3	0.6	0.6	0.6	0.6	0.0	1.4	0.1	3.7	0.2
TRAF	2/2/2005	0.1	13.9	0.4	23.2	1.1	4.0	0.3	5.5	0.2	2.3	0.1	5.8	0.3
TRAF	2/3/2005	0.0	8.6	0.3	10.7	0.5	1.2	0.1	3.2	0.1	1.2	0.1	3.5	0.2
TRAF	2/4/2005													
ZAKO	1/15/2005	0.2	46.3	1.4	81.7	3.7	12.3	0.9	18.8	0.8	9.3	0.5	25.6	1.4
ZAKO	1/16/2005	0.3	52.6	1.6	94.7	4.3	21.0	1.5	23.0	1.0	25.6	1.5	40.3	2.3
ZAKO	1/17/2005	0.3	82.7	2.5	107.6	4.9	21.3	1.5	25.2	1.1	11.1	0.6	43.9	2.5
ZAKO	1/18/2005	0.2	34.9	1.0	58.6	2.7	13.8	1.0	3.1	0.1	1.7	0.1	0.1	0.1
ZAKO	1/19/2005	0.1	13.1	0.4	21.5	1.0	2.1	0.2	3.1	0.1	1.7	0.1	5.6	0.3
ZAKO	1/20/2005	0.1	8.7	0.3	12.1	0.5	0.6	0.6	0.6	0.6	1.3	0.1	0.1	0.1
ZAKO	1/21/2005	0.2	40.0	1.2	68.7	3.1	11.0	0.8	14.4	0.6	7.3	0.4	18.6	1.1
ZAKO	1/22/2005	0.1	11.2	0.3	15.4	0.7	0.6	0.6	0.6	0.6	1.4	0.1	0.1	0.1
ZAKO	1/23/2005	0.1	18.4	0.6	28.3	1.3	4.4	0.3	4.9	0.2	3.1	0.2	8.6	0.5
ZAKO	2/1/2005													
ZAKO	2/2/2005													
ZAKO	2/3/2005													
ZAKO	2/4/2005													
ZAKO	2/5/2005													
ZAKO	2/6/2005													
HOUSE10	1/18/2005	0.05	22.17	0.66	3.58	0.16	5.30	0.37	0.6	0.6	2.83	0.17	9.58	0.54
HOUSE10	1/20/2005	0.02	3.00	0.09	5.01	0.23	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.1
HOUSE10	1/21/2005						0.6	0.6	0.6	0.6				
HOUSE15	2/1/2005	0.03	13.62	0.41	19.86	0.90	0.6	0.6	0.6	0.6	1.32	0.08	0.1	0.1
HOUSE15	2/2/2005	0.04	28.64	0.86	47.98	2.18	0.6	0.6	0.6	0.6	1.71	0.10	10.13	0.57
HOUSE15	2/3/2005	0.03	12.32	0.37	26.20	1.19	0.6	0.6	0.6	0.6	1.33	0.08	7.50	0.42
HOUSE17	2/1/2005	0.02	7.15	0.21	9.79	0.44	0.6	0.6	0.6	0.6	1.03	0.06	0.1	0.1
HOUSE17	2/2/2005	0.03	13.96	0.42	26.41	1.20	0.6	0.6	0.6	0.6	1.87	0.11	0.1	0.1
HOUSE17	2/3/2005	0.02	11.01	0.33	23.13	1.05	0.6	0.6	0.6	0.6	1.36	0.08	0.1	0.1
HOUSE3	1/18/2005	0.04	33.82	1.01	47.28	2.14	4.14	0.29	3.72	0.16	2.81	0.16	0.1	0.1
HOUSE3	1/19/2005	0.03	18.40	0.55	36.42	1.65	0.6	0.6	0.6	0.6	2.13	0.12	0.1	0.1
HOUSE3	1/20/2005	0.02	3.70	0.11	6.11	0.28	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.1

SOURCE	TYPE	OC	UOC	SOOT	USOOT	NO3	UNO3	SO4	USO4
N1, N2, N10	Residential coal combustion	613873	175573	365100	156798	198	55	6230	5090
N5, N6, N9	Residential wood combustion	896312	52608	66540	69934	2533	2919	8651	6310
N20, N21	Power plant coal combustion	51305	4247	1499	10	30374	4310	61277	41401
N14	Industial power plant, coal (and coke-gas) combustion	44943	9483	1400	235	37504	682	27983	4326
N13	Blast furnace	80810	22866	5625	113	0	1301	20436	2253
N11	Iron ore sinter plant	433273	24324	14828	460	43349	1166	67370	8521
N12	Industial power plant, coke-gas (and coal) combustion	572740	120848	17968	3019	15858	458	19777	3044
N19	Cement kiln (coal fired)	266775	56290	7674	1289	3402	209	102844	15897
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	417993	186839	16821	8969	8953	12196	141943	35299
N16-1, N16-11	Coke plant fugitive emissions	613187	179120	97372	40023	30500	29341	19099	6477
N8	Commercial boilers 5MW (Heavy fuel oil)	252819	53345	8427	1416	185261	3234	137816	4698
N15	Basic oxygen furnace steel plant (coke)	554412	181824	17638	5542	28851	4746	31705	10681
N18	Production of fire proof material for steel production (natural gas)	145416	35038	3765	805	800	227	289004	19725

SOURCE	TYPE	CL	UCL	BR	UBR	NH4	UNH4	NA	UNA
N1, N2, N10	Residential coal combustion	6308	9254	96	124	476	170	2708	2725
N5, N6, N9	Residential wood combustion	4314	3707	8	7	605	309	1362	1183
N20, N21	Power plant coal combustion	197760	16982	3096	636	11828	96	7024	1311
N14	Industial power plant, coal (and coke-gas) combustion	89578	5193	1373	70	7325	169	12628	666
N13	Blast furnace	3402	492	53	6	1808	348	5235	1346
N11	Iron ore sinter plant	140600	8282	1322	69	37545	474	0	0
N12	Industial power plant, coke-gas (and coal) combustion	17931	1429	251	13	1939	116	6560	472
N19	Cement kiln (coal fired)	109893	6371	156	8	11573	267	9995	328
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	14576	20351	184	137	2759	1153	46025	37438
N16-1, N16-11	Coke plant fugitive emissions	20022	6324	257	117	120157	10244	19214	7424
N8	Commercial boilers 5MW (Heavy fuel oil)	11650	610	8	9	2683	657	58130	3097
N15	Basic oxygen furnace steel plant (coke)	95736	7144	785	48	38402	1389	46772	5278
N18	Production of fire proof material for steel production (natural gas)	41207	3512	504	26	2442	65	24628	659

SOURCE	TYPE	K	UK	CA	UCA	MGO	UMGO	SI	USI
N1, N2, N10	Residential coal combustion	843	1103	39	67	0	0	156	78
N5, N6, N9	Residential wood combustion	11059	11678	2461	3373	222	303	298	219
N20, N21	Power plant coal combustion	5618	2222	50410	9819	15531	693	26280	8336
N14	Industial power plant, coal (and coke-gas) combustion	10886	716	30388	1631	18243	458	129036	8652
N13	Blast furnace	14181	881	163	215	8	93	2241	657
N11	Iron ore sinter plant	98373	5301	23548	1276	9288	245	3133	1285
N12	Industial power plant, coke-gas (and coal) combustion	5546	504	21688	1244	4387	114	44314	4240
N19	Cement kiln (coal fired)	25602	2847	386055	20188	1591	42	26787	2451
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	28498	19420	14378	5504	2754	1526	47662	39839
N16-1, N16-11	Coke plant fugitive emissions	3092	4373	4264	2959	2043	46	2821	250
N8	Commercial boilers 5MW (Heavy fuel oil)	0	368	12057	1110	5745	250	1419	1334
N15	Basic oxygen furnace steel plant (coke)	8470	1369	62974	3994	22145	746	1550	2609
N18	Production of fire proof material for steel production (natural gas)	191946	10608	175466	9143	474	20	6874	2312

SOURCE	TYPE	CU	UCU	V	UV	MN	UMN	PB	UPB
N1, N2, N10	Residential coal combustion	6	10	0	0	4	6	127	95
N5, N6, N9	Residential wood combustion	29	44	1	1	41	11	19	9
N20, N21	Power plant coal combustion	153	67	339	114	4635	179	191	58
N14	Industial power plant, coal (and coke-gas) combustion	133	53	451	133	3839	393	481	29
N13	Blast furnace	269	23	26	112	888	880	144	15
N11	Iron ore sinter plant	47083	2385	25	14	711	64	14492	731
N12	Industial power plant, coke-gas (and coal) combustion	74	16	116	46	580	113	200	12
N19	Cement kiln (coal fired)	36	5	64	18	289	27	297	16
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	1585	1077	276	228	245	103	6343	4834
N16-1, N16-11	Coke plant fugitive emissions	8	12	17	25	47	66	1298	372
N8	Commercial boilers 5MW (Heavy fuel oil)	11	51	2419	141	49	56	81	20
N15	Basic oxygen furnace steel plant (coke)	736	214	0	64	4176	292	1127	78
N18	Production of fire proof material for steel production (natural gas)	41	10	9	9	97	12	6611	333

SOURCE	TYPE	FE	UFE	AL	UAL	ZN	UZN	TI	UTI
N1, N2, N10	Residential coal combustion	0	0	452	67	84	86	2	3
N5, N6, N9	Residential wood combustion	0	0	720	327	437	472	16	28
N20, N21	Power plant coal combustion	178380	19410	49682	7563	3175	1819	1394	409
N14	Industial power plant, coal (and coke-gas) combustion	158299	8034	58565	7788	1313	72	4977	302
N13	Blast furnace	596484	30314	1916	1001	3857	197	338	100
N11	Iron ore sinter plant	29508	1550	4219	1821	48601	2459	76	28
N12	Industial power plant, coke-gas (and coal) combustion	26942	1425	39366	7228	645	37	1460	99
N19	Cement kiln (coal fired)	7256	404	18609	3790	357	19	1029	69
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	13428	11897	58211	46382	12117	9124	3681	2858
N16-1, N16-11	Coke plant fugitive emissions	0	0	4086	4210	1606	2053	43	60
N8	Commercial boilers 5MW (Heavy fuel oil)	0	2634	4119	2166	6221	379	3	84
N15	Basic oxygen furnace steel plant (coke)	11880	4187	3950	4037	105168	5333	1	155
N18	Production of fire proof material for steel production (natural gas)	236	183	8617	3843	5410	274	140	25

SOURCE	TYPE	NI	UNI	BA	UBA	SR	USR	CR	UCR
N1, N2, N10	Residential coal combustion	34	48	0	0	2	2	69	102
N5, N6, N9	Residential wood combustion	52	89	9	6	11	8	16	26
N20, N21	Power plant coal combustion	10867	1050	448	57	219	35	46570	6006
N14	Industial power plant, coal (and coke-gas) combustion	10467	536	1697	194	638	33	30569	1578
N13	Blast furnace	108	31	13	171	0	5	215	244
N11	Iron ore sinter plant	1217	80	43	215	66	9	16	19
N12	Industial power plant, coke-gas (and coal) combustion	2046	106	473	89	248	13	5952	318
N19	Cement kiln (coal fired)	27	22	240	43	379	19	30	13
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	433	221	1770	1141	1234	731	276	219
N16-1, N16-11	Coke plant fugitive emissions	6	8	55	44	85	74	186	115
N8	Commercial boilers 5MW (Heavy fuel oil)	1394	82	94	388	126	13	110	47
N15	Basic oxygen furnace steel plant (coke)	8634	464	456	769	904	56	379	92
N18	Production of fire proof material for steel production (natural gas)	26	12	0	51	165	10	63	10

SOURCE	TYPE	SB	USB	SN	USN	RB	URB	ZR	UZR
N1, N2, N10	Residential coal combustion	4	2	2	0	4	7	1	0
N5, N6, N9	Residential wood combustion	4	1	3	0	22	23	1	1
N20, N21	Power plant coal combustion	61	5	48	13	134	7	77	17
N14	Industial power plant, coal (and coke-gas) combustion	52	33	35	26	170	12	175	12
N13	Blast furnace	30	39	29	31	119	9	10	5
N11	Iron ore sinter plant	13	53	1	38	1758	91	57	9
N12	Industial power plant, coke-gas (and coal) combustion	29	18	19	14	72	5	58	4
N19	Cement kiln (coal fired)	12	8	5	6	480	24	57	4
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	299	221	419	335	306	223	145	103
N16-1, N16-11	Coke plant fugitive emissions	232	227	111	61	32	46	37	34
N8	Commercial boilers 5MW (Heavy fuel oil)	77	87	26	68	0	13	11	10
N15	Basic oxygen furnace steel plant (coke)	239	176	207	137	209	33	64	24
N18	Production of fire proof material for steel production (natural gas)	13	12	2	9	1189	61	29	3

SOURCE	TYPE	MO	UMO	AS	UAS	SE	USE	CD	UCD
N1, N2, N10	Residential coal combustion	5	8	0	0	6	8	2	1
N5, N6, N9	Residential wood combustion	0	0	1	1	0	0	13	9
N20, N21	Power plant coal combustion	885	239	42	5	22	13	9	13
N14	Industial power plant, coal (and coke-gas) combustion	424	33	51	8	17	4	17	15
N13	Blast furnace	0	25	45	7	16	4	4	17
N11	Iron ore sinter plant	0	23	0	34	18	6	438	41
N12	Industial power plant, coke-gas (and coal) combustion	137	19	30	3	11	1	38	9
N19	Cement kiln (coal fired)	0	8	15	3	1	1	8	4
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	80	76	554	534	48	24	66	49
N16-1, N16-11	Coke plant fugitive emissions	0	0	42	60	12	4	79	52
N8	Commercial boilers 5MW (Heavy fuel oil)	1	95	29	10	5	4	35	40
N15	Basic oxygen furnace steel plant (coke)	0	183	7	25	7	10	340	86
N18	Production of fire proof material for steel production (natural gas)	6	9	14	14	5	2	209	14

SOURCE	TYPE	GA	UGA	FLUO	UFLUO	DMPHE	UDMPHE	PYR	UPYR
N1, N2, N10	Residential coal combustion	1	1	2048	1918	32	12	1514	1456
N5, N6, N9	Residential wood combustion	0	0	1681	1843	3	4	1508	1630
N20, N21	Power plant coal combustion	57	1	51	0	23	4	27	1
N14	Industial power plant, coal (and coke-gas) combustion	103	10	55	8	20	12	29	5
N13	Blast furnace	28	10	144	21	0	1	57	10
N11	Iron ore sinter plant	20	64	579	86	1	1	399	67
N12	Industial power plant, coke-gas (and coal) combustion	48	4	1531	226	128	74	640	108
N19	Cement kiln (coal fired)	14	2	28	5	6	4	14	3
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	1195	1125	481	692	1	0	200	253
N16-1, N16-11	Coke plant fugitive emissions	48	49	8289	3912	210	210	7299	4788
N8	Commercial boilers 5MW (Heavy fuel oil)	6	10	100	16	1	1	59	11
N15	Basic oxygen furnace steel plant (coke)	32	50	157	24	1	2	105	19
N18	Production of fire proof material for steel production (natural gas)	42	15	10	3	3	3	8	2

SOURCE	TYPE	CPCDP	UCPCDP	BAANT	UBAANT	CHRYS	UCHRYS	BBFLU	UBBFLU
N1, N2, N10	Residential coal combustion	277	344	571	580	498	435	483	489
N5, N6, N9	Residential wood combustion	186	257	271	345	271	330	227	293
N20, N21	Power plant coal combustion	11	2	6	2	5	0	9	1
N14	Industial power plant, coal (and coke-gas) combustion	11	3	7	1	7	1	10	1
N13	Blast furnace	31	7	11	2	13	2	23	3
N11	Iron ore sinter plant	74	16	222	33	216	25	183	21
N12	Industial power plant, coke-gas (and coal) combustion	92	19	36	6	40	5	62	7
N19	Cement kiln (coal fired)	4	1	3	1	3	1	3	1
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	53	35	42	54	50	63	68	90
N16-1, N16-11	Coke plant fugitive emissions	3044	1582	8415	5292	9092	6859	4600	709
N8	Commercial boilers 5MW (Heavy fuel oil)	58	13	18	4	15	3	31	4
N15	Basic oxygen furnace steel plant (coke)	85	19	28	5	29	5	49	7
N18	Production of fire proof material for steel production (natural gas)	3	2	2	1	3	2	3	2

SOURCE	TYPE	BKFLU	UBKFLU	BEPYR	UBEPYR	BAPYR	UBAPYR	PERYL	UPERYL
N1, N2, N10	Residential coal combustion	403	384	255	252	479	586	84	91
N5, N6, N9	Residential wood combustion	227	293	128	163	343	460	62	79
N20, N21	Power plant coal combustion	4	1	5	1	5	1	0	0
N14	Industial power plant, coal (and coke-gas) combustion	5	1	6	1	6	1	0	0
N13	Blast furnace	4	1	10	2	4	1	20	2
N11	Iron ore sinter plant	171	19	124	18	197	40	61	7
N12	Industial power plant, coke-gas (and coal) combustion	31	4	36	5	32	7	5	1
N19	Cement kiln (coal fired)	1	1	2	1	2	1	0	0
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	64	104	38	52	34	46	12	11
N16-1, N16-11	Coke plant fugitive emissions	3502	752	2895	137	4402	2045	1267	483
N8	Commercial boilers 5MW (Heavy fuel oil)	5	1	15	3	15	4	35	4
N15	Basic oxygen furnace steel plant (coke)	7	2	24	4	26	6	53	7
N18	Production of fire proof material for steel production (natural gas)	1	1	2	1	1	1	0	0

SOURCE	TYPE	IN123	UIN123	DBAHA	UDBAHA	BGPER	UBGPER	COR	UCOR
N1, N2, N10	Residential coal combustion	321	376	79	63	268	292	413	492
N5, N6, N9	Residential wood combustion	216	292	20	14	169	224	357	489
N20, N21	Power plant coal combustion	7	1	12	3	7	1	13	2
N14	Industial power plant, coal (and coke-gas) combustion	7	2	11	1	7	2	15	4
N13	Blast furnace	8	2	31	3	21	4	72	16
N11	Iron ore sinter plant	152	36	78	8	132	27	269	61
N12	Industial power plant, coke-gas (and coal) combustion	46	11	83	8	47	10	114	26
N19	Cement kiln (coal fired)	2	1	3	0	2	1	4	1
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	62	89	35	23	56	69	143	155
N16-1, N16-11	Coke plant fugitive emissions	2628	1249	475	327	2509	1367	2310	1423
N8	Commercial boilers 5MW (Heavy fuel oil)	23	6	52	5	34	7	84	20
N15	Basic oxygen furnace steel plant (coke)	38	9	79	8	56	12	189	44
N18	Production of fire proof material for steel production (natural gas)	2	1	2	1	2	1	6	2

SOURCE	TYPE	ACRID	UACRID	PANTR	UPANTR	BCACR	UBCACR	DBAHAC	UDBAHAC
N1, N2, N10	Resindential coal combustion	102	102	114	100	60	58	32	28
N5, N6, N9	Residential wood combustion	12	3	12	3	15	6	3	2
N20, N21	Power plant coal combustion	10	1	10	1	10	1	2	0
N14	Industial power plant, coal (and coke-gas) combustion	10	13	10	12	10	12	2	2
N13	Blast furnace	12	14	12	14	12	14	2	3
N11	Iron ore sinter plant	22	27	22	27	50	33	4	5
N12	Industial power plant, coke-gas (and coal) combustion	21	26	21	26	21	26	4	5
N19	Cement kiln (coal fired)	13	15	13	15	13	15	3	3
N3, N4, N7	Commercial boilers <5MW coal combustion, cyclon	22	6	22	6	22	6	4	1
N16-1, N16-11	Coke plant fugitive emissions	1523	1842	2035	2603	1193	924	190	67
N8	Commercial boilers 5MW (Heavy fuel oil)	30	37	30	37	30	37	6	7
N15	Basic oxygen furnace steel plant (coke)	44	54	44	53	44	53	9	11
N18	Production of fire proof material for steel production (natural gas)	40	49	40	49	40	49	8	10

Appendix 5. Quality control of the dataset.

It is well-known, that a major part of the uncertainty of chemical measurements may derive from sampling artifacts. A good indication of a correct PM sampling for the present study is obtained when the gravimetric PM_{10} data obtained from the samplers equipped with quartz filters is compared with the data obtained in parallel with the samplers using nitrocellulose filters (PM_{10} (Quartz) = 0.98 x PM_{10} (nitrocellulose) + 4.0, R^2 = 0.96; Fig, AP5.1). This indication is corroborated by the comparison of the present PM_{10} data with data obtained with different sampling techniques available from the official monitoring network (MVIE), and from parallel measurements by mobile laboratories (Jimenez and Neidzialek, 2006; Putaud et al., 2008; Marelli et al., 2008) which were all in very good agreements.
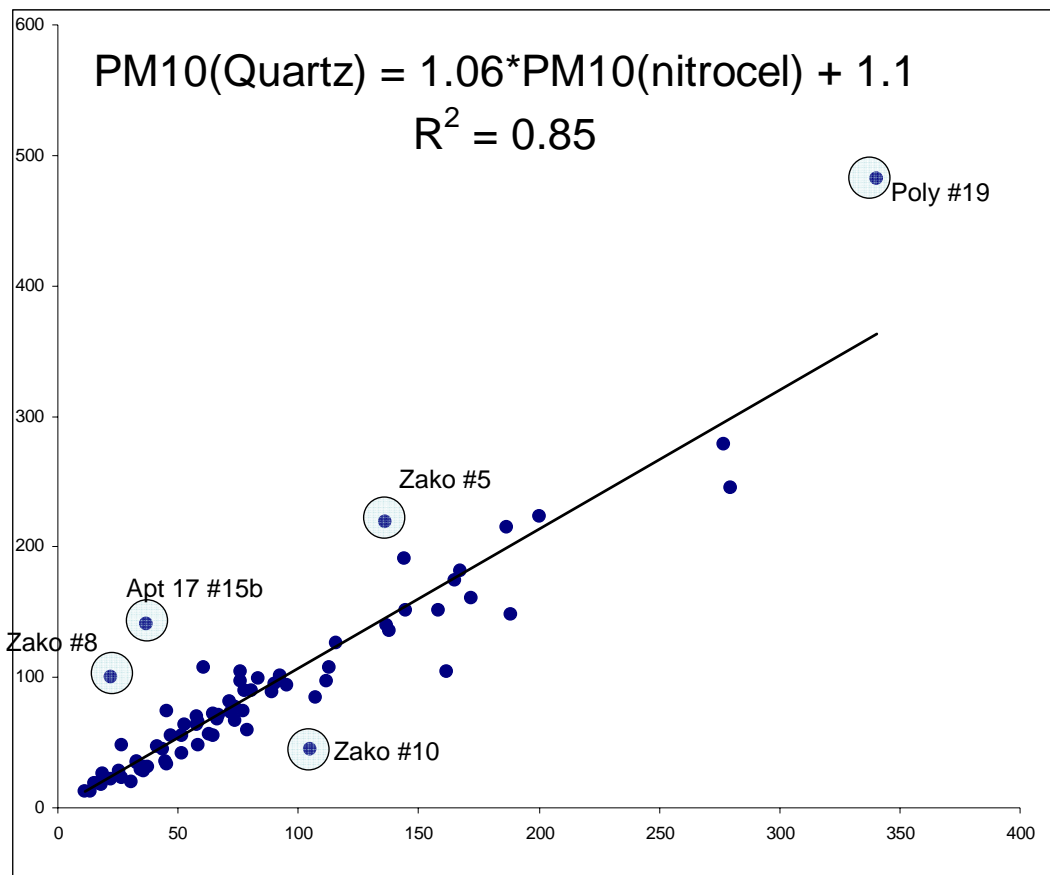
Figure AP5.1 – Comparison of PM10 data obtained with quartz filters and nitrocellulose filters. Five outliers were excluded, from the data set.

As a control of the data quality various approaches were followed. An overall control of the chemical analysis was achieved by mass balancing the gravimetric sum of all analyzed compounds with the collected mass of PM, which, with the exclusion of five outliers, was always better than better than 85% and strongly linearly correlated (PM-mass (μg/m^3) = 0.95 x Sum of chemical compounds + 1.2 (μg/m^3), R^2 = 0.94; Fig. AP5.2).
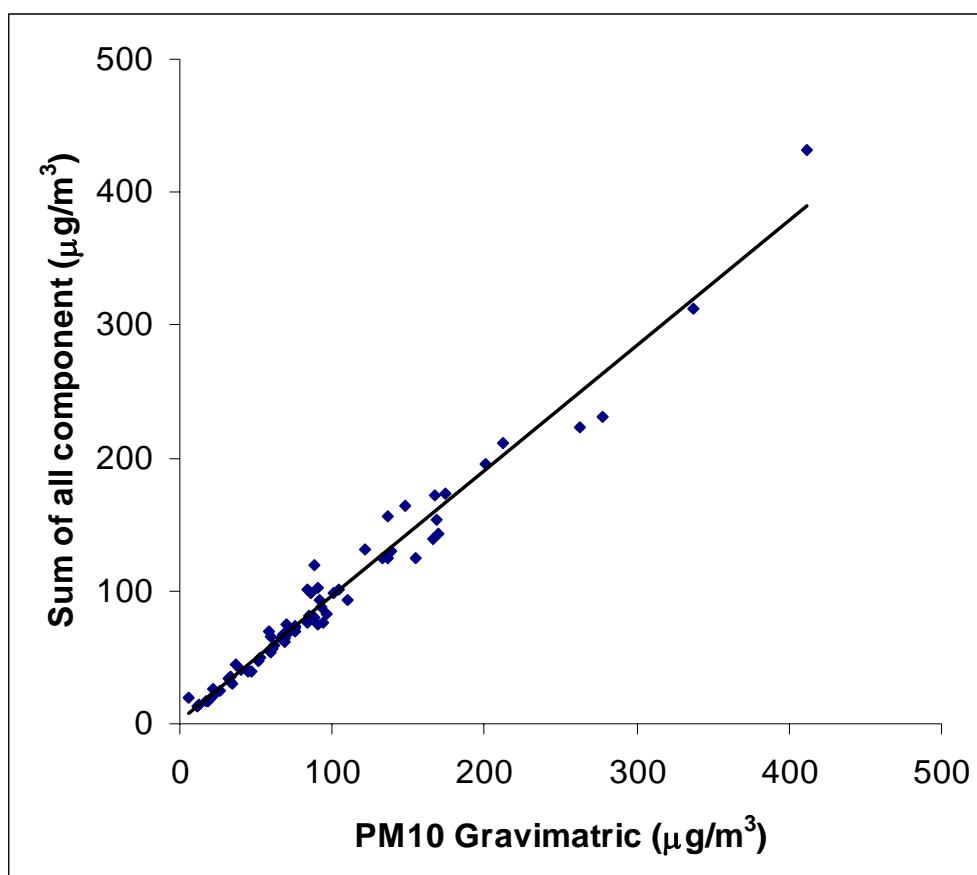
Figure AP5.2 – Mass balance for all receptor samples..

Another overall quality control was obtained by the ion-balance, which indicated that all major anions and cations have been taken into account (Sum of cations (mol/m^3) = 0.94 x Sum of anions (mol/m^3) + 0.00004 (mol/m^3), R^2 = 0.91; Fig, AP5.3). The minor ion discrepancy may be explained by carbonate, which is not analyzed in the present study. Following the regression data the amount of carbonate compared to other anions cannot be more than 3%.
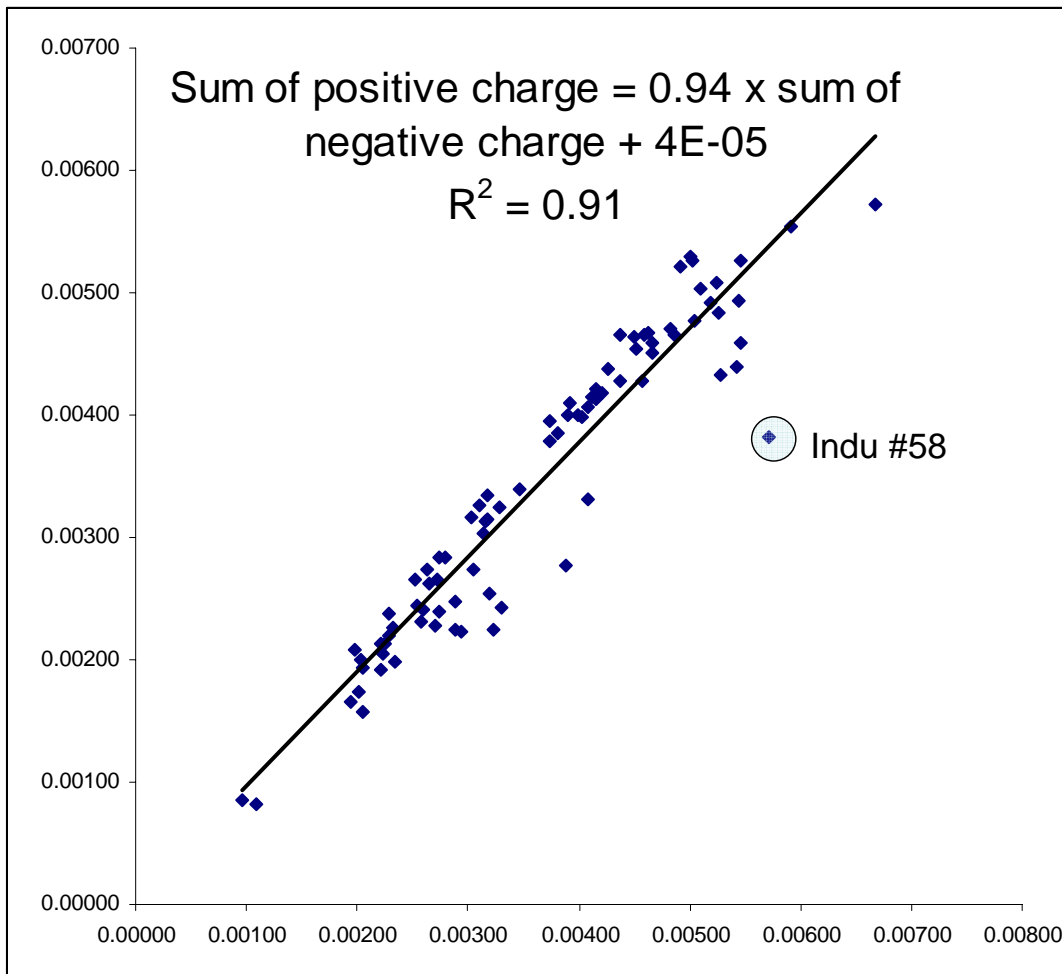
Figure AP5.3 The ion-balance, for all Krakow filters. One outlier was excluded from the data set.

In addition, the results obtained by different methods for individual compounds determined were in good agreement. Thus, the concentration data on Cl obtained by PIXE and Cl^- obtained by IC were well correlated, when it is taken into account that during PIXE analysis the thermal energy developed by the proton beam is known to cause evaporative losses for halogens (Cl-PIXE ($\mu g/m^3$) = 0.85 x Cl^- ($\mu g/m^3$) + 0.4 ($\mu g/m^3$), R^2 = 0.98; Fig. AP5.4).
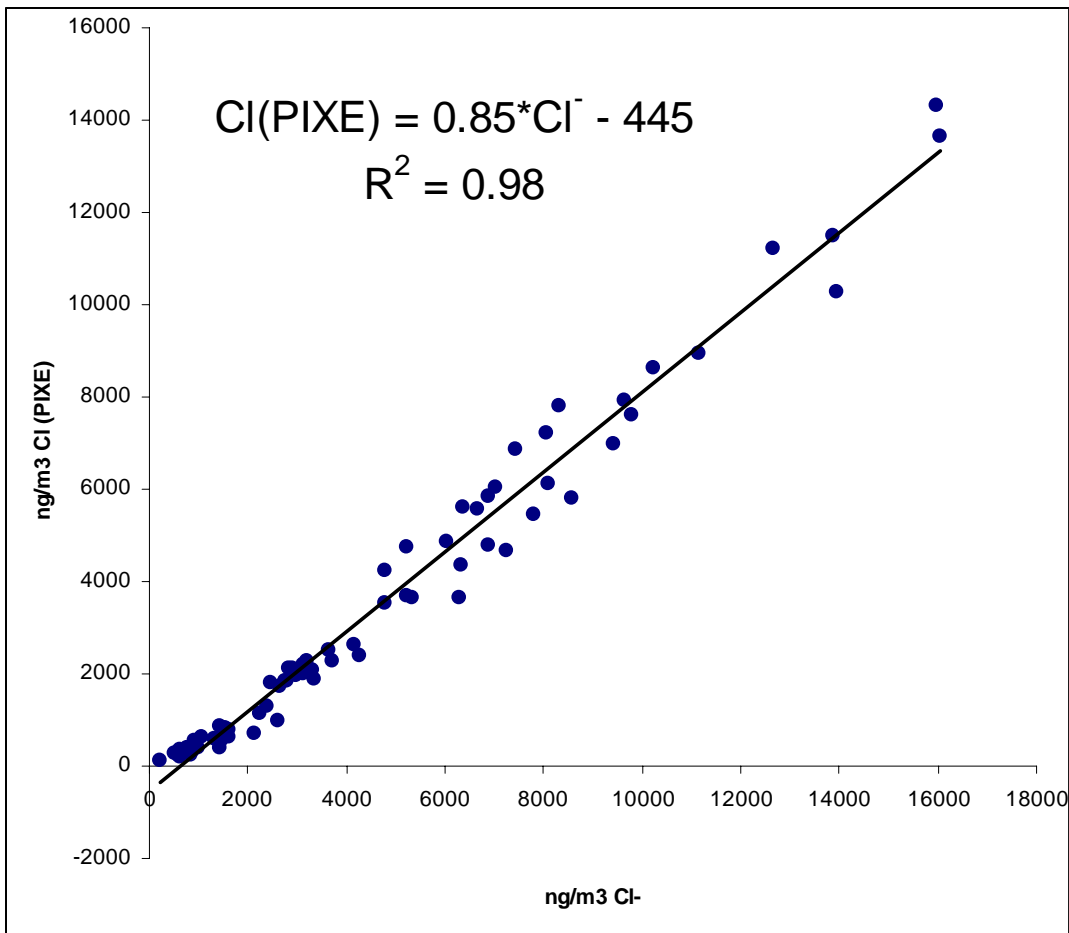
Figure AP5.4 – Comparison of Cl measured with PIXE and Cl⁻ measured with IC.

Moreover, the concentration data for sulfur obtained by PIXE was only slightly higher than the sulfur data derived from sulfate by IC. (S-PIXE (μg/m^3) = 1.15 x S-IC (μg/m^3) + 0.08 (μg/m^3), R^2 = 0.90). However a higher spread for samples with the large concentrations of sulfur indicated a strong heteroscedaficity in the data set and when the regression was done on the logarithmic form a homeoscedafic nearly perfect correlation was obtained (Y = 1.01 x X, R^2 = 0.98, with the slope being statistically non-significant from unity).
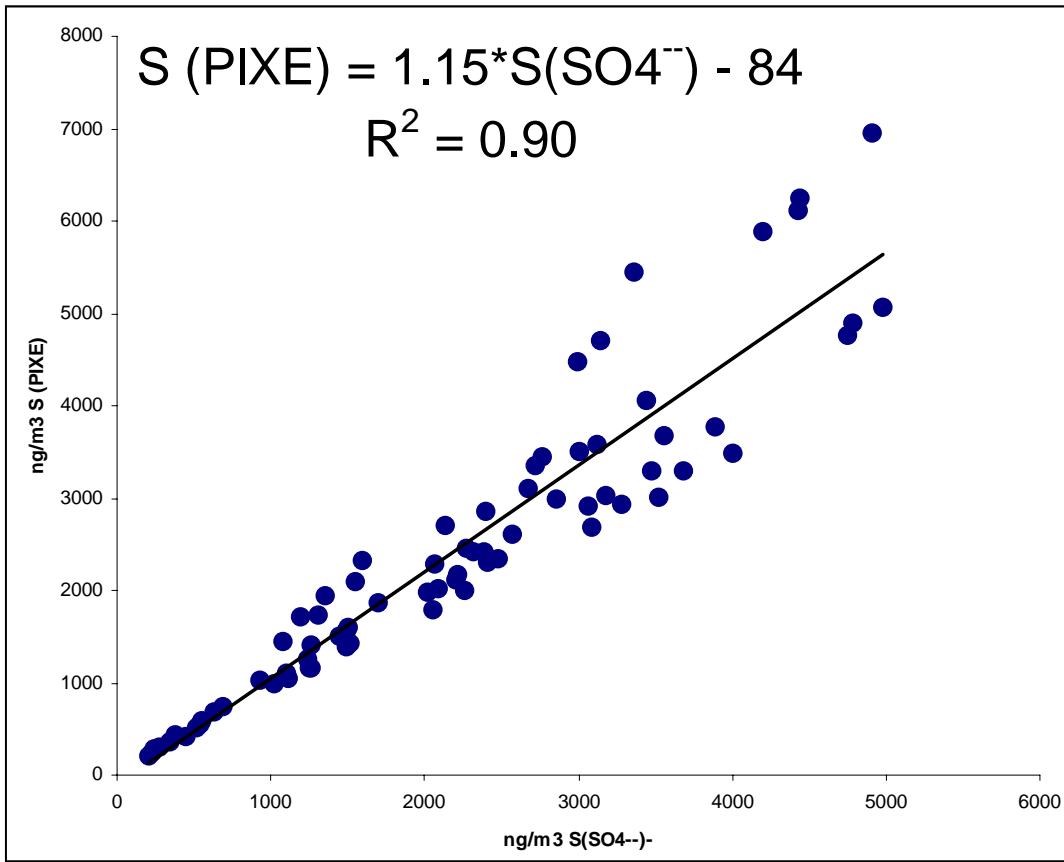
Figure AP5.5 – Comparison of S measured with PIXE and S(SO4⁻) measured with IC.

Appendix 6. PCA and apportionment analysis with data for metals as their oxides.

Table 1   Factor loadings for four latent factors (all variables). Marked loading will be
               commented Total explained variance: 84.81%

	Factor 1	Factor 2	Factor 3	Factor4
OC	0.367	**0.853**	0.144	0.015
SOOT	<u>0.614</u>	<u>0.661</u>	0.019	-0.022
NO3	0.375	0.132	**0.858**	-0.080
SO4	0.384	0.187	**0.766**	-0.065
CL	**0.665**	0.457	0.390	0.277
BR	<u>0.585</u>	<u>0.589</u>	0.341	0.344
NH4	0.423	0.388	**0.764**	0.010
NA	0.206	0.110	0.456	0.213
K	**0.738**	0.478	0.322	0.143
CACO3	**0.929**	0.237	0.003	0.011
MGO	**0.842**	-0.023	0.190	0.184
SIO2	**0.926**	0.309	0.001	-0.048
FE2O3	**0.909**	0.107	0.195	0.145
AL2O3	**0.909**	0.361	0.092	-0.044
ZNO	**0.760**	0.503	0.340	-0.008
TIO2	**0.933**	0.269	0.053	-0.055
CUO	**0.862**	0.043	0.266	0.214
V2O5	**0.885**	0.219	0.271	-0.036
MNO2	**0.863**	0.416	0.078	-0.044
PBO	**0.699**	0.407	0.497	0.078
NI2O	**0.752**	0.181	0.216	0.004
BAO	**0.899**	0.172	0.110	0.0503
SRO	**0.685**	0.099	-0.069	0.097
CR2O3	**0.707**	0.170	0.307	-0.189
SB2O3	**0.833**	0.190	0.302	0.080
SNO2	**0.838**	0.251	0.305	0.119
RB2O	**0.696**	0.291	0.404	0.265
ZRO2	**0.913**	0.187	0.098	0.033
MOO3	**0.834**	0.327	0.049	-0.079
AS2O3	-0.086	0.083	**0.739**	0.170
SEO2	**0.602**	0.360	0.435	0.117
CDO	**0.729**	0.348	0.449	0.008
GA2O3	<u>0.496</u>	0.290	<u>0.547</u>	-0.270
FLUO	0.068	<u>0.666</u>	0.031	<u>0.679</u>
DMPHE	0.158	-0.100	0.093	**0.719**
PYR	0.130	0.644	0.059	**0.695**
CPCDP	0.303	**0.901**	0.060	0.017

	Factor 1	Factor 2	Factor 3	Factor4
BAANT	0.344	**0.908**	0.093	0.180
CHRYS	0.348	**0.905**	0.112	0.174
BBFLU	0.328	**0.917**	0.168	0.006
BKFLU	0.351	**0.911**	0.156	0.052
BEPYR	0.331	**0.924**	0.149	0.022
BAPYR	0.302	**0.936**	0.101	-0.015
PERYL	0.276	**0.909**	0.152	-0.034
IN123	0.193	**0.911**	0.150	-0.203
DBAHA	0.042	**0.884**	0.219	-0.052
BGPER	0.240	**0.949**	0.120	-0.021
COR	0.134	**0.939**	0.180	-0.093
ACRID	0.253	**0.892**	0.170	0.145
PANTR	0.245	**0.824**	0.152	0.303
BCACR	0.083	**0.852**	0.101	0.281
DBAHAC	-0.323	**0.623**	0.074	0.492
Expl. Var. %	36.1	33.6	10.0	5.13

The first step of chemometric data treatment was performance of Principal component Analysis (PCA) in order to identify the latent factors responsible for the data structure. The data of all sampling sites were involved with deletion of rows (days) with missing data. It seems that four latent factors which explain nearly 85% of the total variance are easily interpreted:

Factor 1: Indication of strong correlation between variables (Si, Ti, Al, Ca, Mg etc.) related to soil and paved road dust sources confirms the assumption that this is a "soil and paved road dust" emission source. Additionally, the high factor loadings for V, Pb and Se and moderate loadings for Br, Cl and SOOT assume that Factor 1 is related partially also to stationary and mobile combustion sources.

Factor 2: Indication of strong correlation between variables OC, almost all PAH species and to high extent SOOT and Br related to combustion emission sources.

Factor 3: Indication of strong correlation between variables NH4, SO4 and NO3 obviously related to secondary emission sources. A special comment needs the high factor loadings for As usually being tracer for coal combustion (see high concentration of As in the Commercial boilers <5MW coal combustion, cyclon).

Factor 4: It explains only 5.13% of the total variance and will be not specifically commented. Probably it explains some minor effect of combustion or traffic sources with tracers DMPHE, PYR and FLUO. It could be also effect of insufficient uncertainty (high RSD%, especially DMPHE – 50%). That is why Factor 4 was eliminated for apportioning analysis.

The same procedure was applied to all inorganic variables and the sum of all PAH species. The results confirmed completely the conclusions made above.

Table 2   Factor loadings for four latent factors (all variables). Marked loading will be commented Total explained variance: 81.00%

	Factor 1	Factor 2	Factor 3
OC	0.264	0.221	**0.874**
SOOT	0.517	0.106	**0.758**
NO3	0.286	**0.887**	0.095
SO4	0.296	**0.799**	0.163
CL	<u>0.557</u>	0.496	<u>0.537</u>
BR	0.467	0.445	**0.685**
NH4	0.297	**0.814**	0.405
NA	0.131	0.498	0.139
K	**0.657**	0.428	0.520
CACO3	**0.905**	0.106	0.306
MGO	**0.846**	0.292	-0.010
SIO2	**0.885**	0.100	0.397
FE2O3	**0.889**	0.303	0.150
AL2O3	**0.855**	0.193	0.438
ZNO	**0.662**	0.434	0.564
TIO2	**0.900**	0.152	0.339
CUO	**0.815**	0.365	0.145
V2O5	**0.833**	0.365	0.271
MNO2	**0.796**	0.178	0.501
PBO	<u>0.596</u>	<u>0.586</u>	0.456
NI2O	**0.712**	0.302	0.224
BAO	**0.864**	0.207	0.263
SRO	**0.692**	0.010	0.149
CR2O3	**0.663**	0.373	0.185
SB2O3	**0.759**	0.389	0.301
SNO2	**0.767**	0.403	0.344
RB2O	**0.642**	0.509	0.301
ZRO2	**0.881**	0.200	0.260
MOO3	0.778	0.136	0.422
AS2O3	-0.136	0.744	-0.011
SEO2	0.513	0.510	0.421
CDO	0.629	0.532	0.414
GA2O3	0.401	0.583	0.305
PAH	0.149	0.209	**0.928**
Expl. Var. %	44.1	19.1	17.8

The principle explanation of observed system does not change substantially if three hidden factors are involved. In the case *Factor 1* is "soil and paved road dust", *Factor 2* is "secondary emission" and *Factor 3* is "combustion". The apportioning was performed according to the procedure of Thurston and Spengler (G. Thurston and J. Spengler:1985. "A Quantative Assessment of Source Contributions to Inhalable Particulate Matter Pollution in Metropolitan Boston"; *Atmospheric Environment*, Vol. 19, (1985), pp.9-15.) resembling so called APCS apportioning.

Table 3 Source contribution to the total concentration of each species in % (the columns OBS and EST are in $ng.m^{-3}$)

Analyte	Intcpt	Factor 1	Factor 2	Factor 3	EST	OBS	R^2
OC	32.77	6.12	29.50	31.61	49935.2	50042.4	0.882
SOOT	23.25	23.25		53.50	11939.0	11949.7	0.842
NO3		5.17	94.83		4448.54	4437.12	0.869
SO4		5.75	94.25		5693.01	5765.23	0.727
CL		14.22	64.61	21.18	4220.10	4056.80	0.842
BR		11.80	61.01	27.19	23.31	22.79	0.884
NH4		5.47	82.89	11.63	4189.89	4033.62	0.915
NA	43.21		56.79		967.85	965.29	0.248
K		16.15	63.73	20.12	649.51	652.46	0.885
CACO3	28.67	46.65		24.68	2538.51	2539.18	0.913
MGO	25.88	24.30	49.82		326.45	326.28	0.802
SIO2		44.98	23.70	31.32	1841.08	1802.10	0.951
FE2O3		34.21	57.48	8.31	1537.64	1477.59	0.902
AL2O3		31.67	42.85	25.48	783.52	784.28	0.960
ZNO		16.81	60.85	22.33	339.68	334.06	0.944
TIO2		35.27	43.42	21.32	45.68	46.88	0.946
Analyte	Intcpt	Factor 1	Factor 2	Factor 3	EST	OBS	R^2
CUO		28.30	71.70		54.21	53.57	0.797
V2O5		21.70	66.47	11.83	4.52	4.63	0.897
MNO2		33.70	33.47	32.83	40.46	38.98	0.913

Analyte	Intcpt	Factor 1	Factor 2	Factor 3	EST	OBS	R^2
PBO		12.87	71.78	15.34	91.79	90.59	0.907
NI2O		22.71	65.40	11.89	2.86	2.97	0.647
BAO		33.70	50.09	16.21	17.53	17.63	0.859
SRO	76.52	23.48			6.01	6.01	0.479
CR2O3		22.65	77.35		13.77	13.87	0.579
SB2O3		24.08	61.64	14.28	10.20	9.81	0.815
SNO2		22.44	62.09	15.46	6.75	6.57	0.867
RB2O		15.53	73.08	11.39	4.26	4.26	0.762
ZRO2		38.32	44.39	17.30	5.61	5.52	0.883
MOO3		52.85		47.15	2.98	3.52	0.783
AS2O3			100.00		1.64	1.71	0.554
SEO2		11.56	73.48	14.96	3.08	3.11	0.699
CDO		14.44	70.46	15.10	2.73	2.71	0.851
Analyte	**Intcpt**	**Factor 1**	**Factor 2**	**Factor 3**	**EST**	**OBS**	**R^2**
GA2O3		9.40	80.15	10.45	1.63	1.65	0.593
PAH		5.18	44.53	50.28	388.83	391.02	0.928

Legend to the table: Intct means intercept of the regression model and presents the % of unexplained concentration. OBS and EST mean observed and estimated by the model. The lines marked in red indicate the non-adequate models.

Principal component analysis

Soil and road dust…   **Factor 1**   … possible additives of
traffic and combustion
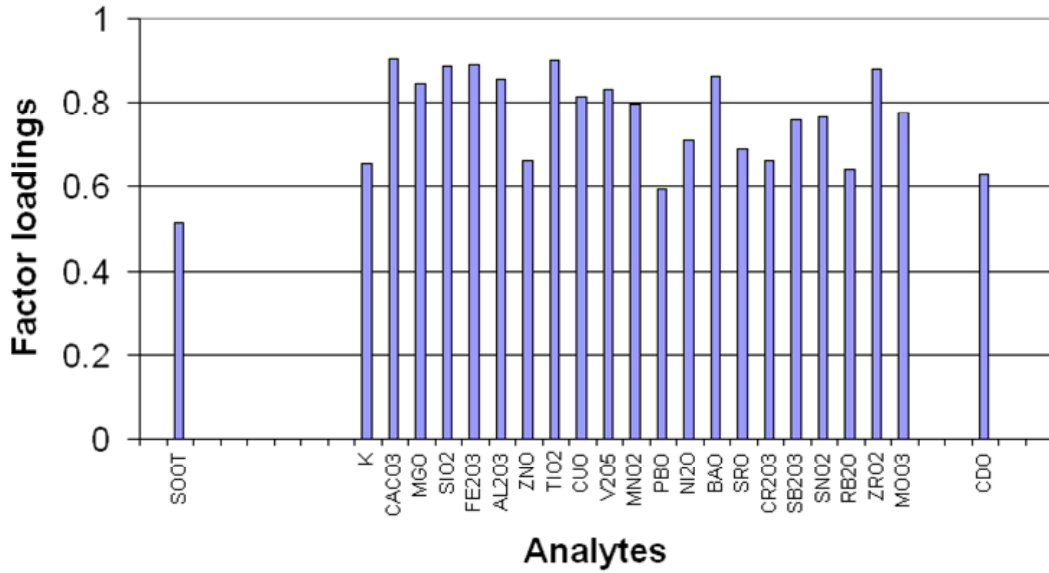
Principal component analysis

Secondary emission…   **Factor 2**   … possible diffusion transfer
of combustion products

Principal component analysis
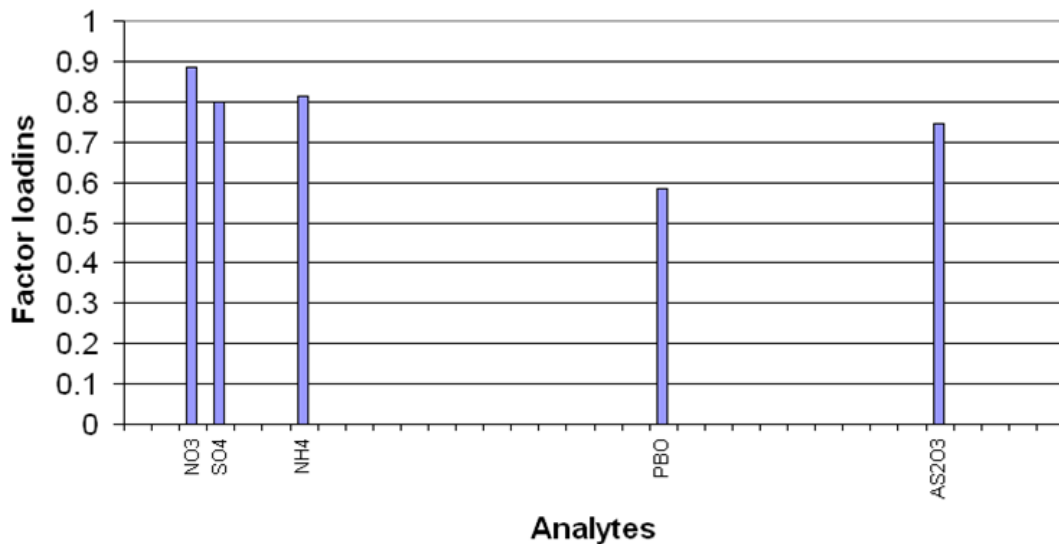
Factor 3 … stationary and mobile sources
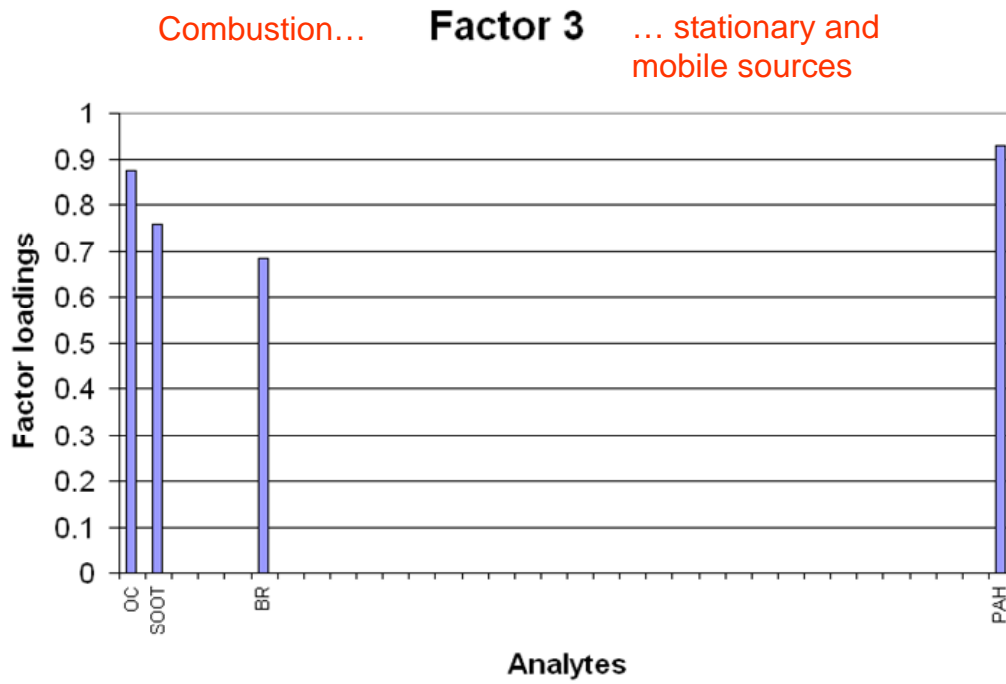
PM10 apportioning
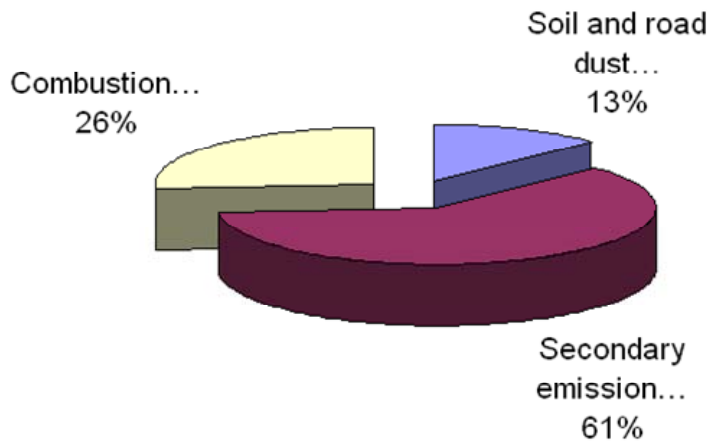
Appendix 7. PCA and apportionment analysis with data for metals as elements.

PCA most vars (incl. PM10), outdoor + indoor
Total % var.=87%

	Factor 1		Factor 2		Factor 3		Factor 4
TI	**0.95**	**FLUO**	**0.96**	**SO4**	**0.85**	**NA**	**0.85**
CA	**0.94**	**PYR**	**0.95**	**NO3**	**0.84**	**CL**	**0.44**
SI	**0.94**	**CHRYS**	**0.85**	**NH4**	**0.77**	**CU**	**0.42**
AL	**0.93**	**OC**	**0.74**	**AS**	**0.70**	SB	0.38
FE	**0.90**	**BR**	**0.72**	**PB**	**0.50**	SN	0.34
V	**0.89**	**PM10**	**0.55**	**RB**	**0.47**	BA	0.24
MN	**0.89**	**SOOT**	**0.54**	**CD**	**0.46**	NO3	0.22
BA	**0.88**	**CL**	**0.53**	**PM10**	**0.41**	NH4	0.21
MGO	**0.84**	**K**	**0.44**	**K**	**0.40**	V	0.17
SN	**0.80**	ZN	0.39	ZN	0.37	ZN	0.17
CU	**0.79**	PB	0.39	OC	0.36	BR	0.16
SB	**0.78**	RB	0.36	CR	0.35	PB	0.15
ZN	**0.78**	NH4	0.33	BR	0.32	PM10	0.14
NI	**0.77**	CD	0.31	CL	0.30	CD	0.14
K	**0.77**	SN	0.30	V	0.27	MGO	0.13
CR	**0.74**	MN	0.29	NI	0.26	AS	0.12
CD	**0.73**	AL	0.26	SN	0.26	PYR	0.11
SR	**0.72**	SB	0.25	SB	0.24	TI	0.09
PM10	**0.70**	SI	0.22	FE	0.23	FLUO	0.09
RB	**0.70**	BA	0.19	CHRYS	0.23	SI	0.07
PB	**0.70**	CA	0.19	NA	0.22	SOOT	0.07
SOOT	**0.69**	TI	0.18	SOOT	0.18	FE	0.07
CL	**0.63**	V	0.17	CU	0.18	MN	0.06
BR	**0.57**	CU	0.17	MGO	0.17	CR	0.05
OC	**0.46**	NI	0.15	AL	0.16	AL	0.05
CHRYS	**0.41**	NA	0.15	MN	0.15	CHRYS	0.04
NH4	**0.41**	FE	0.14	TI	0.11	NI	0.03
SO4	0.37	AS	0.11	BA	0.09	CA	0.03
NO3	0.36	SR	0.10	CA	0.08	OC	0.00
NA	0.13	SO4	0.09	SI	0.08	K	-0.03
PYR	0.06	CR	0.06	PYR	0.02	RB	-0.04
FLUO	0.01	NO3	0.04	FLUO	0.01	SO4	-0.05
AS	-0.15	MGO	0.04	SR	-0.01	SR	-0.13
% Var	67	% Var	9	% Var	7	% Var	3

PCA outdoor

Total % var.=88%

	Factor 1		Factor 2		Factor 3		Factor 4
TI	**0.95**	FLUO	**0.97**	NO3	**0.86**	NA	**0.88**
CA	**0.95**	PYR	**0.96**	SO4	**0.84**	CL	0.39
SI	**0.95**	CHRYS	**0.84**	NH4	**0.77**	CU	0.36
FE	**0.93**	OC	**0.74**	AS	**0.68**	SB	0.32
AL	**0.93**	BR	**0.72**	PB	**0.47**	SN	0.29
V	**0.90**	CL	**0.51**	CD	**0.43**	BA	0.25
MN	**0.90**	K	**0.43**	RB	**0.41**	AS	0.18
BA	**0.89**	ZN	0.36	K	0.37	NH4	0.14
MGO	**0.87**	PB	0.36	OC	0.36	BR	0.14
SR	**0.85**	RB	0.35	ZN	0.34	NO3	0.13
SN	**0.84**	NH4	0.30	NI	0.30	ZN	0.13
CU	**0.83**	CD	0.28	BR	0.29	V	0.12
SB	**0.82**	SN	0.27	CR	0.29	PB	0.09
ZN	**0.81**	MN	0.26	V	0.26	CD	0.08
K	**0.79**	AL	0.25	CL	0.24	PYR	0.08
CR	**0.77**	SB	0.21	SN	0.22	TI	0.08
CD	**0.77**	SI	0.20	SB	0.21	FLUO	0.07
NI	**0.76**	SR	0.20	CHRYS	0.20	NI	0.06
PB	**0.74**	BA	0.19	AL	0.18	MGO	0.05
RB	**0.74**	CA	0.17	SR	0.18	AL	0.04
CL	**0.69**	TI	0.17	NA	0.17	SI	0.04
BR	**0.60**	NI	0.16	FE	0.16	SR	0.02
OC	**0.47**	V	0.14	CU	0.13	OC	0.02
NH4	**0.45**	CU	0.14	TI	0.12	CHRYS	0.01
CHRYS	**0.43**	FE	0.12	MN	0.12	MN	0.00
NO3	**0.40**	NA	0.11	BA	0.12	CA	-0.02
SO4	0.39	AS	0.10	MGO	0.08	FE	-0.02
NA	0.16	SO4	0.05	SI	0.06	CR	-0.03
PYR	0.07	MGO	0.03	CA	0.05	K	-0.05
FLUO	0.02	CR	0.03	PYR	-0.01	RB	-0.09
AS	-0.15	NO3	-0.02	FLUO	-0.02	SO4	-0.10
% Variance	67		10		7		4

PCA outdoor + indoor

Total % var.=87%

	Factor 1		Factor 2		Factor 3		Factor 4
TI	**0.95**	FLUO	**0.97**	SO4	**0.86**	NA	**0.85**
CA	**0.94**	PYR	**0.96**	NO3	**0.84**	CL	**0.44**
SI	**0.94**	CHRYS	**0.84**	NH4	**0.78**	CU	**0.42**
AL	**0.94**	OC	**0.73**	AS	**0.69**	SB	0.38
FE	**0.90**	BR	**0.71**	PB	**0.51**	SN	0.34
MN	**0.89**	CL	**0.52**	CD	**0.47**	BA	0.24
V	**0.89**	K	**0.43**	RB	**0.46**	NO3	0.22
BA	**0.88**	ZN	0.37	K	**0.40**	NH4	0.21
MGO	**0.84**	PB	0.37	ZN	0.38	ZN	0.17
SN	**0.80**	RB	0.36	OC	0.36	V	0.17
CU	**0.79**	NH4	0.31	CR	0.35	BR	0.17
SB	**0.78**	SN	0.29	BR	0.33	PB	0.15
ZN	**0.78**	CD	0.29	CL	0.29	CD	0.14
K	**0.77**	MN	0.28	V	0.27	MGO	0.13
NI	**0.77**	AL	0.24	NI	0.26	AS	0.12
CR	**0.74**	SB	0.23	SN	0.26	PYR	0.10
CD	**0.73**	SI	0.21	SB	0.25	TI	0.10
SR	**0.73**	CA	0.18	CHRYS	0.23	FLUO	0.09
RB	**0.71**	BA	0.18	FE	0.22	SI	0.08
PB	**0.70**	TI	0.17	NA	0.21	FE	0.06
CL	**0.64**	CU	0.16	CU	0.18	MN	0.06
BR	**0.58**	V	0.16	AL	0.17	CR	0.05
OC	**0.47**	FE	0.14	MN	0.16	AL	0.05
CHRYS	**0.42**	NA	0.14	MGO	0.15	CHRYS	0.05
NH4	**0.40**	NI	0.14	TI	0.11	NI	0.03
SO4	0.36	AS	0.11	BA	0.09	CA	0.03
NO3	0.36	SR	0.09	CA	0.08	OC	0.00
NA	0.14	SO4	0.07	SI	0.08	K	-0.03
PYR	0.07	MGO	0.05	PYR	0.03	RB	-0.04
FLUO	0.03	CR	0.05	FLUO	0.01	SO4	-0.06
AS	-0.15	NO3	0.03	SR	-0.01	SR	-0.12
% total Varian	66		10		7		4

PRELIMINARY OBSERVATIONS

- Results are robust: same PCs are obtained in all analyses

- Results for Indoor + Outdoor = very similar to only Outdoor

- When SO_2 was included, it defined an independent PC

- The same occurred with NO_x and CO: not grouped with any PC

Analysis of Variance	
Total	86-88%
Factor 1	66-72%
Factor 2	7-10%
Factor 3	4-7%
Factor 4	3-4%

INTERPRETATION OF PRINCIPAL COMPONENTS (PCs)

Factor 1: Industrial power plants coke + coal (Fe, Si, Al, OC, V, Ni)

Factor 2: Residential combustion wood + coal (OC, K, Cl, FLUO, PYR)

Factor 3: Secondary + pollutant mix (SO_4^{2-}, NO_3^-, NH_4^+, As, Pb, Cd, K).
Probably derived from air-mass re-circulation due to atmospheric stagnation

Factor 4: Road salting + road dust (Na, Cl, Cu, Sb, Sn, Ba)

MULTI-LINEAR REGRESSION ANALYSIS (MLRA)

For all tests performed:

- When intercept included in model $\Rightarrow$ intercept < 0
- When intercept set to zero $\Rightarrow$ B of Factor4 < 0
- p-level of Factor4 >>> p-levels of Factors1-3 $\Rightarrow$ lower significance of Factor4

Regression Summary for Dependent Variable: PM10 (data.sta)					
R= .99181823 R2= .98370340 Adjusted R2= .98242524					
F(4,51)=769.62 p<.00000 Std.Error of estimate: 10365.					
		St. Err.		St. Err.		
	BETA	of BETA	B	of B	t(51)	p-level
Intercpt			-56555.7098	4127.72744	-13.7014157	1.0057E-18
Factor1	0.71194031	0.01799079	51771.8365	1308.27821	39.5724976	5.9398E-40
Factor2	0.45400946	0.01798693	36907.3213	1462.19302	25.2410734	1.7572E-30
Factor3	0.41044945	0.0180762	31735.8349	1397.64628	22.7066285	2.514E-28
Factor4	0.08829443	0.01807478	7805.82794	1597.93308	4.88495298	1.0653E-05

Regression Summary for Dependent Variable: PM10 (data.sta)					
R= .99243808 R2= .98493334 Adjusted R2= .98381730					
F(4,54)=882.52 p<0.0000 Std.Error of estimate: 9653.6					
		St. Err.		St. Err.		
	BETA	of BETA	B	of B	t(54)	p-level
Intercpt			-64392.0255	3240.2014	-19.8728466	1.6839E-26
Factor1	0.70978184	0.01678963	56291.197	1331.54799	42.2750042	4.5402E-43
Factor2	0.46844973	0.01684683	39943.3845	1436.48164	27.8064009	1.1144E-33
Factor3	0.42756829	0.01677711	32540.9491	1276.85577	25.4852191	8.8919E-32
Factor4	0.07723853	0.01677406	6317.72711	1372.03464	4.60464112	2.5529E-05

PCA forced to 3 PCs, outdoor + indoor
Total % var.=83%

	Factor 1		Factor 2		Factor 3
TI	**0.95**	**FLUO**	**0.97**	**NO3**	**0.87**
SI	**0.94**	**PYR**	**0.96**	**SO4**	**0.83**
CA	**0.94**	**CHRYS**	**0.83**	**NH4**	**0.81**
AL	**0.93**	**BR**	**0.72**	**AS**	**0.70**
FE	**0.90**	**OC**	**0.71**	**PB**	**0.54**
BA	**0.89**	**CL**	**0.55**	**CD**	**0.50**
V	**0.89**	**K**	**0.41**	**RB**	**0.45**
MN	**0.88**	ZN	0.37	**ZN**	**0.41**
MGO	**0.84**	PB	0.37	**NA**	**0.41**
SN	**0.81**	RB	0.34	CL	0.39
CU	**0.81**	SN	0.31	K	0.39
SB	**0.80**	NH4	0.31	BR	0.37
ZN	**0.78**	CD	0.29	CR	0.36
NI	**0.77**	MN	0.28	OC	0.36
K	**0.76**	SB	0.25	SN	0.34
CR	**0.73**	AL	0.24	SB	0.34
CD	**0.73**	NA	0.21	V	0.31
SR	**0.72**	SI	0.21	CU	0.27
PB	**0.70**	BA	0.19	NI	0.27
RB	**0.69**	CU	0.19	CHRYS	0.25
CL	**0.65**	CA	0.18	FE	0.24
BR	**0.58**	TI	0.17	AL	0.18
OC	**0.46**	V	0.16	MGO	0.18
CHRYS	**0.41**	FE	0.14	MN	0.18
NH4	**0.40**	NI	0.13	BA	0.15
NO3	0.35	AS	0.10	TI	0.14
SO4	0.33	SR	0.08	SI	0.10
NA	0.18	MGO	0.06	CA	0.09
PYR	0.07	CR	0.04	PYR	0.06
FLUO	0.03	SO4	0.04	FLUO	0.04
AS	-0.16	NO3	0.03	SR	-0.04
% Var	66	% Var	10	% Var	7

PCA forced to 3 PCs, outdoor

Total % var.=84%

	Factor 1		Factor 2		Factor 3
TI	**0.94**	**FLUO**	**0.94**	**NO3**	**0.87**
CA	**0.94**	**PYR**	**0.93**	**SO4**	**0.83**
SI	**0.94**	**CHRYS**	**0.87**	**NH4**	**0.77**
FE	**0.93**	**COR**	**0.77**	**AS**	**0.69**
AL	**0.92**	**OC**	**0.77**	**PB**	**0.48**
BA	**0.90**	**BR**	**0.74**	**CD**	**0.44**
V	**0.90**	**SOOT**	**0.58**	RB	0.39
MN	**0.89**	**CL**	**0.56**	K	0.36
MGO	**0.87**	**K**	**0.45**	ZN	0.36
CU	**0.86**	**ZN**	**0.41**	OC	0.35
SN	**0.85**	**PB**	**0.40**	COR	0.34
SR	**0.85**	RB	0.34	NI	0.30
SB	**0.84**	NH4	0.34	CR	0.30
ZN	**0.79**	CD	0.31	BR	0.29
K	**0.77**	SN	0.30	CL	0.28
CR	**0.76**	MN	0.30	V	0.27
NI	**0.76**	AL	0.28	NA	0.27
CD	**0.76**	SB	0.25	SN	0.25
PB	**0.73**	SI	0.23	SB	0.24
RB	**0.72**	BA	0.22	SOOT	0.20
CL	**0.70**	SR	0.21	AL	0.19
SOOT	**0.69**	TI	0.20	CHRYS	0.19
BR	**0.59**	CA	0.19	SR	0.19
NH4	**0.44**	V	0.18	CU	0.16
OC	**0.43**	NA	0.17	FE	0.16
CHRYS	**0.40**	NI	0.17	BA	0.15
NO3	0.39	CU	0.16	TI	0.14
SO4	0.37	FE	0.12	MN	0.12
COR	0.22	AS	0.10	MGO	0.10
NA	0.21	SO4	0.06	SI	0.07
PYR	0.07	CR	0.05	CA	0.06
FLUO	0.01	MGO	0.03	PYR	-0.03
AS	-0.15	NO3	0.01	FLUO	-0.05
% Var	67		10		7

Appendix 8. Back trajectories. 1: Krakow
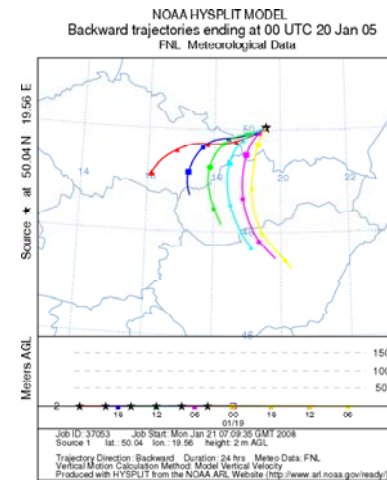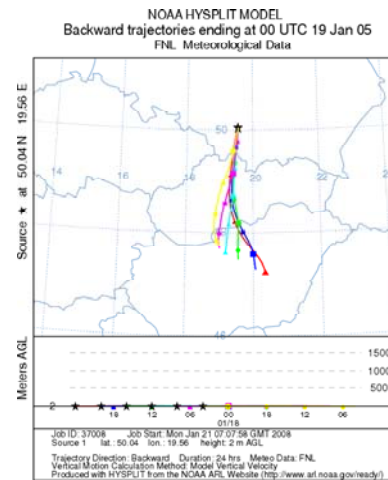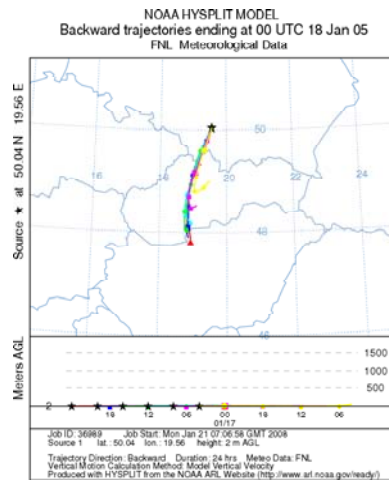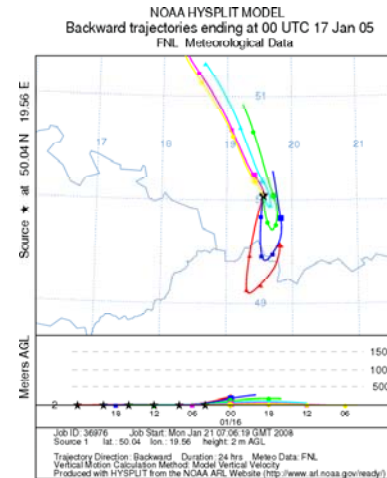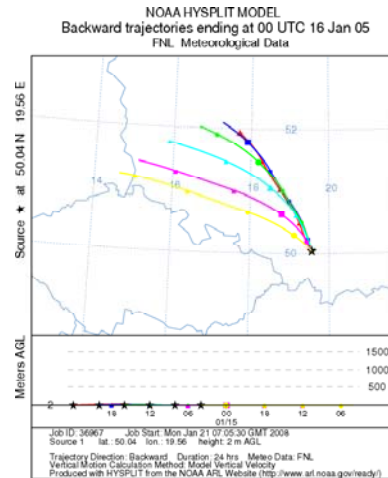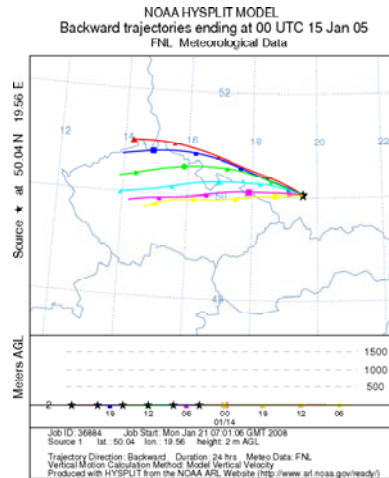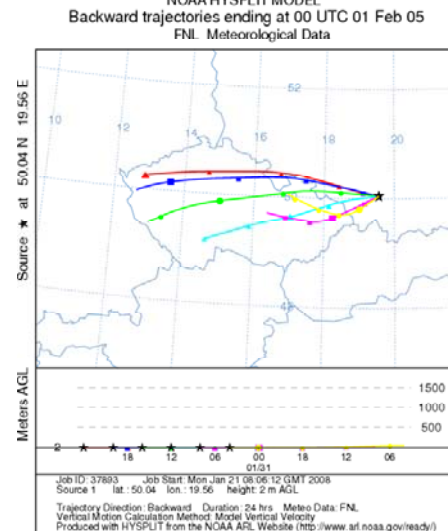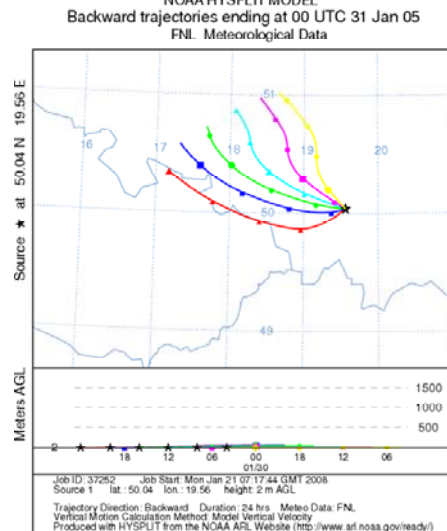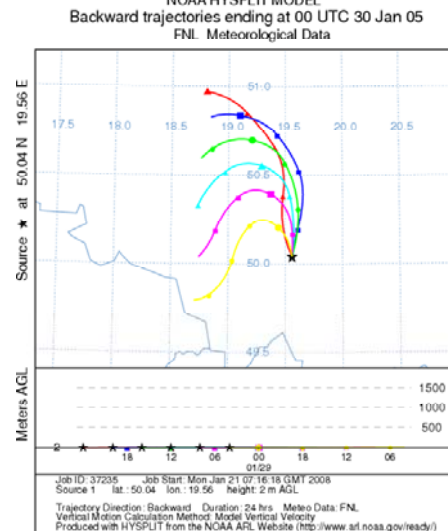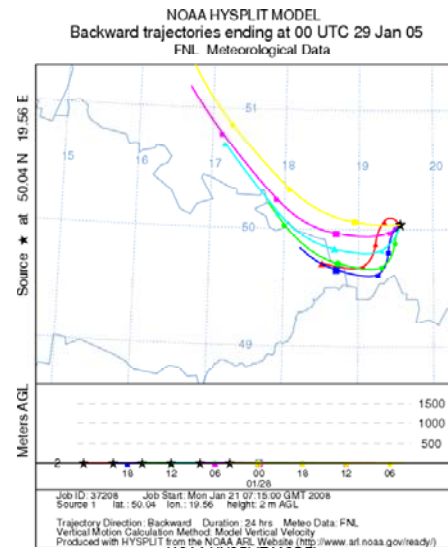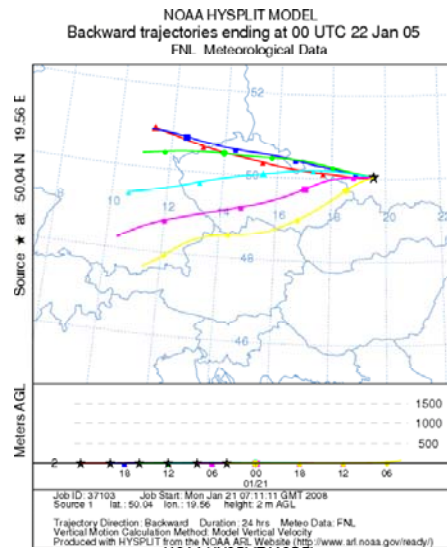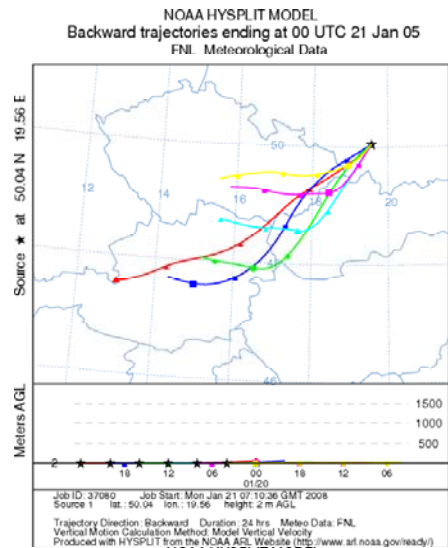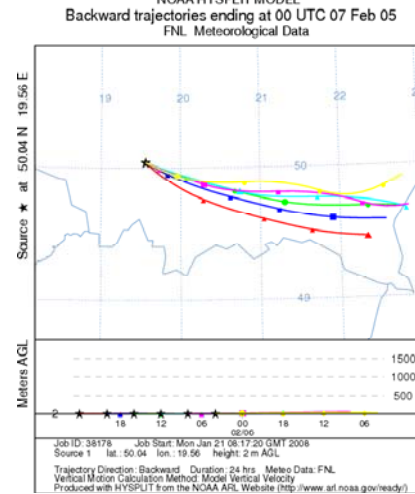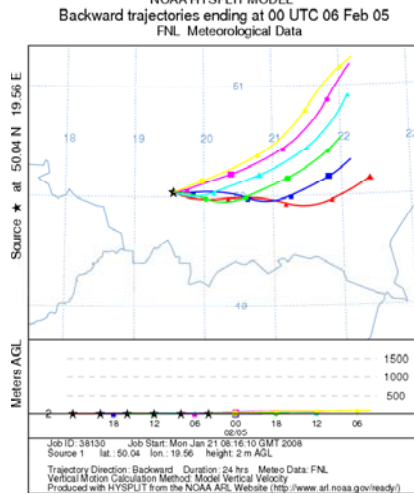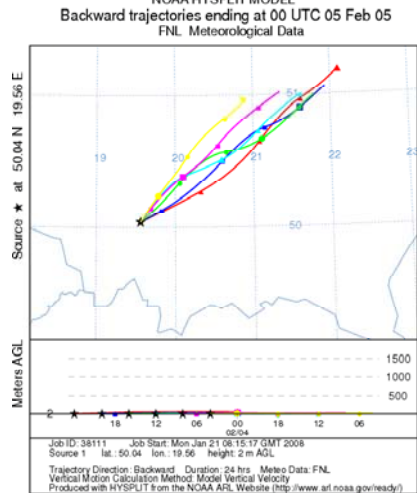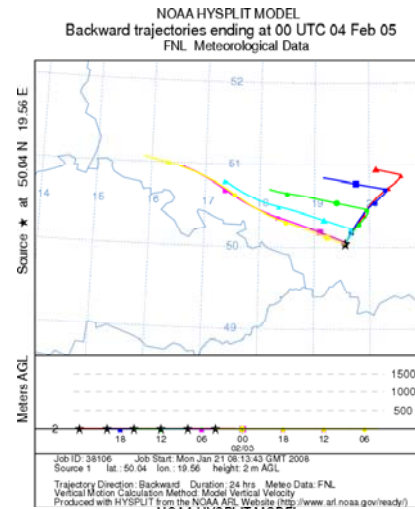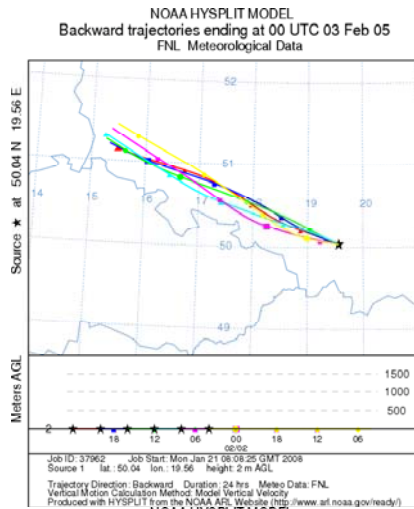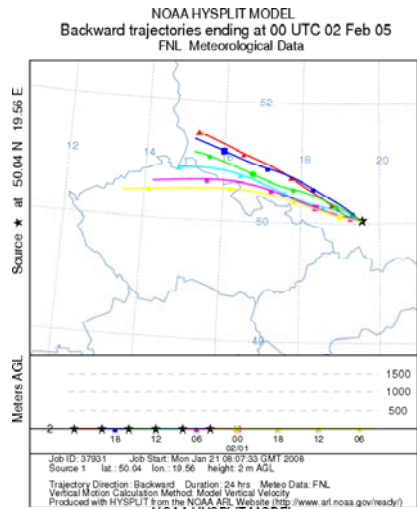
NOAA HYSPLIT MODEL
Backward trajectories ending at 00 UTC 08 Feb 05
FNL Meteorological Data
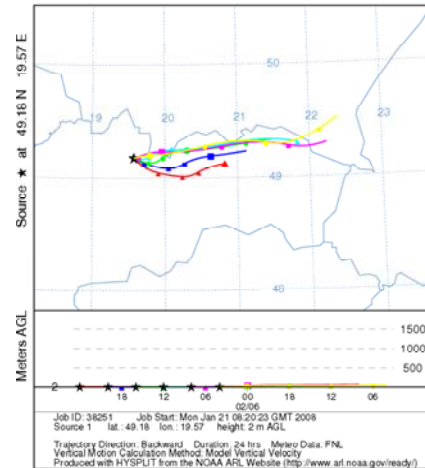
Source ★ at 50.04 N 19.56 E

Meters AGL

1500
1000
500

Job ID: 38213   Job Start: Mon Jan 21 08:18:14 GMT 2008
Source 1   lat.: 50.04   lon.: 19.56   height: 2 m AGL

Trajectory Direction: Backward   Duration: 24 hrs   Meteo Data: FNL
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

2: Zakopane

Abstract
Second to oil, coal is globally the biggest energy source. Coal combustion is utilized mainly for power generation in industry, but in many metropolitan areas in East Europe and Asia also for residential heating in small stoves and boilers. The present investigation, carried out as a case study in a typical major city situated in a European coal combustion region (Krakow, Poland), aims at quantifying the impact on the urban air quality of residential heating by coal combustion in comparison with other potential pollution sources such as power plants, industry and traffic. For that purpose, gaseous emissions (NOx, SO2) were measured for 20 major sources, including small stoves and boilers, and the emissions of particulate matter (PM) was chemically analyzed for 52 individual compounds together with outdoor and indoor PM_{10} collected during typical winter pollution episodes. The data was analyzed using multivariate receptor modelling yielding source apportionments for PM_{10}, B(a)P and other regulated air pollutants associated with PM_{10}, namely Cd, Ni, As, and Pb. The source apportionment was accomplished using the chemical mass balance modelling (CMB) and constrained positive matrix factorization (CMF) and compared to five other multivariate receptor models (PMF, PCA-MLRA, UNMIX, SOM, CA). The results are potentially very useful for planning abatement strategies in all areas of the world, where coal combustion in small appliances is significant.

During the pollution episodes under investigation the PM_{10} and B(a)P concentrations were up to 8-200 times higher than the European limit values. The major culprit for these extreme pollution levels was shown to be residential heating by coal combustion in small stoves and boilers (>50% for PM_{10} and >90% B(a)P), whereas road transport (<10% for PM_{10} and <3% for B(a)P), and industry (4-15% for PM_{10} and <6% for B(a)P) played a lesser role. The indoor PM_{10} and B(a)P concentrations were not much lower than the outdoor concentrations and were found to have the same sources as outdoor PM_{10} and B(a)P The inorganic secondary aerosol component of PM_{10} amounted to around 30%, which may be attributed for a large part to the industrial emission of the precursors SO_2 and NO_X.

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