# Environmental protection: Nuclear analytical techniques in air pollution monitoring and research

*Through IAEA-supported projects in some 30 countries, researchers are tracking and fingerprinting sources of pollution*

by
**Robert M. Parr, Susan F. Stone, and R. Zeisler**

Air pollution has become a matter of global concern, particularly in some of the world's largest cities. It is made up of many different components that affect the environment — and directly or indirectly the health of people. The main components include sulphur dioxide, particulate matter, carbon monoxide, reactive hydrocarbon compounds, nitrogen oxides, ozone, and lead.

Nuclear techniques have important applications in the study of nearly *all* of them. However, it is in the study of *airborne particulate matter* (APM) that nuclear analytical techniques find many of their most important applications. This article focuses on these applications, and on the work of the IAEA in this important field of study.

## What is APM?

APM can be described as a mixture of solid and liquid particles suspended in a gaseous state (air). Generally, the size frequency of the particles has a distribution, with two main peaks at about 0.2 micrometers and at about 10 micrometers . *(See figure.)* One can also classify particles sizes according to sources of origin. Particles of a size less than 2 micrometers can be attributed mainly to combustion processes (anthropogenic activity) or gas-to-particle conversion. Particles larger than 2 micrometers are mostly derived from mechanical processes (e.g. soil erosion) or incomplete combustion.

What is the rationale for wanting to study airborne particulate matter? One of the main reasons has to do with its effects on health. *(See box, next page.)* Health problems associated with APM are starting to be regarded with great concern in many countries — and particularly now in *developing* countries — where, in some highly populated cities, the amounts of total suspended air particulates (TSP) are often far in excess of the World Health Organization (WHO) guideline ranges.

WHO advises that the annual average TSP should not exceed 60-90 micrograms/m$^3$. However, many cities regularly exceed these values. No fewer than 17 of these cities (all of them in developing countries) have moderate to high levels of TSP pollution, mostly derived from coal combustion and industrial sources, and to an extent that is increasing in practically *every* country of the world, from automotive exhausts. In many polluted cities, the most direct consequences are ones that are immediately obvious: reduced visibility of the atmosphere and irritation of eyes and throats. However, much more insidious and important are the longer-term effects on health.

Because health effects are mostly associated with particles in the size range of about 10 micrometers and below (called PM-10 particles) it is these particles that are attracting the greatest attention. Unfortunately, however, there are as yet no internationally recognized air quality standards for PM-10 particles, and most countries do not even monitor them in a regular way (or only started doing so during the last five years). In practice, the air quality standards proposed in the United States are most often used as the basis for comparison, namely that the average annual concentration of PM-10 particles should not exceed 50 micrograms/m$^3$ and the 24-hour average should not exceed 150 micrograms/m$^3$ more than once per year. *(See the graph, next page, for a comparison of these averages with the results re-*

Mr. Parr is a staff member in the IAEA Division of Human Health, and Ms. Stone is a former staff member in that Division. Mr. Zeisler is a former staff member of the IAEA Laboratories at Seibersdorf.

### Typical elements determined by nuclear and related techniques in airborne particulate matter

**Neutron Activation Analysis (NAA):** aluminum (Al), arsenic (As), gold (Au), barium (Ba), bromine (Br), calcium (Ca), cadmium (Cd), chlorine (Cl), cobalt (Co), chromium (Cr), caesium (Cs), europium (Eu), iron (Fe), gallium (Ga), iodine (I), indium (In), potassium (K), lanthanum (La), lutetium (Lu), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), rubidium (Rb), antimony (Sb), scandium (Sc), samarium (Sa), thorium (Th), titanium (Ti), vanadium (V), tungsten (W), zinc (Zn)

**Particle-Induced X-ray Emission (PIXE):** Al, Br, Ca, Cl, copper (Cu), Fe, Ga, K, Mg, Mn, Mo, Na, niobium (Nb), Ni, phosphorus (P), lead (Pb), Rb, sulfur (S), selenium (Se), silicon (Si), Ti, Zn, zirconium (Zr)

**X-ray Fluorescence Analysis (ED-XRF):** Br, Ca, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Se, Ti, Zn

*ported for São Paulo by a Brazilian participant in an IAEA research programme.)*

## IAEA-supported air pollution studies

In response to the above evidence and the apparent need of Member States to assess and control air pollution, the IAEA started a Co-ordinated Research Programme (CRP) in 1992 entitled "Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques"; additionally, four technical co-operation projects have been supported. More recently, in 1995, a regional CRP for the Asia and Pacific region began, which is following the same goals and procedures as the first CRP. It is being carried out within the framework of a joint project of the IAEA, the Regional Co-operation Agreement (RCA) for Asia and the Pacific, and the United Nations Development Programme (UNDP) on the use of isotopes and radiation to strengthen technology and support environmentally sustainable development.

The objectives of the CRPs are threefold: to support the use of nuclear and nuclear-related techniques for practically oriented research and monitoring studies on air pollution; to identify major sources of air pollution affecting each of the participating countries (with particular reference to toxic heavy metals); and to obtain comparative data on pollution levels in areas of high pollution (e.g. a city centre or a populated area

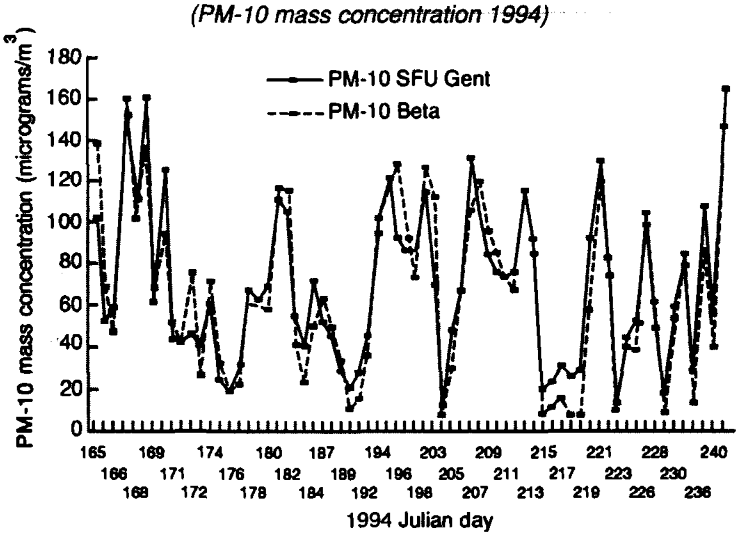
### Health effects of air pollution

That air pollution can kill has been known since at least the time of the infamous great London smog in 1952 which, within the space of about a week, is estimated to have been responsible for the premature deaths of around 4000 people. Such smogs have now gone, but recent research is showing that the numbers of deaths currently caused by air pollution are probably higher than was previously even imagined.

To see why, and what is causing these deaths, it is necessary first to understand how air pollution gets into the body, a process that it is largely a matter of particle size. Particles with a size greater than 10 micrometers are generally too large and heavy to travel very far, and those that do reach a human body are mostly filtered out by the nose. It is the *smaller* particles generally referred to as PM-10, having a size of around 10 micrometers or less, that are the most hazardous. The smaller they are, the *deeper* they can penetrate into the lungs. Exactly what they do there is still not fully understood, but some scientists have suggested that the immune system may be reacting to them as if they were invading organisms. This immune response causes inflammation of the tissues in a similar manner to the allergic reaction of a hay-fever sufferer, but with ultra-fine particles the inflammation is deep in the lungs. The worst effects will be felt by those who are already seriously ill with respiratory disease, so many of those who die during periods of high PM-10 would probably have died within a few weeks or months anyway. This is called *cull* by epidemiologists. However, there is evidence from a comparison between cities in the United States with different PM-10 levels that overall life expectancy falls if PM-10 increases, mainly due to increased death rates from cardiopulmonary disease and lung cancer. This is not a *cull* of the infirm, but a real threat to the health of ordinary people.

The numbers of people affected cannot be estimated accurately, and there is even no consensus yet among scientists who are working in this field on how to do this. Nevertheless, some respected government scientists are suggesting that around 60,000 deaths per year may be caused by air pollution in the United States, and around 10,000 deaths per year in the United Kingdom. If correct, these numbers clearly indicate that air pollution is not only an important environmental problem but also an extremely serious public health problem.

**Aerosol characterization in São Paulo**
*(PM-10 mass concentration 1994)*



## Sampling of airborne particulate matter

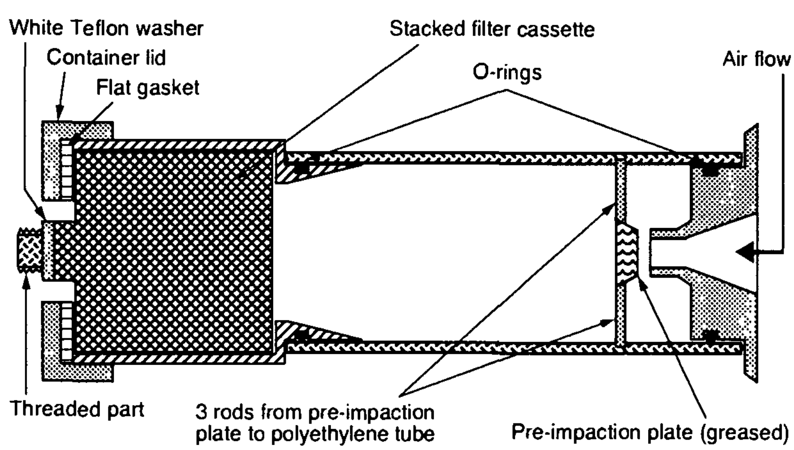
Sampling of APM has much to do with differentiating the size of the particles. Various sampling devices are used for the characterization of APM. The simplest methods involve collection of total suspended matter, without any size selection, and consist of a filter (collection substrate), a pump and a flow meter or controller that draws air through the filter at a known rate. The APM is then collected on the filter. More complicated samplers collect APM in various size fractions.

**Collection of APM without size selection.** ***Collection of dry deposition samples:*** This type of sampler depends only on gravitational settling of particles. It involves the removal of particles onto a surface or collector in the absence of precipitation. This is to be contrasted with wet deposition (which is the removal of particles by precipitation such as rain or snow), and bulk deposition (which is the combination of wet and dry deposition). ***Collection of total suspended particulate matter (TSP):*** Normally, samplers of this type are "high-volume" air samplers, with large volumes of air being drawn through a low resistance (glass or cellulose) filter. Air flow ranges from 1.1 to 1.7 $m^3$/min, or about 2000 $m^3$/day. The inlet duct and collection filter measure 25-30 cm in diameter. This type of sampling is especially useful for monitoring of remote areas, which may have relatively low particulate concentrations, or for monitoring low-level products of anthropogenic nuclear activities.

**Collection of APM with size selection.** ***Samplers with physical impactor stages:*** The principle of these samplers is to separate particles by size using "obstacles" or impactors. Particles are removed onto solid surfaces using inertial forces; air flows around an obstacle (the impactor), and the particles in the airflow either follow the air stream or, depending on the mass (size) of the particle, impact on the obstacle, and are collected. A cascade impactor consists of a series of stages of particle collectors, each stage collecting different particle size ranges. The largest particles are collected in the upper stages. ***Samplers with virtual impactors:*** Separation in these samplers occurs at a "virtual" surface formed by diverging air streams. Coarse and fine particulates are then carried to separate filters. The size segregation of such devices is not as sharp as for physical impactors, and operation below about one micrometer appears difficult, but problems with collections surfaces are largely avoided. An example of this type of air sampler is a dichotomous sampler. This has a size selective inlet to sample particles larger than 10-15 micrometers, and a virtual impactor which further separates particles into two fractions, coarse and fine. These samplers operate at a "medium" volume flow rate. ***Samplers using centrifugal forces:*** These types of samplers, e.g. cyclones, can also provide particle sizing via flow within a cylindrical or conical chamber. Large particles are removed from a constant air flow on the basis of impaction, where the larger particles impact on the walls of the cyclone. These particles remain on the walls or settle to the bottom of the cyclone, and are generally not analyzed. Cyclones are often used for separating out the fine and coarse fractions of APM. ***Stacked filter units (SFU):*** This type of sampler uses the principle of sequential filtration, where particle fractionation is achieved by partially efficient polycarbonate filters. These filters are utilized due to their specific particle capture behaviour for the desired size fractions. An SFU consists of two filters in series, which are located upstream of a pump. The first filter (coarse stage) collects particles between about 3 micrometers and 15 micrometers. The second filter (fine stage) collects the particles which pass through the first filter, that is particles below about 3 micrometers. These samplers are also operated at "medium" volume flow rate (about 18 L/min or 360 $m^3$/day).

**Personal samplers.** These are small, compact air samplers, consisting of a pump and a unit for particulate collection onto a filter. These samplers can either collect total particulate matter, or have some device for particle size differentiation, and are largely low volume samplers (1-5$m^3$/hr). The sampler is then worn by the person being monitored. These samplers are used to assess individual exposure to air particulate matter.

**"Gent" stacked filter unit air sampler.** The "Gent" SFU air sampler is specifically designed for the collection of APM in the inhalable (PM-10) size fraction, using the principle of sequential filtration *(see schematic).* This sampler, designed at the University of Gent, Belgium (and currently being provided by Clarkson University, United States), is being used by all participants in the IAEA's Co-ordinated Research Programmes for air pollution research and related projects. The sampler uses an "open face" type stacked filter unit, in which two 47-mm Nuclepore polycarbonate filters (one filter of 8 micrometers pore size and the other of 0.4 micrometers pore size) are employed for the collection of APM. The filter unit is inserted in a cylindrical container, which is provided with a pre-impaction plate for the collection of particles larger than 10 micrometers. The sampler is designed to operate at a flow rate of 18 L/min, where the pre-impaction stage provides a PM-10 cut-off point at standard temperature and pressure. At this flow rate, the coarse (8 micrometers pore size) Nuclepore filter has a $d_{50}$ value of 2 micrometers, so that it actually collects the 2-10 micrometers size fraction, whereas the fine filter collects particles in the size range less than 2 micrometers.



### Countries participating in IAEA-supported monitoring and research on air pollution

***Participants in global Co-ordinated Research Programme (CRP):*** Australia, Thailand, Bangladesh, China, Kenya, India, Iran, Turkey, Slovenia, Portugal, Hungary, Belgium, Austria, Czech Republic, Argentina, Chile, Brazil, Jamaica, and United States

***Participants in regional CRP:*** Mongolia, China, Myanmar, Thailand, Republic of Korea, Philippines, Viet Nam, New Zealand, Indonesia, Singapore, Malaysia, Bangladesh, Sri Lanka, and Pakistan

***Technical co-operation projects:*** Costa Rica, Chile, Philippines, Sri Lanka, Portugal

downwind of a large pollution source) and low pollution (e.g. rural areas).

In principle, a wide variety of different kinds of samplers may be used to collect APM. *(See box, page 18.)* For practical reasons, however, all participants in the CRPs are using a relatively simple and inexpensive sampling device. All of them have exactly the same design to ensure comparability of the resulting analytical data. A low volume PM-10 stacked filter unit designed at the University of Gent, Belgium, collects air particulate matter in two size fractions. Samplers of this design have already been supplied by the Agency to about 30 countries. *(See box above.)*

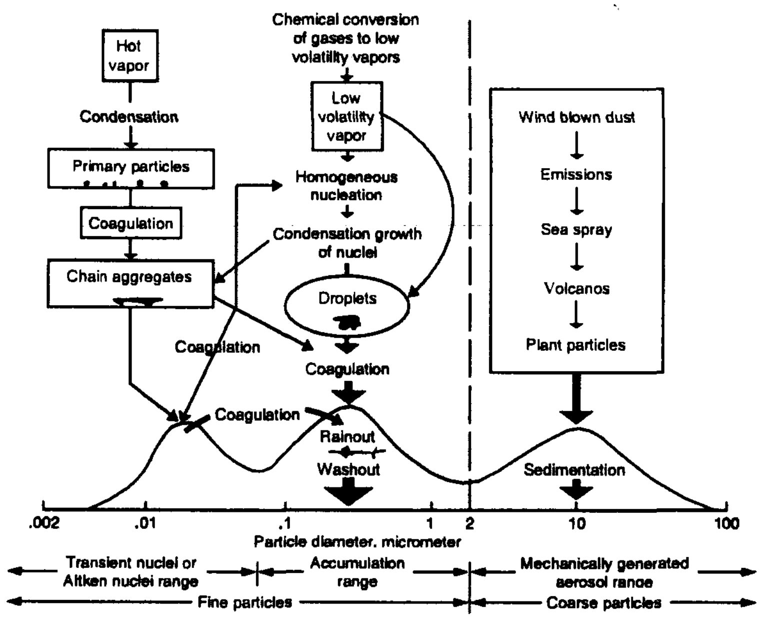
These CRPs are also supported by work at the IAEA's Seibersdorf Laboratories, which have set up one of the Gent samplers for collecting APM in Vienna and at a rural Austrian site. *(See box, right.)* In addition, the Laboratories are actively engaged in developing reference materials for air pollution studies, including reference air filter samples for use by all CRP participants. In this way, it is hoped to be able to ensure that the data collected during the CRP will be of high quality, and that meaningful comparisons can be made between the data reported by different analysts. For the same reason, it has also been decided that most of the data will be evaluated centrally by a single data co-ordinator.

***Applicability of nuclear and related analytical techniques.*** A variety of analytical techniques is being used in these programmes. However, the main emphasis is on nuclear and related techniques, i.e. neutron activation analysis (NAA), energy dispersive X-ray fluorescence analysis (ED-XRF), and particle-induced X-ray emission (PIXE). These techniques have characteristics that make them highly suitable (in fact, *unique*) for conducting non-destructive multi-

### Contribution of the IAEA's Laboratories at Seibersdorf

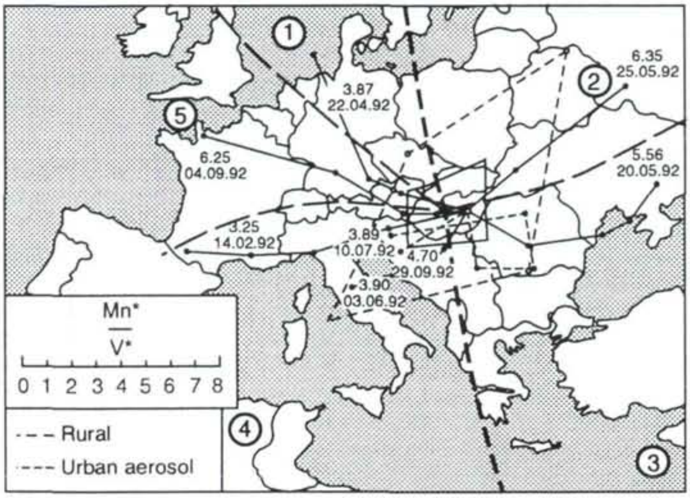
One way the Agency's Laboratories at Seibersdorf are participating in air pollution programmes is through the evaluation of the procedures, including sample collection, preparation, analysis, and data handling. Collection sites for APM using the "Gent" PM-10 sampler were established in an urban residential area in Vienna, and also at the site of the Laboratory in Seibersdorf, as a representative rural area. Possible pitfalls in the sampling and preparation steps, as well as the applicability of different analytical techniques, were investigated, and information on the suitability of the relatively low-volume sampler in developing countries was obtained. Due to the low masses of APM collected by the sampler utilized in the CRPs, highly sensitive analytical methods are required. Nuclear analytical techniques such as NAA and PIXE were shown to be particularly well-suited for analysis of the resulting samples. The multi-technique analytical approach used in Seibersdorf not only provided results for a large number of elements, but, for several elements, provided results from two different techniques, for better confidence in the data obtained. Although the number of samples collected was limited, a small "snapshot" of the trace element composition of APM in the Vienna area, as well as rural Seibersdorf, was obtained. The importance of the characterization of the "blank" (i.e. the trace element composition of the "substrate" or filter), was especially emphasized for samples taken in more remote areas (e.g. a rural site), as many of the trace element concentrations are at, or below, this blank value. Even with the challenges presented in the collection and analysis of APM samples, much information on the trace element composition of inhalable fractions of APM can be obtained by careful analytical work, as well as information on the sources of the APM (both natural and anthropogenic).

### Airborne particulate matter




The diagram shows the size ranges, principal modes, main sources of mass of each mode, and the principal mechanisms by which particles are removed from the air.

**Wind sector distribution diagrams in Debrecen, Hungary for urban and rural air particulates**




Though rather complicated, the graph basically shows that the components of air pollution under investigation had mainly come from two directions: Donets'k, Moscow, and Ural regions of the Commonwealth of Independent States; and northern Italy and the northwestern Balkans. In addition, some particular pollution events could be identified and traced back to specific sources and dates.

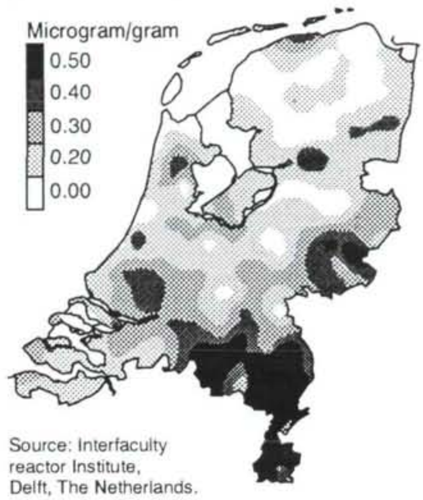
**Apportionment of air pollution (PM-2.5 particles) for a city in New South Wales, Australia**

| Fingerprint | Percentage fingerprint contributions: Winter Month July 1994 | Summer Month December 1994 | Average for 1994 |
|---|---|---|---|
| Motor Vehicles | 68 ± 7 | 19 ± 5 | 54 ± 21 |
| Smoke | 18 ± 7 | — | 8 ± 12 |
| Soil | — | 2.7 ± 0.9 | 5 ± 4 |
| Sea Spray | 3.5 ± 0.9 | 5.4 ± 0.8 | 4 ± 2 |
| Industry | 11 ± 2.6 | 73 ± 7 | 35 ± 21 |
| Total Mass | 30 ± 2 μg/m$^3$ | 9.5 ± 0.6 μg/m$^3$ | 14 ± 8 μg/m$^3$ |

element analyses of airborne particulate matter on filters. *(See box, page 17.)* All other competing methods require a time-consuming dissolution of the filters, and are generally only applicable to one, or a small group, of elements (an exception is ICP-MS, which is also a nuclear-*related* method). Some of these elements, such as lead (chemical symbol Pb) are of *direct* interest

**Calculated contribution from zinc smelters to cadmium air pollution in the Netherlands**

*(based on analysis of moss samples)*




because of their health effects. However, most of them are studied because they can be used to provide a unique kind of *fingerprint* which enables individual sources of pollution to be identified.

***Source identification and apportionment.*** Sources of pollution are characterized by being composed of different mixtures of elements in different proportions. Some examples of elements associated with six fingerprint sources of fine particles appear below, taken from the work of the Australian participant in the IAEA research programme:

- motor vehicles: H, Na, Al, Si, S, Cl, Fe, Zn, Br, Pb, Elt.C (elemental carbon)
- coal combustion: H, Na, Al, Si, P, S, K, Ca, Fe, Elt.C
- smoke: H, Cl, K, Ca, Elt.C
- soil: Al, Si, K, Ca, Ti, Mn, Fe
- sea spray: Na, S, Cl, K, Ca
- industry: H, P, S, V, Cr, Cu, Pb, Elt.C

If several elements that are characteristic of each of these sources are measured in a set of air filter samples, statistical techniques can then be used to estimate the percentage fingerprint contribution from each of them. *(See table.)* This kind of information is extremely useful to environmental authorities because it enables them to see where the pollution is coming from in terms of how it can be apportioned between different kinds of sources.

Another way in which sources of pollution can be identified is by combining information on the trace element content of air filter samples with *meteorological* information, in particular with information on wind direction and recent movements of air masses (so called backward air trajectories). *(See graph on previous page for an example in Hungary.)*

***Biomonitoring.*** The same kinds of analytical and statistical techniques can be applied not only to air filter samples but also to *other* kinds of indicators of air pollution. In recent years there has been a considerable growth of interest in using various kinds of *biomonitors* of air pollution — samples such as moss, lichen, and even tree bark. The "trick" in applying this kind of technique is to choose a biomonitor that obtains most of its nutrients from the air and not from the soil, or other matrix, on which it is growing.

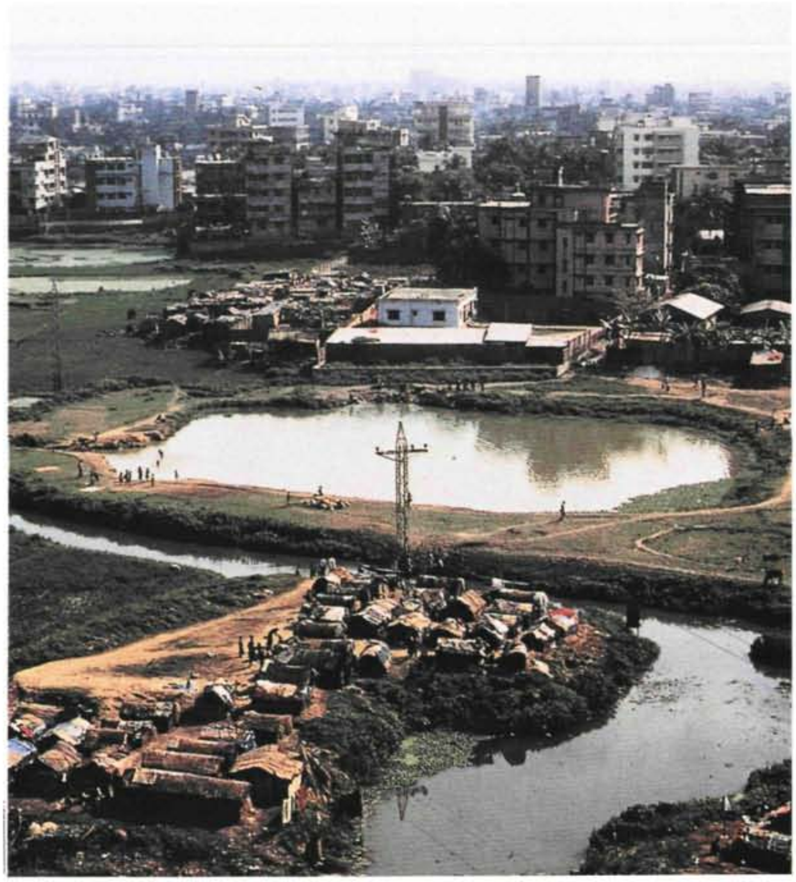
The main advantages of using biomonitors are (1) that the samples can be obtained almost "for free" (it is not necessary to set up expensive air filtering devices, needing electrical power together with frequent supervision and maintenance); and (2) the samples are already "in place" at sampling sites covering large areas (maybe even the whole country).

Surprisingly detailed information on the geographical distribution of air pollutants can be obtained in this way, not only on the *levels* of specific pollutants, but also (by statistical fingerprinting) on the *sources* of this pollution. *(See figure, previous page, for an example in the Netherlands.)* Several participants in the Agency's CRPs are also exploring the use of this kind of technique. The IAEA is well prepared to support further work in this area by having recently certified a suitable analytical reference material, lichen, with the help of 42 research participants from 26 countries.

## Future areas of emphasis

The Agency's global CRP on air pollution is due to be completed in 1997, and the regional CRP in Asia and the Pacific in 1999. The information they provide will constitute a unique database on levels and sources of specific kinds of air pollution in major cities in many developing countries.

Since the particles being measured are the ones that are thought to be of direct relevance to human health, the Agency's database can be used to explore possible associations between air pollution and the incidence of cardiopulmonary diseases in the cities and regions being investigated. For most countries, such data has never been reported before. Since the same kinds of air samplers and analytical quality control procedures are being used by all research participants, a high level of confidence in the results is expected from the standpoint of being able to make meaningful comparisons between different cities and countries.



**Bangladesh, one of the countries participating in IAEA-supported air pollution research.**

New air quality standards are now under discussion in the United States, which are expected to provide guidance not only on PM-10 but also on PM-2.5 particles. The IAEA's programme is already providing information of this kind.

Some of the Agency's work is receiving support in the Asia and the Pacific region within the framework of the joint UNDP/RCA/IAEA project on the use of isotopes and radiation to strengthen technology and support environmentally sustainable development. Discussions are being held with the UNDP with a view to extending this work during the period 1997-99. If approved, air pollution studies will continue to be a major component of this project.

Also in Latin America, within the framework of the ARCAL regional programme, it is hoped to be able to promote the use of nuclear and related techniques for monitoring and research on air pollution, in this case with a major focus on the use of biomonitors.

In all of this work, nuclear and related techniques have been shown to be capable of providing valuable information on levels and sources of air pollution. It is information of a kind that is not only directly useful in itself, but which is practically unobtainable by any other method of non-destructive instrumental analysis. ❐