

# A fresh look at air

Urban air quality makes headline news, and a recent Royal Commission report has stepped up the campaign against pollution from road vehicles. Better detection methods and monitoring mean that we are learning more about the air that we breathe.

In the 1950s and 1960s the problems of urban air pollution in the UK were obvious. The reduced visibility in winter smogs could be severe and in one episode alone, in December 1952, 4000 excess deaths were attributed to the combination of cold stagnant weather and high levels of smoke and SO<sub>2</sub>. The Clean Air Acts of 1956 and 1968, together with a switch to gas for domestic heating, have transformed the situation by causing a great reduction in emissions of SO<sub>2</sub> and smoke within urban areas. Indeed, SO<sub>2</sub> concentrations in most UK towns and cities are now almost indistinguishable from those in the surrounding countryside, and the main source of black smoke in

London is diesel fuel rather than coal.<sup>1,2</sup>

Because the policies for controlling urban smoke and SO<sub>2</sub> were so successful there was a tendency during the 1970s and 1980s to believe that urban air pollution problems had been banished. However, this view ignored the massive growth in road traffic and, despite considerable improvements in emissions per vehicle kilometre, total emissions from motor vehicles have now begun to dominate the urban air pollution scene for many pollutants. Together with concerns that some respiratory diseases may be linked with air pollution, this has led to a recent resurgence of interest in urban air quality. This is manifest in both an increased range of

pollutants monitored, and a greater number of monitoring sites for many pollutants. Additionally, research into urban air quality has expanded, and we are on the point of seeing a considerably greater investment in research into the health effects of air pollutants than has occurred for many years. The government has established a number of expert committees to provide specialist advice on the scientific issues. The content of this article is drawn largely from the work of the Quality of Urban Air Review Group (Quarg), of which I am chairman. Quarg advises the secretary of state for environment on urban air quality issues, including the prediction of future trends.<sup>1,2</sup>

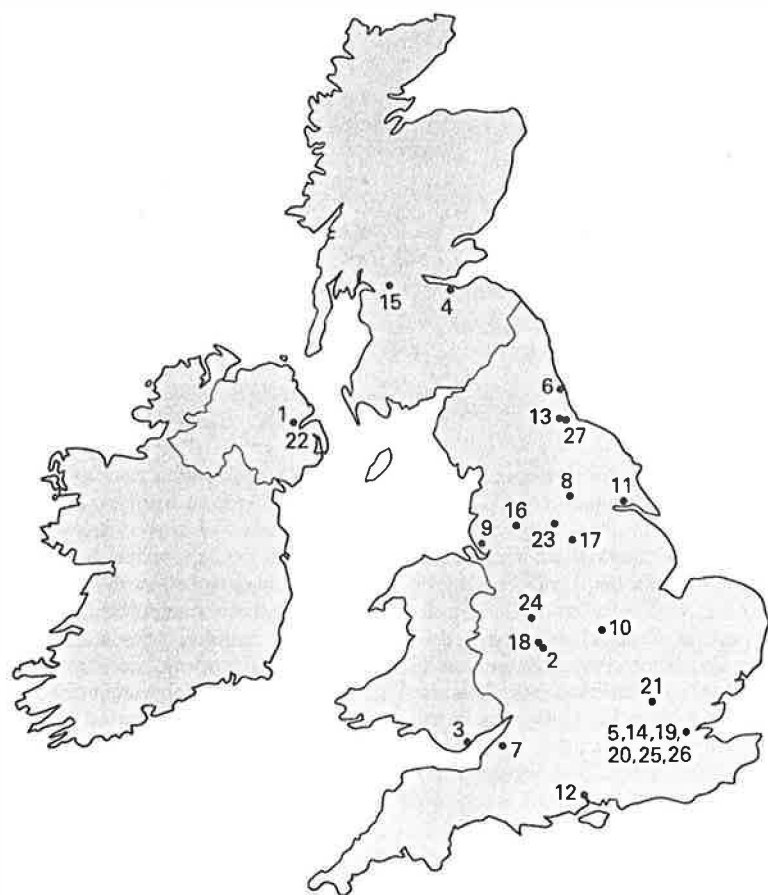
**Table 1. A summary of national air quality monitoring networks in urban areas.**

Network	Pollutants	Type of monitor	Number of sites
EC Directive	nitrogen dioxide	chemiluminescence	7
	sulphur dioxide	UV fluorescence	3
	sulphur dioxide/smoke	bubbler/filter	163
	lead	filter	11
Enhanced Urban	nitrogen dioxide	chemiluminescence	13
	sulphur dioxide	UV fluorescence	13
	carbon monoxide	IR absorption	13
	ozone	UV photometric	13
	PM <sub>10</sub> particles	TEOM	13
Hydrocarbon	benzene	gas chromatography	7
	1,3-butadiene	gas chromatography	7
	other HCs	gas chromatography	7
Toms	PAHs	filter/polyurethane adsorbent	4
	PCBs	filter/polyurethane adsorbent	4
	dioxins/furans	filter/polyurethane adsorbent	4
Others (long-term, urban etc)	nitrogen dioxide	chemiluminescence	2
	nitrogen dioxide	diffusion tube	1 100
	sulphur dioxide	UV fluorescence	3
	sulphur dioxide/smoke	bubbler/filter	241
	carbon monoxide	IR absorption	6
	ozone	UV photometric	2
	lead	filter	7
	metals (urban)	filter	5
	sulphate	filter	1

## Urban monitoring network

The main reasons for monitoring air pollution are to comply with EC directives, to provide public information, and to measure the effectiveness of emission control policies. National networks are funded by the Department of Environment and operated by several organisations on the basis of competitive tendering. In recent years, the management function of some networks has been separated from the quality assurance function, with different organisations in each role. Some air quality monitoring is also funded and operated by local authorities. In future, this activity is to be integrated into national networks where possible.

A summary of urban monitoring activity is given in *Table 1*. EC directives require the monitoring of NO<sub>2</sub>—by chemiluminescence analysis—and of smoke and SO<sub>2</sub>. For the latter, UK networks use predominantly the old manual samplers, as specified in the directive; these estimate smoke from the blackening of the filter paper and estimate SO<sub>2</sub>, as acidity or sulphate, after collection in hydrogen peroxide solution. To provide additional information on SO<sub>2</sub>, the manual sampler network has been augmented with three continuous fast response UV fluorescence instruments sited at locations at risk of breaching the directive. EC directives also require lead monitoring by collection on a filter, and analysis by a technique such as atomic



### Abbreviations

EUN	Enhanced urban network I
H	Hydrocarbons network (EUN II)
Toms	Toxic organic micropollutants
NO <sub>2</sub> D	NO <sub>2</sub> directive
SO <sub>2</sub> D	SO <sub>2</sub> co-located with directive sites

### Key

1	Belfast; city centre	EUN,H
2	Birmingham	EUN (2 sites), H
3	Cardiff	EUN, H, Toms
4	Edinburgh	EUN, H
5	London; Bloomsbury	EUN, H
6	Newcastle	EUN
7	Bristol	EUN
8	Leeds	EUN
9	Liverpool	EUN
10	Leicester	EUN
11	Kingston-upon-Hull	EUN
12	Southampton	EUN
13	Billingham	NO <sub>2</sub> D
14	London; Bridge Place	NO <sub>2</sub> D
15	Glasgow	NO <sub>2</sub> D
16	Manchester	NO <sub>2</sub> D, Toms
17	Sheffield	NO <sub>2</sub> D
18	Walsall	NO <sub>2</sub> D
19	London; Earls Court	NO <sub>2</sub> D
20	London; Cromwell Rd	—
21	Stevenage	Toms
22	Belfast; East	SO <sub>2</sub> D
23	Barnsley	SO <sub>2</sub> D
24	Rugeley	SO <sub>2</sub> D
25	London; Greenwich	H
26	Central London; Marsham Street	Toms
27	Middlesbrough	H

Fig 1. The locations of the national network of automated urban air quality monitoring sites. (Other monitoring is carried out by local authorities and industry.)

absorption, and ozone monitoring by UV photometry. *Box 1* gives further details of these monitoring techniques.<sup>3,4</sup>

The most recent and exciting development in UK air quality monitoring is the Enhanced Urban Network (EUN); the first station opened in January 1992. The first phase of the network involves continuous automated stations measuring the concentrations of NO, NO<sub>2</sub>, SO<sub>2</sub>, CO, ozone and PM<sub>10</sub> (particulate matter with an aerodynamic diameter of less than 10µm). The second phase has involved setting up sites to measure the concentration of 26 individual hydrocarbons by using automated cyclic gas chromatography. Compounds such as benzene and 1,3-butadiene are of particular interest because of their carcinogenicity. Benzene was the subject of the first report of the Expert Panel on Air Quality Standards,<sup>5</sup> which recommended an upper limit to concentrations of 5 parts per billion (ppb) as a rolling annual average, with a target of 1 ppb. At the time of writing this article, the panel was still awaiting a government response to this recommendation. Data from EUN stations are polled hourly by telemetry and used to provide information on air quality for the general public.

Another recently developed network, though smaller in scope, is the Toxic Organic Micropollutants (Toms) network,

which measures both particle-associated and vapour phase polynuclear aromatic hydrocarbons, polychlorinated biphenyls, dibenzodioxins and dibenzofurans.<sup>1</sup> These sites are valuable in providing baseline data on urban concentrations of these pollutants as well as indicating temporal trends. It is only for the polynuclear aromatic hydrocarbons that we have fairly good historic data—concentrations in air going back to the early 1960s. Many of these compounds are showing a substantial decline in concentrations associated with the virtual elimination of coal burning in London.<sup>6</sup> *Figure 1* shows the locations of automated sites in the major networks. There is also a rural network of stations measuring ozone, a few of which also measure oxides of nitrogen.<sup>7</sup>

### Urban air chemistry

The availability of high quality data on a range of air pollutants is leading to questions about the chemical reactions that influence their concentrations. For example, much interest has focused on NO<sub>2</sub> as a pollutant. There are suggestions, as yet largely unsubstantiated, that NO<sub>2</sub> might be associated with the increased prevalence of asthma and may also predispose children to respiratory infective agents.<sup>8</sup> Paradoxically, however, while urban emissions of all nitrogen oxides (NO<sub>x</sub>) have

been increasing appreciably, central urban average concentrations of NO<sub>2</sub> have changed little over the past 20 years, although extremely high concentrations of NO<sub>2</sub> can arise in conditions of stagnant air during winter. Recently, our understanding of these phenomena has advanced appreciably; *Fig 2* and *Box 2* describe the basic chemical reactions in the nitrogen oxide-oxygen-ozone system. Nitrogen oxide emissions from most combustion sources are predominantly NO—motor vehicles produce about 95 per cent NO, the remainder being NO<sub>2</sub>. *Figure 2* shows the relationships of hourly average concentrations of NO<sub>2</sub> as a function of simultaneous hourly average concentrations of NO<sub>x</sub> (ie the sum of NO + NO<sub>2</sub>) at a site in London.<sup>9</sup> The graph indicates that at very low concentrations NO<sub>2</sub> increases with NO<sub>x</sub>, leveling off at around 30–50 ppb. This plateau is believed to be the oxidant-limited region in which the production of NO<sub>2</sub> is controlled by the availability of ozone (*Box 2, reaction a*). Normally, urban atmospheres are within this region and, despite increases in the annual average NO<sub>x</sub> level, there have been imperceptible changes in the annual average NO<sub>2</sub> level at most sites. However, from the viewpoint of possible human health effects, NO<sub>2</sub> concentrations above 100 ppb are probably most significant; in this region the curve becomes

much steeper because of the oxidation of NO by molecular oxygen (Box 2, reaction d). This reaction was long thought to be too slow to play a role in urban air, but it appears that if nitric oxide concentrations exceed about 500 ppb with a residence time of air within the urban area of several hours, it can play a significant role in generating further NO<sub>2</sub>. There is evidence in the literature for surface catalysis of this process, and our own analyses of atmospheric measurements at Birmingham University suggest that it is necessary to invoke catalytic enhancement to explain the observed rate of NO<sub>2</sub> production.

Much of our current understanding of ground-level ozone pollution derives from work based in Southern California. In Los Angeles, the trapping of primary pollutants by meteorological and topographic influences, combined with high sunlight intensities, allows a build-up of ozone at ground level on a horizontal scale of tens of kilometres. It is tempting to think that photochemical ozone episodes are an urban phenomenon. On the contrary, in Western Europe they tend to be a regional phenomenon, expanding over hundreds or thousands of kilometres simultaneously, and urban areas tend to show lower ozone

## 1. Air quality monitoring techniques

A variety of physical and chemical techniques are used for monitoring air pollutant concentrations. The automatic networks use continuous gas analysers, typically capable of measuring concentrations down to 1 ppb by volume with a response time of seconds. The particle analysers are also continuous, but involve a minimum averaging period of 15 min.

- NO<sub>2</sub> is monitored by thermal decomposition to NO, which is then mixed with ozone generated within the instrument. A photomultiplier tube detects light emitted in the chemiluminescent reaction.

- SO<sub>2</sub> is monitored by gas phase fluorescence using an excitation wavelength of 216 nm, and measuring fluorescence in the 240–420 nm range. To limit humidity-dependent quenching phenomena, a diffusion dryer removes water vapour from the air stream entering the instrument.

- CO is measured by IR absorption at 4.6 μm with instruments designed to overcome interference due to varying CO<sub>2</sub> levels.

- Ozone is measured by UV absorption at 254 nm; to avoid interference from other species absorbing at this wavelength, the instrument cycles between measuring the absorbance of ambient air and that of air from which ozone has been catalytically removed.

- Hydrocarbons are measured by cryogenic preconcentration and subsequent gas chromatography with flame ionisation detection using an automated cycling system.

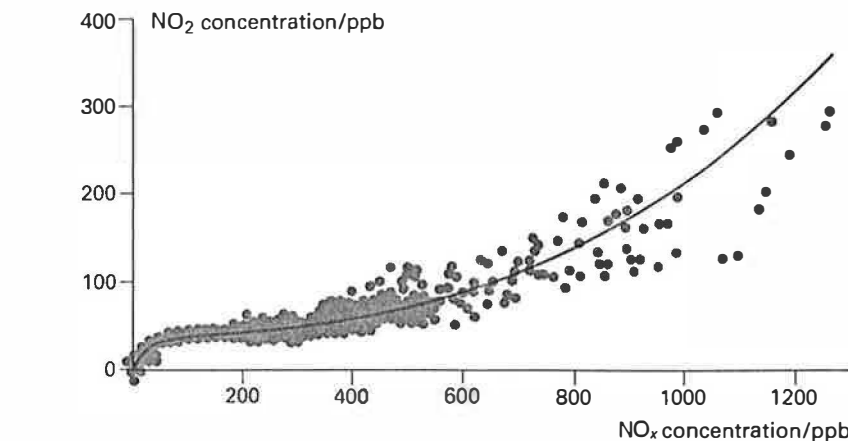


Fig 2. The relationship between hourly mean NO<sub>2</sub> and NO<sub>x</sub> concentrations at Exhibition Road, London.

concentrations than the surrounding rural areas. Figure 3 shows that rural sites such as Lullington Heath on the south coast and Aston Hill on the Welsh border have the highest average ozone concentrations, and central London sites the lowest.<sup>1</sup> This is because fresh nitric oxide emissions from

combustion sources—mainly motor vehicles—destroy ozone, as shown in reaction a. The elevated concentrations of nitrogen oxides and reactive hydrocarbons caused by fresh pollutant injections in large urban areas can significantly enhance ozone concentrations in the downwind urban plume (Box 2). In London, the effect is observed about 80 km downwind, often in the vicinity of the Harwell Laboratory, because photochemical ozone episodes are most common during periods of anticyclonic weather and easterly winds.<sup>10</sup> Paradoxically, the urban area is contributing both to ozone destruction on the local scale and to ozone formation on the larger regional scale.

Recently, the focus of research into the effects of pollution on health has turned to particulate matter. A number of US studies have shown that elevated concentrations of airborne particles are associated with increased mortality from all causes. One of the most recent of these was the Harvard Six-City Study<sup>11</sup> which showed a monotonic increase in mortality rates, after correction for smoking and other potentially confounding variables, with airborne particle loading. Death rates in Steubenville, Ohio, were 26 per cent greater than those in Portage, Wisconsin—the PM<sub>10</sub> concentrations being 46.5 and 18.2 μg m<sup>-3</sup> respectively. Four other cities included in the study had intermediate PM<sub>10</sub> concentrations and mortality rates. The statistical link between airborne particle loading and mortality has yet to be explained in biological terms and will be a rich area for research. It is reassuring that the first phase of EUN provides measurements of PM<sub>10</sub> in our city centres, and these concentrations in international terms are very modest; the average is generally about 30 μg m<sup>-3</sup>.

Airborne particles are very complex in chemical terms. Figure 4 gives a breakdown of the major constituents, although several of these contain many minor components; the fine particle fraction is of greatest health significance. Figure 4 includes primary particles, ie those emitted directly into the atmosphere such as insol-

ble materials and carbonaceous matter, and a major component of secondary particles, *ie* those formed in the atmosphere from chemical conversion of gases such as  $\text{SO}_2$  and nitrogen oxides to solid products, mostly ammonium sulphate and ammonium nitrate. The chemical complexity of this particulate material and the fact that composition will vary significantly both spatially and temporally, make it particularly difficult to understand why fine particle concentrations and death rates in different areas and at different times correlate so consistently.

### Future trends

In predicting future air quality trends we need to make a number of projections about industrial activity, traffic growth and the stringency of pollution control measures. In its first report, Quarg examined future trends,<sup>1</sup> particularly in road traffic emissions of various pollutants as these play such a major role in urban areas. In the third report we will look in more detail at the likely future trends in urban air quality. One factor that came through extremely clearly in our projections to the year 2010 was that three-way catalytic converters—mandatory on all new cars since January 1993—will significantly reduce road traffic emissions of  $\text{NO}_x$ , CO and hydrocarbons over the next 20 years, but emissions may start to grow again as a result of increasing road traffic. However, in the second report<sup>2</sup> we looked specifically at the impact of diesel engine vehicles on urban air quality. The projections in the first report did not take account of the massive recent increase in the market penetration of diesel cars. If this trend of increased diesel sales continues it will have a significant beneficial effect on CO concentrations, a very modest but beneficial effect on hydrocarbons, but deleterious effects on oxides of nitrogen, and a major impact on road transport emissions of particulate matter for which diesel is by

Fig 3. The average diurnal variation of hourly mean ozone concentrations (1 May to 31 July 1992) at five sites.

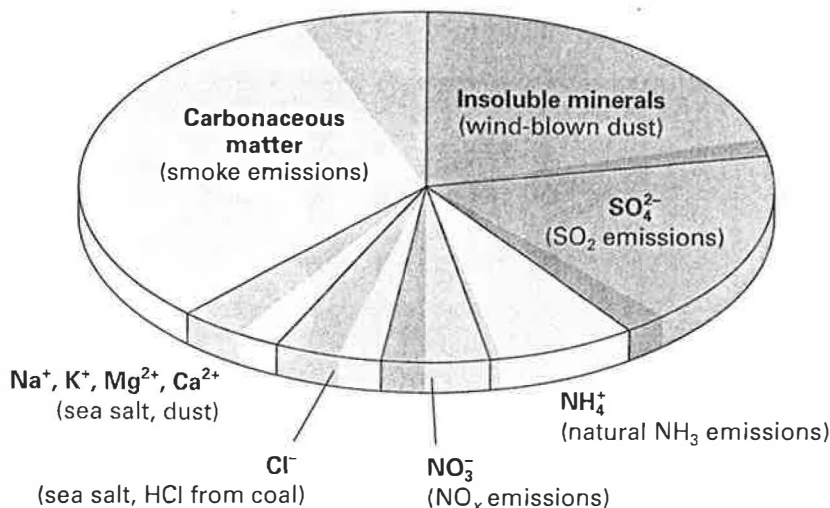
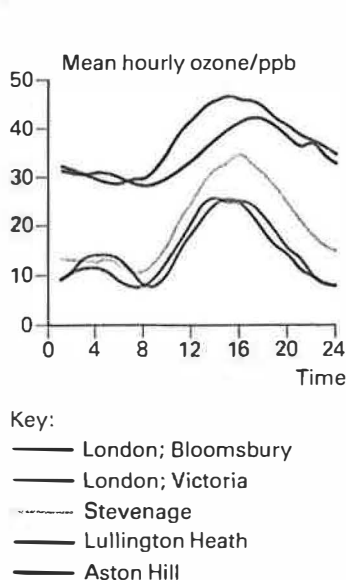


Fig 4. The composition of atmospheric particles collected in Leeds (1982-83). The shaded portions of each segment indicate the proportions of fine particles (< 2.5  $\mu\text{m}$  diameter); the remainder are coarse particles (2.5-15  $\mu\text{m}$ ).

far the major source. Emissions of particulate matter per vehicle are set to decrease because of tighter emission standards on diesel cars, due to be implemented in 1996, and the increasing uptake of unleaded petrol, which gives lower particulate emissions from petrol cars. Our projections of road transport particulate emissions indicate that if diesel vehicles were to maintain a constant 16 per cent share of the new car market, total particulate emission would decrease significantly over the years to a level in 2005 that is *ca* 50 per cent of the 1991 emissions. If, however, diesels were to comprise 49 per cent of the car fleet, particulate emissions will increase significantly to the year 2000 and then decrease by 2005 to a level very similar to that in 1991.<sup>2</sup> Because these diesel particles probably comprise the largest single source of primary particle emissions in urban areas, the current increase in sales of diesel cars threatens to wipe out the benefits of tightening emission control standards in relation to particulate matter. Also, it is clear from Fig 3 that abolishing episodes of high  $\text{NO}_2$  concentrations will require a substantial decrease in  $\text{NO}_x$  emissions, which will take longer, if the number of diesel vehicles continues to rise.

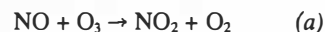
A further implication of the ozone- $\text{NO}_x$  chemistry discussed above is that a decrease in nitrogen oxide emissions (mainly NO) is liable to cause an increase in urban ozone concentrations because of a reduced impact of reaction *a* and a higher  $\text{NO}_2/\text{NO}$  ratio. We have yet to predict the magnitude of this effect quantitatively. Rural ozone concentrations are likely to decline, but the magnitude is difficult to predict as the ozone concentration is not linearly related to the emissions of precursor gases.

The recently published government discussion paper *Improving air quality*<sup>12</sup> suggests policies for future management of air quality. The widespread availability of urban air quality data, combined with a

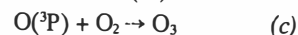
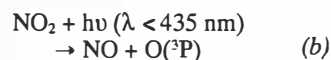
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## 2. Urban nitrogen oxide, oxygen and ozone chemistry

Most emissions comprise NO, which is susceptible to rapid oxidation by  $\text{O}_3$ :



In daylight,  $\text{NO}_2$  may be photolysed to give triplet state atomic oxygen  $\text{O}(^3\text{P})$ , which reacts with molecular oxygen to form ozone:



The equilibrium condition between  $\text{NO}_2$  formation (reaction *a*) and photolysis (reaction *b*) is termed the photostationary state. This occurs when the rates of the two reactions are equal and hence:

$$[\text{O}_3] = \frac{J_b[\text{NO}_2]}{k_a[\text{NO}]}$$

where  $J_b$  is the light dependent  $\text{NO}_2$  photolysis rate constant and  $k_a$ , the rate constant for reaction *a*. Measurements in the atmosphere indicate that the stationary state is widely achieved. Deviations arise when other reactions of comparable rate intervene. The most important are reactions involving peroxy radicals, which convert NO to  $\text{NO}_2$  without consuming ozone. Peroxy radicals are most abundant during periods of bright sunshine, generating high  $\text{NO}_2/\text{NO}$  ratios and allowing high concentrations of ozone to develop. Thus 'plumes' downwind of urban areas can be substantially enriched in ozone.

The alternative route for oxidation of NO is the reaction with molecular oxygen.



This reaction is second order in NO and of insignificant rate until atmospheric concentrations exceed 500 ppb.

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participate in the general assembly as observers. For the small fee of US \$ 50 they have the opportunity to gain some acquaintance with the union before becoming full members. In addition, about 30 other international associations are associated with the union; these are active in science, technology and engineering. About 1500 experts from government, industry and academe are engaged in the Union's committees and commissions. IUPAC has a worldwide membership programme operating in 75 countries. Almost 7000 chemists have registered as affiliates, including about 600 chemists from Third World countries.

IUPAC is responsible for regulating, standardising and codifying the international language of chemistry. Over 160 chemical companies from 25 countries participate in the IUPAC Company Associate Scheme, which was introduced in 1977 to improve collaboration between the chemical industry and the union. The union also works closely with international organisations, resulting in ventures such as the joint IUPAC-Unesco-Unido training programme, which allows safety experts from developing countries to learn about safety and environmental protective measures by visiting plants of IUPAC Company Associates in the industrialised world.

Every year IUPAC organises dozens of conferences, symposia and other events all over the world. Among these are the bien-

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growing clutch of air quality standards, will generate pressure for improvements in air quality which will require further reductions in emissions. The paper envisages empowering local authorities, singly or in combination, to designate air quality management areas for which an air quality management strategy would be devised. A comprehensive, scientific strategy will require the construction of pollutant emissions inventories broken down on a fine spatial scale. Together with topographic and meteorological data this will be input to numerical dispersion models, which will allow us to calculate ground-level pollutant concentrations for a grid of receptor points. Such air quality management models will allow us to assess the impact on air quality of source reductions, new roads, pedestrianisation schemes or other emissions changes, before the schemes are implemented. Currently, a detailed emission inventory is available only for London, although work is in hand for an inventory of the West Midlands conurbation.

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cial congresses and general assemblies, as well as conferences launched under the Chemical Research Applied to World Needs programme. In the latter conferences, the union identifies important global or multinational problems to which chemistry can contribute significantly.

Recently the union has launched a series of collective monographs under the general heading *Chemistry for the 21st century*. Among the recent titles are the *Chemistry of advanced materials*, *Chemistry of oxide superconductors*, *Perspectives in catalysis*, and *Medicinal chemistry for the 21st century*.

Given the rapid advances that are currently affecting chemistry, IUPAC faces a number of challenges. But we can be confident that the collaborations of chemists under IUPAC's umbrella will come up with appropriate answers. In doing so, chemistry will, among other things, deliver its input to some of the more burning questions that society has today.

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### Further reading

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