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Eva Leoz-Garziandia, Martine Ramel

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# METROLOGICAL STAKES IN THE MONITORING OF AIR QUALITY : PAH EXAMPLE IN FRANCE

Eva LEOZ-GARZIANDIA and Martine RAMEL  
INERIS, Institut national de l'environnement industriel et des risques  
Parc technologique Alata, BP 2, 60550 VERNEUIL-EN-HALATTE, FRANCE

## Résumé

La surveillance de la qualité de l'air représente un enjeu considérable pour prévenir et réduire les effets des polluants sur la santé humaine et l'environnement. Le Laboratoire Central de Surveillance de la Qualité de l'Air, créé par le Ministère chargé de l'environnement vise à apporter un appui technique au dispositif national de surveillance de la qualité de l'air en France, en particulier dans le cadre de la mise en oeuvre des Directives européennes.

Le développement d'une stratégie nationale de surveillance des HAP est une des missions du LCSQA depuis plusieurs années, avec l'accompagnement d'un programme pilote, qui vise à mieux connaître les niveaux de concentration dans l'air ambiant, à définir et valider des stratégies de prélèvement et d'analyse, à quantifier les incertitudes et à évaluer les coûts.

## Introduction

Air does not respect international boundaries and therefore any strategy for improving air quality has to take into account the European and wider international dimensions. The European Commission has established the basic principles of a common strategy to define and set objectives for ambient air quality in order to avoid, prevent or reduce harmful effects for human health and the environment. The European directives contain provisions concerning the assessment of ambient air quality in the Member States and public information, notably by means of alert thresholds.

The French Air Quality Monitoring Network (there are 40 different networks spread throughout France, figure 1), which was set up from the 1970's, is the response to this European strategy.



Figure 1. Air quality monitoring networks in France

## The Central Laboratory for Air Quality Monitoring (LCSQA)

The Ministry of the Environment with three partner organisations formed the Central Laboratory for Air Quality Monitoring (Laboratoire Central de Surveillance de la Qualité de l'Air - LCSQA) :

- The Douai School of Mines (Ecole des Mines de Douai)
- The National Institute for Industrial Environment and Risks (Institut National de l'Environnement Industriel et des Risques - INERIS)
- The National Testing Laboratory (Laboratoire National d'Essais - LNE).

The general LCSQA's objectives is to promote, together with the Ministry of the Environment and the Agency for Environment and Energy Management (Agence de l'Environnement et de la Maîtrise de l'Energie - ADEME), the development of ways and means that will enable each air quality monitoring network to carry out its own mission, under conditions of satisfactory metrology, within the national framework and within the framework of the European Union.

The various technical and scientific missions cover the following items :

- Measurement quality and development of measuring ways and means
- Development and use of complementary modelling techniques
- Support for data processing
- Relationship between atmospheric pollution and health

## Polycyclic Aromatic Hydrocarbons (PAH) in ambient air

PAH monitoring strategy in ambient air is one mission of particular interest for LCSQA.

PAH compounds consist of two or more fused benzene rings in linear, angular or cluster arrangements. They can be formed in any incomplete combustion or high temperature pyrolytic process involving fossil fuels and other organic material.

PAH are found in the atmosphere in very small quantities ( $\text{ng}/\text{m}^3$  of air) and under two forms : adsorbed on suspended particles and in gas phase. This partition between gas and particulate (adsorbed) phases depend on physico-chemical properties, e.g. vapour pressure and ambient conditions, e.g. temperature, and humidity.

Some PAH are mutagenic and they are classified by the International Agency for Research on Cancer (IARC) as being "probably or possibly carcinogenic" in humans (Classes 2a and 2b of IARC). Toxicity of Benz(a)pyrene (B(a)P) (figure 2) is for example very studied.

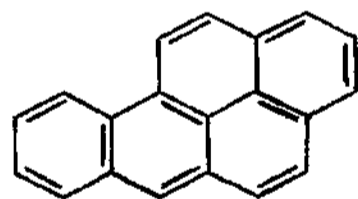


Figure 2. Benz(a)pyrene

They are too, very reactive and the knowledge of chemical reactions is very important because the products of reactions may, in some instances, be more toxic than PAH.

After inhalation these compounds can be adsorbed by the organism and they could conceivably play a role in both genotoxic and non-genotoxic carcinogenesis.

## Needs for a PAH reference method at an European level

Though PAH pollutants have been monitored in ambient air for a long time, the repeatability and reproducibility of the various sampling and analysis measurement methods is still lacking, as well as the number and the phase (particle or gas) of PAH must be measured...

An European Commission steering group, prepared a "position paper" which started to answer at some of those questions.

The 27<sup>th</sup> of September of 1996 European directive 96/62/CE about ambient air quality assessment and monitoring requires that the PAH have to be taken into account. A proposal of the new daughter directive relating to arsenic, cadmium, mercury, nickel and PAH in ambient air has been already written and submitted for comments in the European countries. This daughter directive is based on recommendations from the "position paper" and proposes benzo(a)pyrene as a marker of carcinogenic risk of the total PAH usually measured.

A target value of  $1 \text{ ng}/\text{m}^3$  for B(a)P referred to an annual average of the PM10 particle fraction in ambient air will be proposed in order to prevent non-cancer effects from PAH and ensure a reasonable protection of the population from carcinogenic effects.

Parallel, a CEN working group is preparing at this moment an European standard for B(a)P sampling and analysis in ambient air. INERIS as a LCSQA partner, participates in both European groups.

## PAH monitoring strategy in France

Prior to those European activities, a French pilot program was launched to develop the monitoring of PAH in France by 2001. Based on the position paper, and on French expertise in PAH monitoring, INERIS proposed a sampling and analysis procedure for PAH in ambient air.

Nine air quality monitoring networks (in red on figure 1) are involved which perform sampling. Analyse is subcontracting to associated laboratories. This pilot phase is convened by ADEME and INERIS, and the objectives are :

- to assess concentration levels in different sites in France
- to elaborate a validated monitoring strategy
- to choose a good sampling and analytical method
- to quantify uncertainties
- to evaluate costs

Some preliminary studies were performed before to start :

- a comparison study between different sampling systems to choice the more suitable device
- an inter-comparison exercise between all laboratories participants in order to evaluate the comparability of results.

### Inter-laboratory tests

Different materials were sent to the laboratories :

- a liquid standard in two different concentrations containing 10PAH
- a sample extract from INERIS
- a filter blank extract from INERIS
- samples of a NIST Standard Reference Material

Table 1 shows results obtained for B(a)P recovery from NIST material for each laboratory.

Laboratory	B(a)P recovery
Lab A	21 %
Lab B	94 %
Lab C	56 %
Lab D	97 %
Lab E	89 %
Lab F	73 %
Lab G	68 %
INERIS	96 %

Table 1. B(a)P recovery from NIST material

In base of Dutch an Italian reference methods, a recovery bigger than 75 % and 60 % respectively are need for B(a)P on standard material. This test could show a recovery problem for laboratories A and C which were resolved before the start of the sampling campaign.

### First results of the French pilot program

Nine French cities participate in this program : Caen, Lille, Rouen, Paris, La Rochelle, Lyon, Grenoble, Marseille and Fos-Berre. Different sites were chosen in each city, samples were performed in industrial, urban and traffic sites.

A 24 hours sampling of PM 10 particles is made on a fibre quartz filter and the gas phase is adsorbed on polyurethane foam plugs. Samples are performed once a week, all of six days, in order to have the more representative annual average.

The PAH monitoring program started in October 2001 and is not still finish. In figure 3, results obtained for the first year are shown. We can see that in the winter period B(a)P concentrations are bigger than in summer period, a diminution about 90 % is observed.

Results show that in some periods and locations the target value (1 ng/m<sup>3</sup>) will be proposed by the European Community in the daughter directive would be probably exceeded. But as the target value is referred to an annual average, we found that only in one city B(a)P concentration was close to this value.

The pilot program and the preliminary studies will enable not only the implantation of PAH monitoring in France but as well, will help CEN working group on PAH to organise, by 2003, an European inter-laboratory and field campaigns, in which France will participate.

Figure 3. Concentration of B(a)P in some French cities

