

nally planned that there would be only one such document, ILAC has published a similar guide (ILAC Guide 12). Thus, a difference in classification of reference materials exists and should be resolved between ISO and ILAC.

- **Consistency between ISO Guides and GUM:** The ISO Guide *Expression of Uncertainty in Measurement* (Geneva, 1995) has, in the last few years, influenced almost all fields of analytical chemistry. The requirement of ISO Standard 17025 that analytical results need to be reported together with their associated measurement uncertainty also strongly underpins ISO REMCO's new *Certification of Reference Materials—General and Statistical Principles* (ISO Guide 35). This viewpoint is understandable, because RMs are often applied in field laboratories for quantification of combined uncertainty or separate sources of measurement uncertainty. At the moment, revision of ISO Guide 35 is around 50% complete. Its publication is not to be expected before summer 2001. ISO Guide 35 is also a basis for future classification of RMs. However, the principles of the new guide are clear, and they will, to a certain extent, influence all reference materials producers dealing with matrix RMs. Principles of ISO Guide 35 include the following:

1. Characterization of the candidate material through large international laboratory comparisons, which normally results in a consensus value, is no longer regarded as appropriate. Comparison of results from a small number of laboratories is preferred; however, all participants must demonstrate traceability of their results and report their measurement uncertainty.
2. When a number of laboratories participate, as described at the beginning of paragraph 1, the results should be treated in the same way as if they were produced by a single laboratory. Statistics applied in combining these results and their uncertainties does not break a traceability chain when each laboratory separately reports traceable results. At the same time, a small number of participants can better communicate to clarify eventual discrepancies, and the entire certification project can be processed faster. Exclusion of outliers on the basis of statistics alone is not allowed. Unfortunately, in large worldwide inter-comparisons, it is almost impossible to control and to achieve these requirements.
3. In preparing the revised ISO Guide 35, no distinction will be made between "primary" methods of measurement and "other" methods. There is a common requirement that methods applied for CRM characterization are "fit for purpose" and that measurement uncertainty is as small as

reasonably achievable. These decisions were based partially on the latest developments at the Consultative Committee on Amount of Substance (CCQM) at BIPM, Sevres, France (see report on page 163). CCQM has recognized that methods of analysis cannot be declared as traceable as methods *per se*. Rather, a combination of analyte, measurand, matrix, and technique is important. For various analytical techniques, the ability to produce results that are "fit for purpose" has already been demonstrated, although not declared as "primary".

- **Similarities and Differences between Materials Used in Measurement Processes:** Several different types of materials are used in measurement processes (e.g., CRMs, RMs, proficiency-testing materials, internal quality control samples, calibration standards, etc.). A clear distinction between them, based on the quality requirements for these materials and their intended use, has to be made. The first draft of a paper on this topic was expected by the end of this year. As the topic also concerns chemical terminology, strong cooperation with IUPAC is foreseen. The result of IUPAC Project 501/9/97, "Compilation and clarification of quality assurance-related nomenclature" and Alphabetical Index of Defined Terms and Where They Can Be Found, prepared by Mr. David Holcombe and published in three parts in *Accreditation and Quality Assurance* [see *Accred. Qual. Assur.* **4**, No. 12, pp. 525–530 (1999); **5**, No. 2, pp. 77–82 (2000); and **5**, No. 4, pp. 159–164 (2000)] will serve as a starting point. For a summary of the project and links to the abstracts of the *Accred. Qual. Assur.* articles, please visit the IUPAC web site at [www.iupac.org/divisions/current\\_projects/1997/501\\_9\\_97.html](http://www.iupac.org/divisions/current_projects/1997/501_9_97.html).

The next two ISO REMCO Meetings are planned to take place at the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA, 21–23 May 2001 in conjunction with the 100<sup>th</sup> anniversary of NIST; and in Ljubljana, Slovenia in May 2002, respectively.

#### Overview of the International Symposium on Atmospheric Deposition and its Impact on Ecosystems, with Reference to the Mideast Region, Tel Aviv, Israel, 4–5 June 2000

Prof. René E. Van Grieken (Departement Scheikunde, Universitaire Instelling Antwerpen, Universiteitsplein 1, B-2610 Antwerpen [Wilrijk], Belgium; E-mail: [vgrieken@uia.ua.ac.be](mailto:vgrieken@uia.ua.ac.be)), a National Representative on

IUPAC's Chemistry and the Environment Division's Commission on Atmospheric Chemistry (VI.2), and Dr. Yehuda Shevah (TAHAL Consulting Eng., Ltd., 54 Ibn Gvirol Street, POB 11170, Tel Aviv 61111, Israel; E-mail: tahalcmp@netvision.net.il), Chairman of IUPAC's Commission on Soil and Water Chemistry (VI.3), have submitted the following report:

### Introduction

Atmospheric supplies of nitrogen and phosphorus, heavy metals, polychlorinated biphenyls (PCBs), chlorinated pesticides, and other persistent organic pollutants (POPs) may play a major role in ecosystem dynamics, particularly in oligotrophic marine areas such as the Southeast Mediterranean, in terrestrial ecosystems, and in inland freshwater bodies. The interface between the atmosphere and the sea plays a central role in the exchange of matter. Trace elements, such as lead, cadmium, and mercury, enter the sea to a considerable extent via the atmospheric pathway. Over 50% of the nitrogen input to the North Sea may be supplied by the atmosphere, with most of this amount being derived from anthropogenic sources. In estuaries and seas, extra nutrients can cause eutrophication, with enhanced growth of algae populations, and subsequent oxygen deficiency when the dead algae material decomposes.

Hundreds of lakes and streams can no longer sustain life, while the threat to forests and watersheds in many parts of the world is growing. In Israel, the freshwater Sea of Galilee—providing 35% of the water supply—is now showing a very unstable quality. It is likely that the dustfall, which can amount to 60% of the total solid input into the lake, may exert a profound influence on the properties and behavior of the lake in general and on the water quality in particular. In the Dead Sea area, ozone depletion was reported to coincide with an interaction of atmospheric oxidants with bromide at the Dead Sea salt pans.

In view of the growing threat of atmospheric deposition and the increasing need to expand our knowledge in the field, an International Symposium on Atmospheric Deposition and Its Impact on Ecosystems was convened 4–5 June 2000 in Tel Aviv, Israel. The symposium, organized by IUPAC's Division of Environmental Chemistry and by the Israel Chemical Society, brought together about 70 internationally recognized experts from the United States, Europe, the Mediterranean Region, and Israel.

### Symposium Issues

- Atmospheric processes related to the Mideast Region as a zone in which air mass trajectories can trace both local pollution and the influence of Europe and the Sahara as sources.
- Effects of the large efforts that have been made to

reduce or control emissions to air of SO<sub>2</sub> and NO<sub>x</sub>, volatile organic compounds (VOCs), and, more recently, of metals and POPs.

- Cycling of pollutants between the atmosphere and the ecosystem compartments and new developments in experimental techniques for flux measurements.
- Review of atmospheric deposition studies covering the work of the Cooperative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP), the EUREKA Project on the Transport and Chemical Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe (EUROTRAC), ASE, the Biosphere Atmosphere Exchange of Trace Gases and Aerosols (BIATEX), and interaction with regional and local studies in the Middle East.

### Topics of Discussion and Main Sessions

- backward trajectories of air masses over the Mediterranean
- effects of atmospheric pollutants on the Southeast Mediterranean Region
- Saharan dust
- impact on ecosystems
- research cooperation

### Wet and Dry Atmospheric Deposition

Atmospheric removal occurs by dry deposition of aerosol particles and gases, or by wet deposition in rain, fog, hail, and snow. The relative importance of these two processes varies between locations and is primarily a function of the rainfall intensity. For example, at the Northern and Western European temperate latitudes, wet deposition amounts to about half of the total atmospheric input of nitrogen to natural ecosystems.

The processes of dry deposition were described by C. Davidson to include three major steps. The first step, aerodynamic transport, carries contaminants from the free atmosphere into the relatively quiescent layer close to the surface, which can be described using the friction velocity, stability class, and other parameters pertinent to turbulent flow. The second step is boundary layer transport of contaminants across the viscous layer of air, immediately adjacent to the surface. Analogies with momentum and heat transport across boundary layers are often used to describe contaminant mass transport in the viscous layer. The third step refers to interactions of the contaminants with the surface. For gases, this step describes adsorption and absorption interactions. For particles, it is important whether they adhere to the surface or bounce off.

The processes that govern the formation of rain, the scavenging of aerosol particles both within and below clouds, and the effects of aerosol size on these processes were discussed by L. Spokes, including problems as-

sociated with the collection and determination of wet fluxes, chemical reactions occurring in rainwater and controlling the pH and the aerosol solubility, and the importance of episodic high-concentration deposition events and their effect on surface water biogeochemistry.

### Long-Range Transport

The East Mediterranean Region is influenced by "European" air masses that are high in anthropogenic pollutants. This import is compounded by the scavenging of alkaline Saharan dust, which has a magnified effect on cloud physics and chemistry and, subsequently, on natural precipitation, cloud seeding, and deposition onto terrestrial and aquatic ecosystems.

Recent investigations of long-range transport of European pollutants to Israel were discussed by P. Alpert, who calculated monthly cyclonic tracks over the Mediterranean based on European Center for Medium-Range Weather Forecasts (ECMWF) data. Summer back trajectories from Tel Aviv pointed to sources spreading from Southeast Russia to Southern Europe, Spain, and North Africa. Z. Levine speculated that transported particles that pass through clouds are affected by wet chemical reactions and by physical processes, leading to the formation of dust particles coated with soluble salts such as sulfates from industrial origin or from dimethyl sulfide naturally emitted by the Mediterranean itself. Gas scavenging and subsequent liquid-phase oxidation add additional sulfate. The soluble coating of the mineral dust particles could significantly change their ability to serve as cloud condensation nuclei (CCN), causing cloud water to redistribute into larger concentrations of smaller droplets.

Sulfur-coated particles were reported by D. Rosenfeld to prevent rain droplets from forming in low clouds and, possibly, to cause lower rainfall. "Polluted" clouds are composed of much smaller droplets, without any precipitation echoes detectable by precipitation radar.

The Regional Atmospheric Modeling System (RAMS) for meteorological simulations and the Hybrid Particle and Concentration Transport (HYPART) package for dispersion modeling were used by M. Luria to explain the transport of polluted air masses toward the coast of Israel. Specific synoptic and wind conditions over the Eastern Mediterranean govern the movement of polluted air masses toward Israel. In one case study involving aircraft measurements, prevailing northwest winds forced the pollution from Southern Europe and the Balkans into the Eastern Mediterranean coast along the 180-km flight path, significantly increasing the average measured concentrations of  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{O}_3$ , and particulate sulfate.

### Short-Range Transport

W. Kordel described aerial short-range-transport for pesticides; direct spray drift occurred during applica-

tion and by volatilization from the target area in the post-application phase. Pesticide concentrations in nontarget plants exceeding 10% of the actual pesticide concentration in the target plants were observed in neighboring nontarget ecozones, which may cause unintended effects on fauna and flora. Particularly for semivolatile pesticides with vapor pressures between  $5 \times 10^{-3}$  and  $10^{-6}$  Pa, this relationship is important. The observed shelter effects of downwind hedges were low.

### Ozone Depletion

Photochemistry of  $\text{NO}_2$  is the main source of  $\text{O}_3$  in the ground and boundary layer. L. Klasinc showed that, in Croatia, the  $\text{O}_3$  concentration has more than doubled recently and is still rising. Vertical fluxes of  $\text{O}_3$  and energy over a plant growth cycle in a large coniferous forest of Southwest France were reported by Lopez et al.; they indicated the effects of dry, wet, and dew conditions on  $\text{O}_3$  deposition velocity, and the effect of stomatal conductance on increased deposition velocity during the day.

Atmospheric reactive BrO was measured, and its effect on  $\text{O}_3$  ozone chemistry was assessed over the Dead Sea in Israel by Peleg et al., who reported a negative diurnal repeating cycle of  $\text{O}_3$  and BrO variations, correlated with solar radiation and wind direction. During the elevated BrO events,  $\text{O}_3$  regularly decreased from noontime levels of 50–80 ppb or higher down to 10–30 ppb and occasionally to levels below the detection limit of 5 ppb. Interaction of atmospheric oxidants with bromide at the salt pans of the Dead Sea were stipulated to be the source of BrO. The only other places where this kind of chemistry occurs are over the Arctic and Antarctic.

### Trace Metals

A literature survey of published concentrations of atmospheric trace metals above the North Sea and the English Channel over the period 1971–1994 was conducted by Van Grieken et al. Of the six trace metals—Cd, Cu, Pb, Zn, Ni, and Cr—that were evaluated, Pb, Zn, and Cd showed a very strong decreasing trend with time. Similarly, a seasonal variability of atmospheric Pb concentrations over the English Channel was reported by Puskaric et al.; they indicated a decrease by about one order of magnitude over the last fifteen years and a different isotopic signature for Pb aerosols from Eastern Europe versus those originating in Western Europe. Cd, Cu, Pb, Zn, and natural elements (Al, Fe, Mn, and Cr) were also measured in dry atmospheric inputs at the coast of Israel, where mixing and dilution effects of European emissions with local emissions are taking place (Herut et al.).

Fossil fuel combustion sources and incinerators are the major sources of reactive gas phase Hg (RGM). Compared to elemental  $\text{Hg}^0$ , which has a slow removal

rate from the atmosphere (low solubility in water), RGM is extremely water-soluble and efficiently removed from the atmosphere during rain events. Hg deposition studies are being conducted by Mamane et al. for Hg, RGM, and total particulate mercury (TPM) to model the Hg emission in Europe, as well as its transport and deposition on the South Baltic Sea and the Mediterranean Sea.

### Organic Pollutants

Gas-phase POPs over Lake Michigan have been studied by Hornbuckle et al., who employed the Lake Michigan Mass Balance Project to identify the large summertime “plume” of gas-phase PCBs from Chicago, differentiating between short-range (higher molecular weight congeners) and long-range atmospheric transport (lower molecular weight congeners).

### Nitrogen and Sulfur Compounds

Owing to the discontinued use of soft coal, emissions of SO<sub>2</sub> over Europe have been reduced by 55% since 1980, resulting in lower concentrations of S-components in air and precipitation. In the meantime, the emissions of NO<sub>x</sub>, contributing to acidification and to photochemistry, remain very much the same today as in 1980, although long-term studies of nitrate concentrations in precipitation from the early 1980s to the present seem to indicate that concentrations have been falling (Schaug et al. and N.O. Jensen). It was shown that large inputs of alkaline species and a relatively high abundance of Ca and NH<sub>4</sub><sup>+</sup> cause neutralization of the acid rain. In this context, a rather neutral value of pH 6.4 in the precipitation of Ankara, Turkey was reported by Incecik.

### Saharan Dust

The Saharan dust is an important component in wet deposition, accounting for approximately half of the annual deposition of Al and Fe in the Eastern Mediterranean region. Tuncel et al. showed that the dust particles are potential CCNs, an atmospheric sink for trace gases, and a major factor in the neutralization of rain acidity by CaCO<sub>3</sub>. Rudich et al. further suggested that mineral particles are coated with organic compounds, which can potentially influence the hydrophilic behavior of the particles and their optical properties. Danin also speculated that airborne dust trapped in vegetation is an important factor in the amelioration of growth conditions and functions as a trap of eolian dust, thereby avoiding soil erosion. Ganor et al. showed that dustfall generated locally and dust storms originating in North Africa are deposited over the Sea of Galilee in Israel. Calcite, quartz, feldspar, dolomite—and, to a lesser extent, gypsum and halite, and clay minerals, such as kaolinite, illite, and palygorskite—can be as much as 60% of the total solid input into the lake.

### Conclusions

The symposium and the associated discussions focused on the issue of atmospheric deposition and its impact on ecosystems and highlighted ongoing research and problems that still need monitoring. The symposium provided the scientific basis for effective emission, mitigation, and adaptation policies, emphasizing the:

- numerous sources of polluting emissions;
- chemical transformation processes of pollutants in the atmosphere;
- relationship between sources and effects, which is not always easy to establish;
- deficiency of point measurements, which are not sufficient to characterize air quality in a particular region because the information about transport or atmospheric chemistry is missing; and
- need for integration of atmospheric pollutant concentrations and deposition, which are intricately related and need to be studied together.

The symposium also emphasized the need for:

- improving the knowledge of cause–effect relationships between air pollution and factors affecting conditions and health of ecosystems,
- improving prediction and detection,
- better ways of monitoring the environment,
- international standards for measuring and reporting emissions, and
- necessary regional and international cooperation.

These issues are of a global dimension, and regional and international coordination is highly essential. Therefore, the role of conventions, for example, the Helsinki Commission (HELCOM) for the Baltic Sea, the Oslo and Paris Commission (OSPAR) for the North Sea and Northeast Atlantic, the Barcelona Convention for the Mediterranean, and the UNDP Regional Seas Program, should be strengthened, as well as the institutions involved in measurement of air and precipitation quality and database formation, such as the Norwegian Institute for Air Research (NILU).

### Acknowledgments

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### Epilogue: Coding Scheme for Properties in Laboratory Medicine

Since 1995, the Committee on Nomenclature, Properties, and Units (C-NPU of IFCC and IUPAC) has published nine papers on a coding system (i.e., a structure or a framework for the pairs of codes and meanings) and a coding scheme (i.e., the pairs of codes and their meanings) for properties in laboratory medicine.