Indicator Measurements
for Assessing the Impacts of Anthropogenic Air Pollutants on Human Health and Ecosystems

by **George Allen, NESCAUM, Douglas A. Burns**, U.S. Geological Survey, **Christine Negra**, The Heinz Center for Science, Economics and the Environment, and **George D. Thurston**, New York University School of Medicine. Contact George Allen at gallen@nescaum.org.

Emission control policies are designed to protect human health and our environment from air pollution. To track the success of these policies, an approach is required that includes measurements—both of the pollutants and their effects (indicators)—and various kinds of modeling. Measurements and modeling should be closely coupled because each supports and drives progress in the other, and both are used in indicator or impact assessments.

One favored approach is an integrated assessment approach that recognizes interactions among different aspects of pollutants as well as multi-media chemistry and exposure pathways. Figure 1 shows the inter-related nature of many pollutants. This article examines several high priority air pollutants or pollutant classes in this context, and discusses key indicators for assessing the impact of those pollutants. Information gaps and measurement needs are also noted. The linkage from emissions to health and ecosystem impacts has several intermediate steps.

Starting from the pollutant emission source, modifiers include transport (such as chemical transformations and removal or fate), endpoint concentrations and resulting exposure, and finally the actual dose that drives the observed effects. From an accountability perspective, this pathway can be followed in reverse. Although most of the pollutants here have both natural and anthropogenic sources, we will address the latter in this article since the results of human activities over the last few hundred years have dramatically increased air pollutant emissions.

Mercury

Mercury (Hg) is a powerful neurotoxin to humans and animals. Because Hg has multiple chemical forms in the environment, exposure can occur through several pathways. The most widespread human-risk exposure pathway, however, is the ingestion of the methyl form of mercury (MeHg) through fish consumption. MeHg bioaccumulates in cells, and therefore biomagnifies in both aquatic and terrestrial food webs. The primary source of Hg in most environmental settings is atmospheric deposition, and the largest sources of atmospheric Hg emissions to the atmosphere are coal-burning and other industrial and mining-associated activities.

Relative to other common air pollutants, elemental Hg has a longer atmospheric residence time and Hg emissions are transported longer distances prior to deposition. Additionally, after deposition, Hg can be re-emitted and further transported in the atmosphere.[1] As a result, Hg deposition at any location originates from varying amounts of local, regional, and global emissions. Decades of enhanced rates of atmospheric deposition of Hg have resulted in large Hg stores in soils which can be mobilized and transported into lakes and streams. The rate at which Hg moves from terrestrial to aquatic ecosystems depends on landscape factors such as the presence of wetlands that provide anoxic conditions conducive to the methylation of Hg. Additionally, low pH conditions from acid rain generally favor higher bioaccumulation of Hg in fish, and bacteria that transform the sulfate in acid rain in wetlands and also produce MeHg.

No national scale ecosystem monitoring network yet exists for Hg in waters and biota. Most current information originates from state-level monitoring of Hg in fish (based on diverse sampling strategies) as well as from local ecosystem studies of short duration. Currently, a group of scientists representing universities and federal and state agencies (MercNet) is working to design and establish a comprehensive national monitoring program for Hg in ecosystems. Once national scale data are available, MeHg levels in prey fish, piscivorous fish, and birds can be better linked to watershed sensitivity and mercury deposition levels to assess differences in ecosystem response to atmospheric Hg deposition in slow and fast responding watersheds.

Figure 1. *Movement of Contaminants and Potential Effects*
Source: Adapted from The State of the Nation's Ecosystems 2008: Focus on Contaminants. The H. John Heinz III Center for Science, Economics, and the Environment; graphic by Grabhorn Studios.

Acid Rain

Acid rain includes rain and snow (wet deposition) as well as gases, particles, and fog (dry deposition) that is excessively acidic due primarily to the burning of fossil fuels. Acid rain has been recognized across wide regions of the U.S. since the 1960s. Acidification and the associated release of aluminum to soils and surface waters has damaged both terrestrial and aquatic ecosystems. Research in the 1980s as part of the National Acid Precipitation Assessment Program clearly demonstrated the link between acid rain, acidification of ecosystems, and harmful biological effects such as extirpation and habitat limitation of many species of aquatic biota including fish, insects, and microscopic organisms.[2] Later work identified effects on terrestrial ecosystems including mortality of red spruce and sugar maple trees.[3]

> Data from soils provide an important link to understanding ecosystem recovery from reduced levels of acid rain.

Decreases in the atmospheric deposition of sulfur (S) and nitrogen (N) and increases in the pH of precipitation have been documented by the National Atmospheric Deposition Program (NADP) National Trends Network from the 1980s to the present. This network measures wet deposition at more than 200 sites across the U.S. Notable exceptions to these trends include increasing N deposition in the Rocky Mountains of Colorado and in some agricultural areas affected by high levels of ammonia deposition. Corresponding improvements in water quality have been documented by the U.S. Environmental Protection Agency (EPA) Long–Term Monitoring Program (LTM) which measures water chemistry at a network of lakes and streams in the Eastern U.S.[4] Thus far, improvements in the acid-base status of waters have not kept pace with the improvements documented in acid rain, and little recovery towards a mix of species believed to exist before acidification began has been observed. This sluggish recovery has been attributed to a variety of factors such as expected lags in ecosystems and the slow pace of species dispersal, but widespread evidence points to the depletion of calcium (Ca) and magnesium (Mg) from soils. Decades of acid rain has mobilized aluminum from soils and stripped Ca and Mg from these soils in sensitive areas such as the Adirondack Mountains of New York and Blue Ridge Mountains of Virginia and North Carolina, where native soils have little of these elements and where the rock breaks down at very slow rates. Evidence of acid rain effects on soils has come from a variety of studies, but a soil-monitoring network has not been established to document the status of Ca and Mg in soils at regular time intervals in a variety of locations. Data from soils provide an important link to understanding ecosystem recovery from reduced levels of acid rain.

In summary, wet and dry acid deposition are well monitored by existing networks, and despite the limitations of LTM/TIME in geographic scope and ability to address short-term changes in surface water chemistry associated with rain and snowmelt events, this is the primary network that provides long-term monitoring of acid rain effects on surface water chemistry. Long-term monitoring of effects on aquatic and terrestrial biota and soil chemistry, a key component of acidification models, are insufficient to fully understand the effects of changing deposition levels on ecosystems.

Ozone

Ozone (O_3) is a gas that occurs throughout the atmosphere. In the stratosphere, O_3 is produced naturally and filters the sun's ultraviolet rays. But O_3 that occurs in the lower atmosphere near the earth's surface (the troposphere) is a harmful pollutant. A key component of what is generally called smog, "ground level ozone" results from complex sunlight-driven reactions of volatile organic compounds (VOCs) and nitrogen oxides (NOx), which are emitted primarily by motor vehicles, industrial facilities, and electrical utilities, etc. Emission controls for O_3 precursor pollutants have resulted in a downward O_3 trend over the last few decades at most locations, although in most years the majority of monitoring stations in or near urbanized areas measure O_3 levels greater than 80 ppb on one or more days.[5]

Ozone can cause a variety of respiratory problems in humans and animals and has a direct toxic effect on vegetation. Cumulative effects on individual plants can lead to reduced yields for agriculture and forestry, increased vulnerability to stresses such as disease, pests and harsh weather and declines of whole plant populations. An analysis of O_3 impacts on ecosystem function at a national scale, including agricultural and non-agricultural ecosystems, estimated a 2.6 to 6.8% reduction in annual net primary productivity between 1950 and 1995, depending on agricultural management and land use assumptions.[6] Projected increases in temperature are likely to contribute to increases in tropospheric O_3 levels. Sitch et al.[7] found that O_3-induced reductions in plant productivity may offset the carbon dioxide "fertilization effect", leading to a net reduction in terrestrial carbon storage.

EPA maintains a database of ambient O_3 levels through a network of approximately 1900 monitoring sites that provide important information about ambient O_3 exposure for both human and ecosystem effects. The U.S. Forest Service's Ozone Biomonitoring Program employs established protocols to measure foliar injury in ozone-sensitive plants at over 1100 sites nationwide. These data can be used to track changes in O_3-induced plant injury over time. Monitoring changes in crop yield in areas affected by high O_3 levels can help to assess the impact of changes in O_3 on agricultural productivity.

The adverse health consequences of breathing O_3 are serious and well documented. Effects include impacts demonstrated in controlled chamber exposures of humans and animals, and observational epidemiology showing consistent associations between O_3 and adverse impacts across a wide range of human health outcomes. The damaging nature of O_3 is also evidenced by the way it can visibly "eat away" at materials such as rubber, which shares its elastic characteristics with human lungs. Airway inflammation in the lung is among the serious effects that have been demonstrated by controlled human studies of O_3 at levels typically experienced by most Americans. Airway inflammation is especially a problem for children and adults with asthma, as it makes them more susceptible to having asthma attacks. For example, controlled human studies have shown that prior exposure to O_3 enhances the reactivity of asthmatics to aeroallergens such as pollens, which can trigger asthma attacks.

There is no indication in health studies of a threshold concentration below which sensitive populations (children and the elderly) are safe from the effects of elevated O_3 concentrations. More recently, O_3 has been confirmed to increase the acute and chronic (cumulative) risk of human mortality.[8] Tropospheric O_3 levels are expected to increase under likely future climate change scenarios, creating additional human health implications.

Although O_3 is widely monitored, its precursors and important, but intermediate oxidants (such as the OH radical) are either rarely or sparsely monitored. The EPA Photochemical Assessment Monitoring Stations (PAMS) network that monitors NOx and VOCs was designed to assess O_3 precursors in and near large urban areas with elevated levels[9] but no routine network exists to measure related oxidants or O_3 breakdown products which can also be highly reactive and harmful.

Nitrogen Enrichment

An important nutrient for plant growth, nitrogen is found in both inert and biologically available forms. The production and use of synthetic fertilizers, burning of fossil fuels, and production of nitrogen-fixing crops (e.g. soybeans) have increased biologically available nitrogen to the point that it has become a problem pollutant in some ecosystems.[10] Nitrogen emitted into the atmosphere from industry,

transportation, agriculture, etc. returns to terrestrial and aquatic ecosystems through wet and dry deposition. Over time, chronic nitrogen enrichment can have major effects on an ecosystem's chemical composition and lead to changes in biological composition by inducing potential changes in productivity and competitive interactions.

Once the capacity of an ecosystem to store or make use of added nitrogen is exceeded, the element is exported through the soil profile and into surface waters. The movement of nitrogen from land to rivers and streams, where it is eventually carried to coastal waters, contributes to algal blooms and low oxygen levels or "dead zones".

Streamwater nitrate levels are a useful indicator of terrestrial nitrogen enrichment. The USGS National Water Quality Assessment (NAWQA) gathers nitrate data monthly in 51 major hydrologic systems in the U.S. (http://water.usgs.gov/nawqa/). The EPA Wadeable Streams Assessment provides nitrate data, based on summer stream conditions, for three major U.S. regions (www.epa.gov/owow/streamsurvey/web_data.html). These datasets are based on different sampling schemes and would ideally be harmonized to provide a more robust picture. In addition, national-scale data for nitrogen levels, dissolved oxygen status, and chlorophyll in coastal waters would be useful for tracking the effects of nitrogen enrichment in coastal systems.

The Role of Particulate Acidity in the Effects on Human Health and Ecosystems

There are demonstrated links between the ecosystem effects discussed above and the health effects of O_3, Hg, and acid rain. The major source of particulate-phase acidity in the air is via atmospheric transformation of gaseous sulfur dioxide (SO_2), which is also the major gaseous source of acid rain. Throughout the world, the major anthropogenic source of SO_2 emissions is the burning of fossil fuels, especially coal burning for the production of electrical power. The transformation of gaseous SO_2 to particulate acids in the air usually occurs on the surface of existing atmospheric particles (e.g., heterogeneous gas-solid reactions) resulting in the production of SO_3, which then combines with water vapor to produce sulfuric acid coatings on ambient particles.

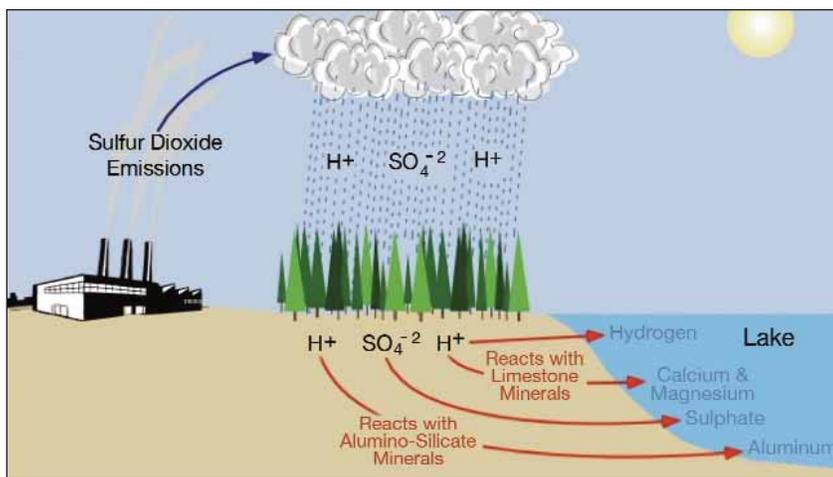The adverse health consequences of breathing O_3 are serious and well documented.

Figure 2. Mobilization of metals from atmospheric acidic deposition
Source: www.physicalgeography.net/fundamentals/8h.html

It is now thought that aerosol acidity may have its greatest ambient environmental effects on human health via this acidity-particle interaction, as the resulting lowered pH of the particle increases the solubility of metals in the particle, mobilizing the transition metals (such as iron and vanadium) within the particle upon which it is adsorbed.[11] This causes these toxic metals to become more bio-available, and more likely to adversely affect the person who breathed the particles before the lung's clearance defense mechanisms can remove the particle from the lung, thereby increasing the toxicity of the particles compared to those without an acid coating. This is analogous to what happens with acid rain in a lake when lowered pH of the water increases the solubility of aluminum, causing increased toxicity to aquatic life (Figure 2). Thus, acidity is a marker for both the human and environmental health effects of fossil fuel combustion.

Future Needs

The pollutants we have considered undergo transformation reactions as they are dispersed and transported across the globe. As a result, they present considerable challenges in predicting their national and trans-border impacts. As discussed in the article *Integration of Air Quality Modeling and Monitoring Data for Enhanced Health Exposure Assessment*, by Denby et al. on p. 46, ambient concentrations of pollutants over a regional domain may be estimated through emissions-based mechanistic modeling, ambient-data-based modeling, or a combination of both. Air quality models provide spatially-resolved descriptions of pollutant concentrations, though the model outputs can be inaccurate due to data

uncertainties, and these errors tend to be compounded as atmospheric reactions are modeled. When modeling is combined appropriately with observations, one can generate an improved air pollutant surface characterization relative to using only one approach.

One ambient-data-based approach that does not rely on often highly uncertain emission estimates is source-apportionment analysis, employing source-specific tracers that are carried with the pollutant as it is diluted, transported, and converted over time in the environment. In such receptor-oriented source apportionment modeling based upon ambient trace constituents, one measures concentrations of various species (e.g., elements) at an ambient sampling site (the receptor) and then uses statistical methods to identify the type and number of major particle sources, their source compositional "signatures" or elemental tracers, and finally obtains a pollution apportionment among the various source contributors. Such source apportionment methods have been well documented in the literature over the past two decades.

In the U.S., the EPA Speciation Trends Network routinely measures tracer elements in particulate matter in the air that are sufficient for the conduct of source apportionment of air pollution in most major U.S. cities. The major pollution sources for which common tracers are measured by the Speciation Network in the U.S. include: smelting industry (Pb, Zn); soil particles (Ca, Si); motor vehicles (EC, NO_3); steel industry (Fe, Mn); coal combustion (As, Se); oil combustion (V, Ni); salt particles (Na, Cl); and biomass burning (K). By following the temporal trends in these tracers, the contribution of their associated sources to pollution can be tracked. However, such data are only collected at a limited number of sites in each U.S. city, and are lacking in most other countries around the globe. If such data were consistently collected and reported, then the changes in impacts from these various sources in the air could be tracked in a consistent manner using source apportionment methods.

Chemical elements such as selenium (Se) and Arsenic (As) can serve as environmental tracers of coal combustion, which is a large and growing source of acid rain, Hg, and O_3 precursors. While both of these elements are pollutants in their own right and have other possible sources in the

environment (e.g., from smelting operations in certain localities), coal combustion is the predominant global source of each of these tracer elements, and when elevated concentrations of both are observed, they provide a useful index of coal impacts over time. Thus, there is a need to build upon and expand the U.S. Speciation Network that monitors these metals in the U.S. and to make similar measurements throughout the rest of the world so that the global impacts of rising coal emissions can be better documented. In addition, similar monitoring of these coal tracers in soils and waterways would help to better track the impacts of coal in these media as well.

Another approach for assessing source attribution is to use highly time-resolved measurements (minutes to one hour) instead of the more traditional 24-hour integrated samples often used at present. This approach can be used with appropriate meteorology to separate and distinguish between different sources of the same pollutant or pollutant indicator. This applies to chemical composition, and for particles, physical parameters such as number concentration (an indicator of ultra-fine particles). Although these measurements can now be made for many pollutants, there is a great need to develop simpler and less expensive methods that can be more widely deployed and are easier to operate. Very little fundamental change has been made in most environmental measurements over the last few decades. Examples of new approaches are the "sensor[s] on a chip" and quantum cascade laser technologies that are presently in the early research phase. Until simpler and less resource-intensive measurement methods are available,

it will not be feasible to obtain these types of time-resolved data routinely across the U.S.

Summary

Few pollutants act in isolation when both human health and ecosystem effects are considered. There are often multiple and highly non-linear or threshold interactions with other pollutants or human and ecosystem health characteristics that are often not initially obvious. While there may be challenges to implementing a multi-pollutant and multi-media integrated approach, the outcome would likely be more realistic with regard to the nature of air pollution. Modeling and source apportionment can benefit from additional monitoring data, and the availability of highly time-resolved data would allow additional analytical approaches. Data that are available in near-real time have additional uses, such as the fine particulate matter and O_3 data now available through AIRNow (http://airnow.gov).

There is a widely held belief that increased integration is likely to result in significant short- to medium-term cost savings, although consultations with managers, funders, and those who oversee monitoring programs suggest that such savings are not easily achieved. Coordination and integration may compete with existing monitoring and reporting activities for money and staff time resources. If efficiencies can be built into programs at the outset, and are reevaluated periodically as new technologies with lower operating costs become available, longer term savings are possible and can help move us towards a more integrated system of pollutant monitoring. **em**

References

1. Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C. A Synthesis of Progress and Uncertainties in Attributing the Sources of Mercury in Deposition. *Ambio*. **2007**, 36, 19-32.
2. Baker, L.A.; Herlihy, A.T.; Kaufmann, P.R.; Eilers, J.M. Acidic Lakes and Streams in the United States: The Role of Acid Deposition. *Science* **1991**, 252, 1151-1154.
3. Driscoll, C.T.; Lawrence, G.B.; Bulger, A.J.; Butler, T.J.; Cronan, C.S.; Eagar C.; Lambert, K.F.; Likens, G.E.; Stoddard, J.L.; Weathers, K.C. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. *BioScience* **2001**, 51: 180-198.
4. Kahl, J.S., and 15 others. Have U.S. Surface Waters Responded to the 1990 Clean Air Act Amendments? *Environmental Science and Technology* **2001**, 38, 484A-490A.
5. The Heinz Center (2008). The State of the Nation's Ecosystems: Measuring the Lands, Waters and Living Resources of the United States. The H. John Heinz III Center for Science, Economics and the Environment, Washington, DC.
6. Felzer, B.; Kicklighter, D.; Melillo, J.; Wang, C.; Zhuang, Q.; Prinn, R. Effects of Ozone on Net Primary Production and Carbon Sequestration in the Conterminous United States Using a Biogeochemistry Model. *Tellus Series B-Chemical and Physical Meteorology* **2004**, 56(3):230-248.
7. Sitch, S.; Cox, P.M.; Collins, W.J.; Huntingford, C. Indirect Radiative Forcing of Climate Change Through Ozone Effects on the Land-Carbon Sink. *Nature* **2007**, 448, 791-794.
8. Jerrett, M.; Burnett, R.T.; Pope, C.A. III; Ito, K.; Thurston, G.; Krewski, D.; Shi, Y.; Calle, J.; Thun, M. The Contribution of Long-Term Ozone Exposure to Mortality. *New England Journal of Medicine* **2009**, 360(11)\, 1085-95.
9. U.S. Environmental Protection Agency (1996). National Air Quality and Emissions Trends Report, Chapter 4: PAMS: Enhanced Ozone and Precursor Monitoring, available at: www.epa.gov/air/airtrends/aqtrnd96/chapter4.pdf.
10. United Nations Environment Programme (2007). Reactive Nitrogen in the Environment: Too Much or Too Little of a Good Thing. The Woods Hole Research Center, Falmouth, MA.
11. Costa, D.L.; Dreher, K.L. (1997). Bioavailable Transition Metals in Particulate Matter Mediate Cardiopulmonary Injury in Healthy and Compromised Animal Models. *Environmental Health Perspective* 105S (Suppl 5):1053-60.