

US EPA ARCHIVE DOCUMENT

# VI. How Do I Design an Air Deposition Assessment Strategy?

The most important question to ask yourself when designing an assessment strategy is “What question am I trying to answer?” What to monitor for, what type of monitoring equipment to choose, where it is placed, how often samples are collected, how deposition data are coordinated with water quality data, and whether models are used (and if so, which one(s) and how) are all dependent on what question(s) need to

be answered. It is also important to remember the “assessment” part of the project. To answer any questions, you must dedicate sufficient time and resources to interpret or analyze the data collected. This is not a negligible cost. Most atmospheric deposition studies have to dedicate 30% of the budget to data analysis. The advisory group will help design the strategy, but here are some things to keep in mind as you go through that process.



- What questions need to be answered?
- What information is needed?
- What else should be considered?

## What Questions Need to be Answered?

When thinking about the questions that need to be answered, you need to look ahead to how you plan to use the information gathered. It is likely that most of the users of this handbook want to gather information that can be used in making management decisions, rather than primarily for basic research. Some of the typical questions are

- How important is atmospheric deposition of a particular pollutant compared to other sources?
- How does it affect the bay/estuary/lake?
- Are there biological or ecological effects?
- How much deposition is falling on the watershed and ending up in the bay/estuary/lake?
- How much is coming from in-state sources versus out-of-state sources?
- How much is coming from a source or source category (e.g., utilities, certain agricultural practices, pulp and paper mills, automobiles, etc.)?

- How much is coming from a single source (e.g., a particular industry or animal-feeding operation upwind)?
- What do I want the data to do? (Objectives defined, along with statistical uncertainty.)
- What degree of certainty in the answer is required for decision makers?

The first step is to clearly identify your specific objectives and prioritize the question(s) that need to be answered. There may be more than one. You also need to ask yourself how much certainty you need in the results to make decisions or to support various management approaches you may use. These questions will help the partners and experts focus on the problem at hand (and design a better assessment strategy). They will guide decisionmaking throughout the study and will help assess the results of the study and determine if it has been successful. That is not to say the study won't uncover questions you didn't know you had or open up paths that hadn't been thought of before. But if you need answers to specific questions, you'd better make sure you have them when the study is

complete (or a good explanation of why you don't). It is a good idea to prioritize the questions that need to be answered so strategic decisions can be made if it is not possible to answer all the questions given the time and/or resources available.

The quality of the data to be collected must be defined during the design stage. A confidence interval or some other statistical parameter by which data quality can be assessed should be developed. The advisory board will prove useful, if not essential, in this effort.

### What Information is Needed?

The information needed depends on the question(s) that need to be answered and the tools used to answer them. Details on different methods of atmospheric deposition assessment are in the sections on **What You Need to Know About Air Deposition Monitoring** and **What You Need to Know About Air Deposition Modeling**. Here is a short discussion of what types of information are needed to get particular kinds of data.

**Wet Deposition Rates.** Wet deposition rates are the easiest to measure directly because wet deposition can be measured with a precipitation sampler. Several wet deposition collectors are commercially available that open and close automatically. For more information on how to monitor wet deposition, see page 34.

**Dry Deposition Rates.** Estimating dry deposition is more complicated. As noted earlier, dry deposition depends on many factors, including meteorological conditions, characteristics of the pollutants being deposited (e.g., particle size), and

characteristics of the surface on which the deposition occurs. There are several different types of dry deposition methods to choose from (see page 34 for descriptions). The data from each type must be converted into deposition rates using a modeled deposition velocity or one taken from the literature. To accurately calculate deposition rates, detailed meteorological data must be collected on wind speed and direction, as well as temperature and humidity at a specific reference height above the ground. This is usually several meters off the ground, so dry deposition sites are also called towers.

**Indirect Deposition Load.** To determine indirect deposition load, you need to know not only how much is deposited to the watershed, but also how much of the deposited pollutant reaches the waterbody of concern via surface runoff or groundwater. The proportion of pollutant retained versus the proportion transported (transmission coefficient) is estimated either from a set of runoff coefficients or a watershed transport model. These values vary greatly for each pollutant and each watershed. They are influenced by land use, soil type and permeability, vegetation slope, and stream density, depth, temperature, and discharge. For more information on how to calculate indirect deposition loads, see page 38.

**Percentage of Load Due to Atmospheric Deposition.** To know the percentage of load due to atmospheric deposition, you need both an estimate of the load due to atmospheric deposition and estimates of the loads due to other pathways. The estimate will only be as accurate as the estimated loading rates from the various pathways. Depending

#### What Role Does the Microlayer Play?

**Microlayer:** The microlayer is the thin (several microns—millionths of a meter—thick) surface layer of water. Pollutants that are hydrophobic (don't mix well with water) tend to collect in the microlayer. Oil forming mats on the surface of the water is an extreme example of this. This means that plants and animals who live in the microlayer, or who eat food from the microlayer, are exposed to far higher concentrations of hydrophobic pollutants than those who do not. Therefore, in order to fully understand the ecological impact of hydrophobic pollutants, you have to study the microlayer separately from the rest of the water column. If the microlayer is thick and the waterbody shallow, then the microlayer can play a significant role in affecting the rate of deposition and volatilization. However, some scientists believe for deeper lakes the microlayer is not a large enough reservoir to be important. Some hydrophobic pollutants include: PAHs, PCBs, organic metal compounds, dioxins/furans and pesticides/herbicides.

on your information needs, you may group these other loads into categories (e.g., point sources and nonpoint sources) or break them into more specific categories (e.g., wastewater treatment plants or stormwater runoff).

**Source Attribution.** Once the total deposition rate is known, the process of identifying sources can begin. This is done in one of two ways: either by using some sort of tracer or modeling. To use tracers, samples must be analyzed for the tracer(s) used and the unique chemical composition or fingerprint of a source or source category must be known. To do back-trajectory modeling related to deposition, you need deposition data collected over a day or less and access to meteorological data temporally resolved on a short-term basis. To do source-receptor modeling, you need sophisticated meteorological data sets and complete emissions inventories. For more information on source attribution see page 57.

**Ecological Impacts of Deposition.** This is complicated for several reasons. One is that the effects of atmospherically deposited pollutants are not easy to separate from the effects of the same pollutants coming from other sources. The second is that many potential environmental effects and indicators can be measured. Another complication is differences in waterbodies, such that the same level of pollutant in one system can have a greatly different response than it would have in another system. Some of the common environmental effects are lake acidification (for sulfate and nitrogen deposition), fish/bird tissue loads and microlayer assays (for toxic bioaccumulating pollutants), forest health (both tree and soil), and symptoms of eutrophication. In addition to measuring specific ecological indicators, it is necessary to know the percentage of the total pollutant load that comes from atmospheric sources and possible (or even proven!) mechanisms for the atmospheric load to cause the observed ecological effects.

Types of data ideally needed in some aspect of atmospheric deposition studies include:

- Wet deposition rates
- Dry deposition rates
- Ambient air quality data and deposition velocities (to calculate the dry deposition rate)
- Meteorological data (rainfall amount daily or weekly, wind speed, wind direction)
- Good inventories of sources that emit pollutants of concern locally, regionally, and perhaps nationally. An ideal inventory should include all sources, emission heights, speciation of emissions, rates of emissions, the exit velocity, and the stack gas temperature.
- Sophisticated meteorological data sets (to input into transport models)
- Watershed transport ratios or models
- Loading rates from sources other than atmospheric sources
- Emissions chemical “fingerprints”
- Ecological data showing impacts of atmospheric deposition.

**It is important to note** that while this is a list of ideal data, it is highly unlikely you will have all of it. This list should be considered a goal, not the bare minimum you need to know before any decisions can be made.

### What Else Should be Considered?

#### *Do I Monitor or Model First?*

Most studies monitor first. Unless there is already a good set of data to put into the model you want to use, that is a good example to follow. You should know what kind of modeling you plan to do before you begin monitoring, however.

Modeling and monitoring are really two parts of an iterative process. Generally there will already be some monitoring or modeling done in the watershed before your project begins, so part of the decision is based on what data are already available. Many assessment strategies monitor first and use modeling to fill in gaps in monitoring data, identify sources, and make predictions about what emissions reductions are needed. Some of the modeling may be already done on a national scale, so check with your state air quality agency and the EPA Air-Water Coordination group or the Great Waters Program to see what is available or “in the works.” (For a list of federal contacts see the **Resources** section on page 73; for state contacts see the EPA Aerometric Information Retrieval System database.)

Air deposition monitoring and modeling are best thought of as complementary strategies that, together, can provide a large amount of information for managers and for the public about the sources and importance of atmospheric deposition in a watershed. For this to happen, however, monitoring and modeling researchers need to communicate their needs to one another and understand the strengths and limitations of each approach. Any manager who uses monitoring and modeling data must, in turn, be clear about how they plan to use

#### **Isopleth Maps**

Monitoring networks use statistical methods such as kriging or the least-squares fit to estimate patterns in wet deposition over large areas between monitoring sites. The results are often turned into isopleth maps, which have contours of deposition amounts or concentrations that look similar to topographic maps. However, unlike topographic maps which are presenting data that actually exists on the ground, isopleths are presenting statistical estimates of deposition rates between monitoring sites. This is the technique used to create the nationwide deposition maps NADP prepares from its 200+ sites. It is really only useful over large areas with many wet deposition monitoring sites. It cannot be used for dry deposition data because the rates are too dependent on the surfaces and immediate meteorology. An example of an ammonium deposition isopleth map (NADP's 1999 data) is on page 29.

it and what kinds of questions they need answered. A given model may be used to answer some questions, but it usually cannot do all of them. The choice of which model(s) to use—or the decision to create a new one—will be guided in large part by what questions need to be answered.

If you think of monitoring and modeling as complementary techniques and if you know what data you have and what data the model(s) you might use require, it will often be obvious what to do first. Your advisory group should be able to help you make the final decision.

#### ***Should I Coordinate with Other Air and Water Monitoring Stations?***

For practical purposes, the more you can coordinate the better. Existing air monitoring stations already have power and security, there is access to the site, and there may be some equipment, particularly meteorological equipment, that you can share instead of buying your own. Perhaps most importantly, coordinating almost always saves operator time (and therefore costs) for sample collection and site maintenance.

It is, however, not essential to collocate air deposition monitoring with either existing air or water quality monitoring sites. Generally it is easier to compare results if the sites are relatively close by, but that is not a good enough reason to locate an air deposition site in a particular location. Develop a set of criteria for the air deposition site based on the questions you need to answer and carefully evaluate whether an existing site will meet those criteria. If they will, go ahead and collocate. But if they will not, locate the air deposition site in an area that will allow you to answer the key questions.

#### ***Should I Join an Existing Monitoring Network?***

The decision to join an existing monitoring network or create an independent site or network of sites depends (once again) largely on the question(s) the data need to answer. Generally, national networks are designed to measure deposition rates on a large scale. They are not designed to show differences in deposition rates over small areas (although

sometimes they can), show the impacts of particular sources on a particular area, or identify sources. They do show long-term trends of “regional” deposition rates and are important databases for scientists studying the effects of deposition. For example, NADP data clearly show the gradient in deposition from the Midwest that spreads north and east into New York and northern New England. They also clearly show the impacts of the 1990 CAA amendments (CAAA) on reductions in sulfate deposition in New England and New York. NADP sites do not indicate which particular sources affected by that legislation caused the original deposition or the decrease. AIRMoN sites can be used in back-trajectory analyses to identify source regions, but may not be adequate for all source identification needs.

National network sites are very important because they allow us to see the big picture on a national scale and identify how local areas and regions fit into that big picture. They are usually not good at differentiating deposition rates over a small area, although they can in some instances. Many local managers have discovered that they end up needing both national network sites and independent sites over the course of a many-year study to answer all their questions.

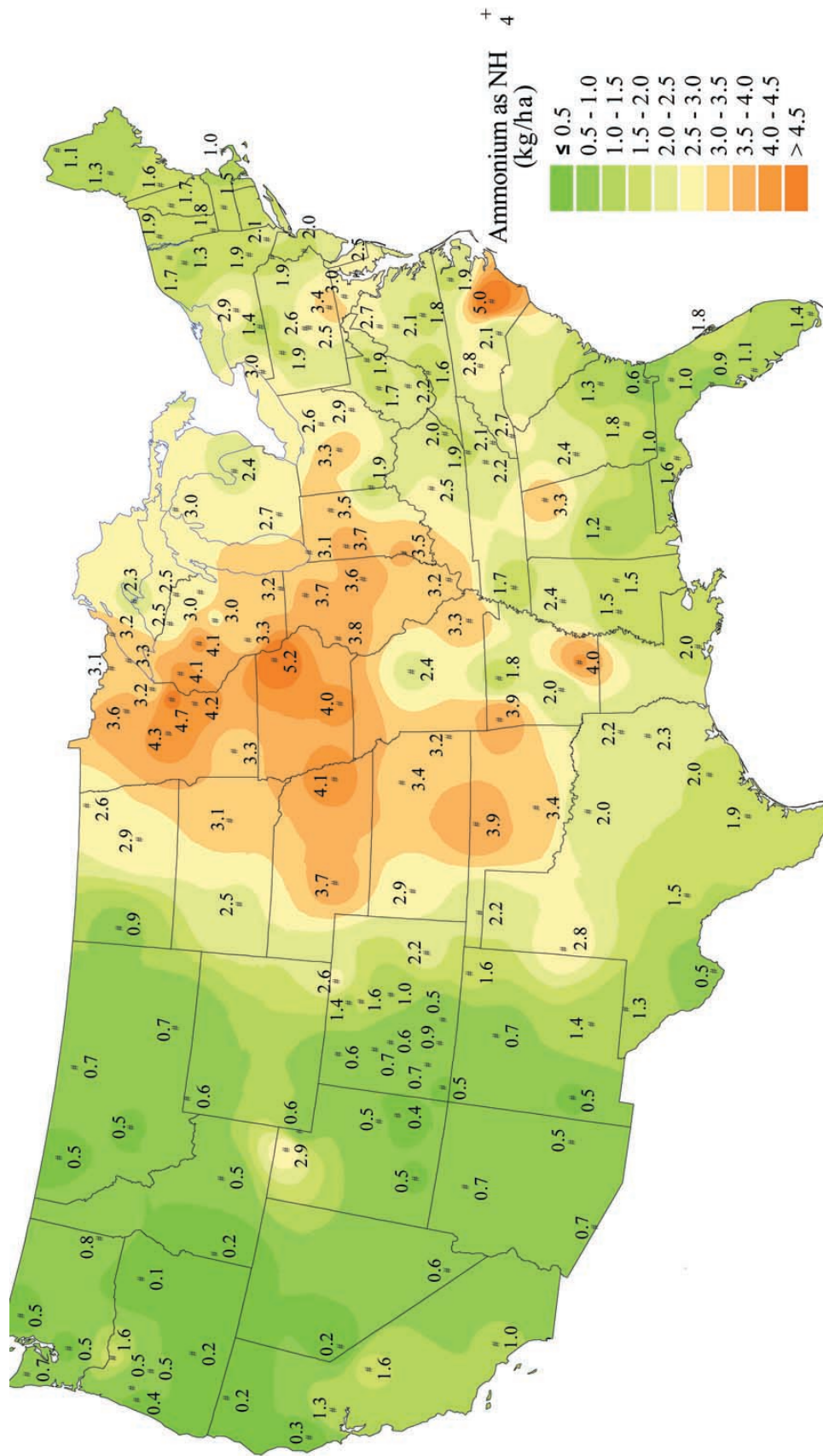
A benefit of national networks is that sampling, analyses, and quality assurance are all done uniformly, in accord with established methods, which makes it easier to compare data between sites or geographic regions. Networks can also provide a source of expertise and can provide a forum to exchange ideas among experts in the field. The national networks ask for a minimum five-year commitment to maintain the site and collect samples. This requirement ensures that inter-annual variation can be measured. However, this commitment is a cost consideration. These networks were discussed in general on pages 14-19. More detail is provided below, such as estimated site operation costs.

To join the NADP-NTN or -MDN, the site needs to be approved by the NADP. This includes agreement that the network needs a site in the general

location of interest. (Because the NADP strives to get regional representation of deposition rates, it is not interested in having sites clumped together.) Once the NADP agrees that a site in the general area is needed, the actual site location, maintenance plan, and quality assurance plan require approval based on NADP criteria. This involves submitting the paperwork requested by the NADP. For examples of NADP siting criteria, see Appendix 4. The NADP does not provide funding to install or maintain the site, collect samples, or analyze samples. The NADP charges a small fee for program coordination that includes data analysis/interpretation and the production of national maps showing spatial variability of deposition. The analysis does not include local watershed-scale data analysis and, by itself, is not useful for most source identification. NADP sites can be used in some situations as reference sites to show lower deposition rates upwind of major sources. The NTN sites measure wet deposition of a handful of pollutants (sulfate, nitrate, orthophosphate, ammonium, calcium, magnesium, potassium, sodium, and pH). The MDN sites measure total wet mercury deposition or, for additional sample analysis fees, wet methylmercury deposition.

In 1999, the first-year costs (buying the equipment and a year’s worth of monitoring) for the NTN cost approximately \$17,000. This does not include the actual installation costs (digging the hole in the ground and installing the monitor and rain gauge). These site-specific costs can vary significantly. Each additional year costs approximately \$15,000 (for site operation, labor, electricity, and sample analysis). MDN sites are more expensive than the basic NTN sites because the equipment has to be modified before sample collection can begin, and mercury analysis is expensive. In 1999, the first-year costs (buying the equipment and a year’s worth of sampling) were approximately \$21,000. Annual operating (sampling and analysis) costs are approximately \$12,000, and more if methylmercury samples are analyzed. Samples are collected weekly (9 am on Tuesday) by operators at each NTN and MDN site and shipped to a single laboratory (one for NTN and another for MDN) for analysis.

### Estimated Ammonium Ion Deposition, 1999



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.sws.uiuc.edu>

AIRMoN, the smallest subnetwork of the NADP, is sponsored by the Air Resources Laboratory of NOAA. The first sites were installed in 1992, but additional sites can still be added to the network. New sites are approved by the NOAA Air Resources Lab. AIRMoN consists of about 22 sites and measures a range of pollutants (for both wet and dry deposition) on a daily (instead of weekly) basis. The network also refrigerates samples to preserve them (which NADP-NTN does not). The pollutants measured (wet, dry, or both) include nitrogen oxides ( $\text{NO}_x$ ) and sulfur dioxide ( $\text{SO}_2$ ). This allows AIRMoN data to be used for back-trajectory analysis (a source attribution method) because data can be matched with meteorological patterns to identify source regions of the pollutants. This is not possible with weekly samples since the wind shifts so many times during a seven-day period. A typical AIRMoN wet site costs approximately \$28,000 for the first year (excluding installation costs). Each additional year costs approximately \$20,000, primarily for sample analysis. A typical AIRMoN dry site costs approximately \$35,000 for the first year and \$30,000 to run for each additional year.

The other national dry deposition network is CASTNet, which was established in 1987 to determine spatial patterns and geographic trends in air pollution (and to measure the effectiveness of the CAAA of 1990). There are approximately 80 CASTNet sites in the country. CASTNet sites use filterpacks to collect ambient air samples, and deposition velocities are calculated using the Multi-Layer Model. Deposition rates are then calculated from the ambient air samples and the deposition velocity. Various pollutants are measured at each site, but there is the capability to measure ambient gaseous nitric acid and sulfur dioxide; particulate sulfate, nitrate, and ammonium; and base cations (potassium, calcium, etc.).

CASTNet sites are expensive to operate because of the large number of pollutants being analyzed and the process required to analyze dry deposition. In 1999, the first year costs were approximately \$78,000. Each additional year costs approximately \$42,000. These costs include installation (roughly \$30,000), operating site costs (\$10,000 and up annually), and annual analysis (\$38,000 to \$43,000).



## VII. What You Need to Know About Air Deposition Monitoring

Although the concept of air deposition monitoring is pretty simple, the reality is rather complicated. There are a variety of methods to choose from and a laundry list of things to watch out for, as well as dozens of decisions to make about all the details. This section lays out many of the options you have to choose from and issues you have to consider, outlines background information on the pros and cons of different methods of monitoring, and provides estimates of the scale of monitoring you can achieve given a certain amount of resources.

A word of caution about monitoring is probably appropriate here. Air deposition monitoring data, like any other type of monitoring data, are only as good as the monitoring design allows them to be. In other words, there are dozens of reasons why the results you get may not be really representative of what deposition is happening now, what has happened, or what generally occurs in the watershed. Monitoring sites should be chosen carefully and maintained for as long as possible to minimize these problems, but you should always ask yourself (as with any other monitoring effort) how accurate and representative your data need to be for their intended purpose.

This section contains information on



- Station setup
- Deposition monitoring
- Estimating the indirect deposition load
- Uncertainty, errors, and quality assurance
- How much data can I get for \$15,000, \$50,000, \$400,000 a year?
- How much monitoring is enough?

### Station Setup

#### *Picking a Site*

Picking a good site is one of the most important things to do when designing a monitoring strategy. A monitoring site must meet the goals of the study—it must be placed to answer the questions that need to be answered—and the data it produces must be scientifically defensible.

If you can place just one monitoring site, it should almost always be where it can measure “regional” deposition. That is, it should measure some sort of average of what happens in the area, not “hotspots”

from particular sources. NADP sites are regional sites; following their site location criteria will give you a good estimate of representative deposition rates. A copy of the NADP site criteria is included in Appendix 4. Dry deposition sites also are located to get regionally representative results, but this is much more difficult to do than it is for wet deposition sites because of the acute sensitivity of dry deposition to the surrounding landscape.

If you can put out two or more sites, things get more complicated. Often two sites are organized in an “upwind, downwind” system where one site is upwind of suspected sources (often well inland) and

### How to Locate Multiple Monitoring Sites

The rule of thumb is to balance getting the best temporal coverage (lots of data points at one site over a long time) and the best spatial coverage (data points from many different sites). Temporal coverage allows more accurate results to be concluded for a particular point; but without spatial coverage, it is not possible to know how representative those results are for the entire watershed. Some networks use a master-satellite approach to get the best of both worlds. In the master-satellite approach, there is one master station where deposition is measured frequently and several satellite sites spread out through the watershed where deposition is less frequently measured. Master sites can also be used to collect speciation data that would be too expensive to collect at all the sites. An example of a master-satellite network is IADN (see page 18 for more information in IADN).

The decision of where to locate sites depends on the question(s) to be answered. For example, if a particular local source is suspected, and the study would like to confirm its significance, sites should be located upwind and downwind, and the results compared. If the goal is to accurately measure the average deposition reaching an estuary or lake, the sites should be geographically spread out around the area of concern, and none of them should be directly downwind of a large source. Sites should be located in suspected “hotspots” of especially high deposition rates only if they are what you want to specifically characterize.

the other is downwind on or near the coast. With additional resources, sites can also be set up upwind of other source areas or located close to large suspected sources in an attempt to characterize the influence of a particular source. Often local or regional networks with multiple sites do not measure every pollutant at every site; the samples are strategically analyzed based on either initial measurements or the researchers’ best understanding of what pollutants are important to measure where. In that situation, unanalyzed samples are usually stored for future analysis for additional pollutants at a later time, if necessary.

Every site requires some type of deposition sampler and some type of equipment to measure

meteorological data. Dry deposition sites require more sophisticated meteorological equipment than wet sites. When choosing site location, think about access (hard for other people, not extremely difficult for you), availability of power (if you can go with battery- and/or solar-powered equipment, great; if not, you’ll have to bring power in or choose a site where it already exists), and security. Almost all sites have fencing around them or are located on rooftops or in some other access-restricted area such as an Army base. These practical concerns are as important as choosing a site without interference from nearby sources or objects and that is the right distance and direction from suspected sources.

Sampling on islands or from boats is attractive because this is often as close as you can get to measuring deposition rates over water. Another advantage of sampling from boats or ships is that, due to their mobility, they can be used to sample at various locations around the waterbody. Few sampling programs end up collecting samples from either boats or ships, however, because the logistics are so difficult. Sampling from boats, in addition to being very costly, also has the drawback that emissions from the boat can contaminate the samples, and the boat disturbs the air flow around it, making it difficult to sample ambient air. This seriously compromises the accuracy of the measurements. If you decide to sample from boats, make sure your quality assurance plan addresses how you will avoid contamination from the boat exhaust and avoid interference from the boat structure itself. Sometimes samplers are set up on buoys and the samples collected by boat (but not *from* a boat), but this also makes access (and getting adequate power supply!) difficult and has the potential to contaminate samples.

### Sampling Frequency

Several sampling frequencies are regularly used (e.g., 12-hour, daily, or weekly). Which one is chosen has a large impact on what the data can be used for. It also has a large impact on how much it costs to do the monitoring. Although the cost of equipment

for different methods varies dramatically, in general, the more samples that have to be analyzed, the more expensive the monitoring.

Longer sampling frequencies (weekly/monthly) are usually adequate for measuring deposition over a longer term, while shorter frequencies (daily/12-hourly) are required for determining depositional processes and delineating emission sources.

**Twelve-hour sampling** is recommended by many experts to get accurate dry deposition measurements. Temperature and humidity changes have a significant influence on measurements; therefore, samples can become altered while waiting for analysis. Twelve-hour sampling minimizes the temperature and humidity changes that any particular sample undergoes. This is often done by having one filterpack or denuder switch on to collect a sample during the day and another switch on to collect a sample at night. This can be done with a series of denuders or filterpacks for several days.

**Daily sampling** can be done for wet or dry samples. Daily sampling allows the data to be used in back-trajectory analyses (a method of matching wind direction and pollutant load to help identify sources). This also tends to be the most accurate for wet deposition samples because there is the least opportunity for any particular sample to be contaminated or otherwise altered. AIRMoN uses a daily sampling frequency.

**Weekly sampling** is probably most common for both wet and dry deposition. Weekly samples cannot be used for back-trajectory analyses (because the wind direction shifts frequently over that period). NADP-NTN, MDN, and CASTNet use a weekly sampling frequency.

### **Types of Samples of Ambient Air**

**Integrated samples** are used to measure ambient air concentrations to support dry deposition calculations. In integrated sampling, air samples are collected on a filter (particles) or reactive/absorbing medium (gases) and subsequently taken to a laboratory for analysis. Samplers are set out for

anywhere from a few days to several months, and the data are averaged over that period. This leaves a large amount of time for samples to be contaminated or altered by humidity and temperature changes. This may affect how well deposition velocities (and therefore deposition rates) can be calculated. It is done regularly anyway to minimize the cost of sample analysis and, in some cases, because shorter sampling frequencies do not collect enough trace pollutants (such as dioxins/furans) to be accurately measured. As samplers become better at detecting very small amounts of pollutants, this technique will probably be used less and less because of the issues with contamination and alteration. It should be emphasized that although pollutant levels may be low enough that samplers must stay active for a long period of time, the small amount of pollution measured may cause significant water quality impacts.

**In situ continuous/semi-continuous samplers** collect and analyze air samples at the sampler location at very small time intervals (such as 5 seconds or 15 minutes) and store the data until they are retrieved by an operator. Typically, data are aggregated to one-hour reporting periods for interpretation and comparison with predictive models. An assortment of techniques is available to capture gases and particle-bound ions, metals, and carbon. Sampling at small time intervals is good for comparing data with results from an airplane study or to measure extremely precise differences in meteorology and air concentration over a short period of time.

### **Deposition Monitoring**

There are only a handful of ways to measure atmospheric deposition. Which one you choose depends to a large extent on what question needs to be answered, what needs to be measured, what assumptions the advisory group is most comfortable with, and the resources available. The preferences of the scientist(s) actually doing the monitoring are also important.

Measuring atmospheric deposition is not a simple process. “Clean techniques” are especially important

for toxic pollutants, which are often (but not always) measured in small quantities. All staff or volunteers who collect atmospheric deposition samples should have some basic training, and those collecting dry deposition samples should be especially well prepared. NADP provides good training materials for wet deposition monitoring methods, but dry deposition training often must be on an individual basis by researchers or experienced field staff. Don't pinch pennies with training. Many data sets have been shown to be virtually worthless because proper sampling and handling techniques were not observed or analytical techniques were employed that were not sensitive enough.

### Wet Deposition

Wet deposition is measured by collecting rain and snow. Almost any pollutant can be measured using this method, and some isotopes of some pollutants can also be measured (for more information on isotope analysis see page 61). The basic equipment is a collector, such as a bucket, tray, or funnel connected to a bottle. A collector typically has an automated cover that keeps dry deposition and debris out when it is not raining and slides away from the collector to uncover it when it is raining.

Snowfall also triggers the collector to be uncovered, so deposition in snowfall is measured. However, the capture efficiency for snowfall may be poor due to the aerodynamics of trying to capture blowing snow. It is also possible for something else, like bird droppings, to trigger the collector to open. This can contaminate the sample. Sometimes samples fall as rain, but freeze before they are collected, which complicates the analysis. Special handling procedures, materials, and other considerations are required for collecting samples for metals, organic compounds, or isotope analysis.

Regardless of whether they measure regional deposition or hotspots, it makes sense for wet deposition sites to follow the local NADP siting criteria (located in an open area where trees and buildings will have a minimum amount of interference). Sites measuring regional deposition rates should also not be too close (either upwind or downwind) to any major sources. (The regional

NADP siting criteria address these issues. See Appendix 4.)

### Dry Deposition

Dry deposition can be measured in several ways: 1) collecting dry particles and gases on some sort of surface (surrogate surfaces method), 2) measuring the amount of dry particles and gases in the air and calculate a deposition rate (ambient air sampling), and 3) measuring deposition at a specific location with a dry collector. See the section on **Resources** for references on dry deposition sampling.

Ambient air sampling methods are considered the most accurate by many researchers. In these systems, the deposition rate is calculated by models based on an equation that includes a deposition velocity and an air concentration. Unless the monitoring is research-grade, use deposition velocities from the literature or a commonly accepted model in lieu of site-specific data.

A table of some dry deposition velocities from the literature is provided in Appendix 2. For more sophisticated estimates, check with experts for the best rate to use.

Measuring dry deposition also requires collecting meteorological data. This must be done at the same interval the model requires. The data you need to collect usually include wind speed, wind direction, humidity, temperature, solar radiation, and rainfall. The deposition rate also varies depending on the characteristics of the surface the pollutant falls on, although these differences are usually estimated rather than measured. For example, dry deposition rates are very different over a parking lot than over a forest of broadleaf trees. Similarly, they can differ over a waterbody and its adjacent shoreline. The key is to know how you will calculate deposition rates before setting up the station so the appropriate data are collected.

Dry deposition sites are very difficult to locate well. This is because the samplers are highly sensitive to local meteorology and the surrounding surfaces. Buildings divert wind much the same way rocks in a stream disturb the smooth flow of water. The type of surface also changes the way the wind flows.

The optimum dry deposition site has a long uniform fetch (smooth open area over which wind can blow) and is not close to any known sources. Since that does not happen very often in real life, pick the best site you can and accept its limitations in the data interpretation.

From a practical point of view it is recommended that you collocate dry deposition samplers with wet deposition samplers. This minimizes the headaches involved with setting up and maintaining sites and buying extra rain gauges. Collocated samplers also provide a more complete picture at one location which is sometimes more useful than half the picture at two different locations.

**Filterpacks.** Filterpacks are basically systems in which air is pulled through a series of filters. Pollutants collect on the filters based on their size and chemical characteristics. Filterpacks collect all particle sizes through an “open” inlet. Many particle samplers, like those used for regulatory purposes, collect specific particle size fractions, such as particulate matter up to 2.5 microns in diameter ( $PM_{2.5}$ ) and particulate matter up to 10 microns in diameter ( $PM_{10}$ ). Ideally, one benefit of using this method for toxic deposition monitoring is that the samples can be easily and cheaply analyzed for a large number of pollutants. This method also can provide data useful for characterizing the signature of a particular source or source category when using the chemical mass balance method of source identification. For more information on chemical mass balance sampling, see page 59. Filterpacks are attractive because they are relatively cheap compared to other types of active samplers (denuders and dichotomous samplers). The downside of filterpacks is that they are often put out for long periods of time (more than one week). The night/day cooling and heating cycle can cause the ratio of gases and particles collected in the system to change. This is fine for measuring the total amount of pollutant, but severely compromises your ability to measure deposition velocity (because gases and particles fall at different rates). CASTNet, however, uses them on a weekly basis. If filterpacks are used for short periods of time (12 or 24 hours), they can be highly effective (and cheap) measurement tools.

**Gas Trap Samplers.** Gas trap samplers are very similar to filterpacks except that they are specifically designed to capture semi-volatile organic pollutants. Examples of pollutants for which these would be used include PAHs, PCBs, and dioxins/furans. The sample is pulled through a filter and then through a tube containing some sort of polyurethane or sorbent resin material (some use a material very similar to foam seat cushioning!) that acts as a filter to capture the organic pollutants. The pollutants are extracted from the material in the tube and the filter in the lab. These systems can be highly accurate for measuring small amounts of organic pollutants if proper clean field techniques are used. They are not cheap, however; and technical assistance with them is required to select the appropriate materials for the pollutant of concern.

**Denuders.** Typically, denuders are used to separate gas phase chemicals from those bound in particulate. In this system, air is pulled through tubes coated with a chemical that will “stick” to the pollutant being measured and filters to catch additional pollutants. The order of the denuders and filters is important because different pollutants are captured by each component. Some denuders have a device to sort particles on the front called a cyclone that blocks large particles from entering the tube. It was originally designed to keep soot and other large particles out of the denuders to prevent contamination. Evidence is mounting, however, that the device also keeps large nitrogen particles out. This is a problem only in coastal areas where sea salt in the air strips nitric acid and sulfates from the air and forms large particles of sodium nitrate ( $NaNO_3$ ). These particles get caught on the cyclone and are not counted in the measured nitrogen load. Therefore, denuders probably underestimate nitrogen deposition in coastal areas. This is thought to be a solvable problem, but no precise method has yet emerged as a standard way to solve it. Even with this limitation, denuders are considered by many experts to be the best samplers to measure dry deposition of nitrate and ammonia. However, they are significantly more expensive than filterpacks. The specific chemicals used on the denuder and the order of denuder tubes and filters will vary depending on what you are trying to measure and

the chemistry of the air in your area. So this is yet another place where help from technical experts will be necessary to make the technology meet your specific needs.

**Dichotomous samplers (dicots).** A dichotomous sampler measures the amount of particles of different sizes, but does not differentiate between different types of pollutants in the air. This is helpful in some circumstances where data from a denuder or filterpack do not clearly indicate what form of the pollutants are being deposited. Since the size of a particle is a key factor in how quickly it deposits, using a dicot with a filterpack or denuder often allows you to estimate more accurate dry deposition rates. Often dicots are set to differentiate particles smaller than 2.5 microns from those that are larger. This breakoff point is commonly used in air sample analysis because particles smaller than approximately 2.5 microns behave very differently (more like gases) than those that are larger.

**Continuous air quality samplers.** Continuous air quality samplers may do what you need either on their own or with some modifications. Generally they collect ozone precursors ( $\text{NO}_x$  and VOCs),  $\text{SO}_x$ , and particulate matter. They are common and easy to obtain. Existing continuous air sampler data may already be available through the NAMS/SLAMS/SPMS network or from  $\text{NO}_x$ ,  $\text{SO}_x$ , or PM monitoring stations already in place in many urban areas and national parks. The ambient air quality data require significant translations to get estimated deposition rates. It is possible to do this as long as all the other data needed (deposition velocity, particle size, meteorology) are also collected.

**Dry bucket/tray/funnels.** This design attempts to measure dry deposition directly by doing the opposite of the wet deposition sampler: the collector is covered when it rains. Because the collector is open for long periods of time, it is highly susceptible to contamination from windblown dust or debris. The collector tends to over-collect large particles and under-collect small particles or gases. The deposition surface is also not very similar to any situation found in nature. For

these reasons, particularly the concerns about the “unnaturalness” of the surface, data from these samplers are considered inaccurate by most researchers.

**Wet bucket/tray/funnels.** This is the same concept as the dry collector, except there is water in the collector. The purpose of this design is to simulate deposition to a body of water (rather than a dry surface). It has the same problems with contamination as the dry design, but it does have a somewhat more realistic deposition surface (the water). However, the deposition of certain gaseous pollutants (such as  $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{Hg}^0$ ) to the water surface strongly depends on the pH of the water. It is difficult to maintain pH conditions in the collector similar to those that would be found in the waterbody. It is still considered highly inaccurate by most researchers.

**Surrogate surfaces.** Surrogate surfaces are a variation of the dry collector design where the deposition sampling surface is constructed to resemble a natural surface. Unfortunately, it is extremely difficult (some say impossible) to construct a surface that resembles a natural surface (let alone lots of different kinds of natural surfaces). Many different surfaces can be used, but usually they are “distressed” in some way to provide an uneven surface (instead of the artificially smooth surface of most man-made materials). While this sample design appears to have potential, it also can be contaminated very easily. Some scientists believe it may be useful for larger particle species, but less so for smaller particles or gases. Therefore, many (but not all) experts are highly skeptical of data coming from these types of sampling devices.

**Passive samplers.** Passive samplers rely on passive diffusion to trap a gaseous species on an impregnated filter. No air is pulled through the sampler. One passive sampler design is a badge sampler, which looks like a small petri dish made out of nylon-like material. There is a top filter/screen to keep out larger particles and an internal filter saturated with different compounds depending on the type of pollutant being measured. The passive sampler is placed in the field in a location protected

from rain (under some type of roof) for anywhere from a few days to a few weeks.

These samplers are attractive because they are extremely cheap, and a watershed could be blanketed with them for relatively little money. They do have to be referenced to other active samplers (filterpacks or denuders), however; and some researchers still consider them inaccurate. Some studies have been able to develop correlations between badge samplers and any other type of dry deposition sampling. They are probably most useful as a scoping method to identify deposition “hotspot” areas. Once the badge samplers have identified those “hotspots,” another sampling method should be used to quantify the actual deposition load accurately. They are less accurate for low rates of deposition than for intermediate rates; to measure very high deposition rates just leave them out for a shorter period of time.

As you surely noticed, none of these methods of measuring dry deposition is as accurate as scientists would like; and there is a pressing need to develop better (and cheaper!) methods. This is not to say that scientists don't know anything about dry deposition; just that cost-effective methods in many cases have not kept up with the science.

**Inferred dry deposition.** Because the technology for measuring dry deposition has not kept up with science or management needs, and because the more accurate sampling systems are expensive, dry deposition of a few pollutants is sometimes simply inferred from wet deposition. This crude estimate assumes that dry deposition is equal to wet deposition, i.e., total deposition equals wet deposition  $\times 2$ . This ratio comes from some initial measurements made in a few locations on the east coast for nitrogen (nitrate) and mercury, and appears to be holding up well as newer research confirms that it is a reasonable estimate. It probably works well for annual averages of nitrogen (nitrate) and mercury (if you want to know seasonal averages it is not very accurate) in places that get about a meter of rain per year. It does not necessarily hold true for other pollutants (e.g., most metals) or in other climates. For example, in southern California,

dry deposition is a larger portion of the load of most pollutants simply because rain is infrequent. The pollutant speciation of nearby sources can also make this estimate grossly inaccurate. Further, divalent mercury is highly water soluble. Sources that emit a large amount of divalent mercury, such as medical waste incinerators, may cause local (within approximately 10 to 25 km) wet deposition to be significantly more than 50% of the total deposition.

The decision whether or not to measure dry deposition depends on several factors, including the frequency of rainfall in your climate, whether or not there are standard methods for analyzing dry deposition for the pollutants of concern, and how accurately the atmospheric load needs to be estimated.

### **Revolatilization**

Revolatilization is the opposite process from deposition. It happens when volatile pollutants are released from lakes and estuaries to the atmosphere. Only volatile or semivolatile pollutants can do this; the most common ones are mercury, DDT/DDE and other banned pesticides, PCBs, and HCB. Recent research suggests that ammonia also has this behavior. Revolatilization is not measured directly; there is no collection system to catch the gases wafting off the surface of the water the way buckets of rain are collected. Rather, it is calculated based on the concentration of pollutant in the air and in the water column and the chemical/physical properties of the pollutant.

Revolatilization rates are generally determined by short-term measurements that are extrapolated over long time periods (not on a weekly or daily basis the way deposition rates are calculated). For example, surface water and air sampling data indicate that the annual loss of PCBs from Chesapeake Bay from net volatilization (-403 kg/yr) is 10 times greater than inputs from wet and dry deposition (37 kg/yr) and at least two times greater than the loadings from the Susquehanna River (165 kg/yr). (A negative “net gas exchange” is volatilization, positive “net gas exchange” would be deposition).

### Watershed Pass-Through Rates

These rates apply only to inorganic nitrogen and vary even within the same land use type because of differences in age of vegetation, soil type, ecological history, rainfall, slope, the presence of vegetative stream buffers, and other factors. But they are a good place to start for nitrogen compounds; for other pollutants the pass-through rates may be very different.

Forests: Pass-through estimates range from 0-5% in one study to 20% in two others

Pasture: Pass-through estimates range from 0.4-6% in one study, 20% in another, and 30% in a third.

Cropland: Pass-through estimates range from 0.3-24% in one study, 30% in a second, and 40% in a third.

Residential: Pass-through estimates range from 5-38% in one study, 65% in a second, and 75% in a third.

Data from Valigura *et al.*, 1996 NOAA Coastal Ocean Program Decision Analysis Series No. 9 *Atmospheric Nutrient Input to Coastal Areas: Reducing the Uncertainties* (<http://www.cop.noaa.gov/pubs/das/das9.html>).

### Estimating the Indirect Deposition Load

The indirect load is the deposition to the watershed that makes its way into the waterbody of concern. The deposition rate is measured in exactly the same way, but not all of the deposition reaches the waterbody. Some percentage is retained in soils, some may be taken up by plants on land, some may settle to the bottom of lakes or slow sections of rivers, and some may be taken up by aquatic vegetation. The importance of each of these “storage” or “retention” processes depends on the watershed characteristics and the behavior of the pollutants. The percentage of pollutants that actually reach the waterbody of concern is called the “pass-through” rate. The actual amount of deposition that reaches the waterbody by way of the watershed is called the indirect atmospheric load. Original estimates of indirect loads used a 5 to 10% pass-through rate for no reason other than that it was the best guess anyone had. It is now considered too much of an oversimplification to be useful, but many older estimates of indirect load rely on it.

There are two methods to estimate the indirect load. The first is to estimate pass-through rates more accurately than the simple 10% guess by

assigning different rates to different land use types. Using this method, forests could be given a pass-through rate of 10%, but urban areas a pass-through rate of 90%. An additional pass-through rate can be assigned to the stream or river transporting the pollutant to the waterbody of concern. This gives a good back-of-the-envelope estimate. If you choose this method, it is often useful to do it twice, once with conservative (low) estimates of pass-through rates and once with higher ones. For an example of how this works, see the box on the next page.

The second method is to do more complex watershed modeling that simulates the transport of pollutants through the watershed. A model like this includes runoff rates such as those used above to get the pollutants into the waterways, and then represents the complex ecology that transports the pollutants to the waterbody of concern. These models are significantly more complex and can require substantial resources to run, but they are good at capturing the complex in-stream chemistry for pollutants where this is important (such as nitrogen and mercury). The runoff coefficients used in the back-of-the-envelope calculations are usually calculated from this kind of model. One national watershed transport model is the United States Geological Survey (USGS) SPARROW model. There are many other watershed models that can be used instead, many of which may be based on local watersheds. It may be useful to use the same model used to calculate tributary loads to the bay or estuary. Using the same model for all watershed

### Watershed Transport Models

Many watershed transport models can be used to calculate how much deposition reaches a lake, bay, or estuary. Some are national models and can be used anywhere; others are specifically designed for use in specific watersheds or areas. Not all existing watershed models can be used to calculate indirect deposition loads; some do not allow atmospheric loads as an input. Check on the models you currently use to see if they will work. The USGS SPARROW model can also work in any watershed, but must be run by the developers and it may take a long time to get the results you need. For a list of resources on watershed transport models see page 75.



transport (both air deposition and upstream nonpoint source and point sources) makes it easier to put the atmospheric load in context of other loads because all the loads are calculated based on the same assumptions.

Once the indirect atmospheric load is calculated, it is added to the direct load that was calculated earlier (by multiplying the deposition rate by the area of water). As you can imagine, it is more accurate to use a watershed model to estimate indirect loads, but coefficients are a good first step.

### Uncertainty, Errors, and Quality Assurance

Early in the process of designing an air deposition study, it is important to figure out the performance criteria of the data, meaning the quantity and quality of the data needed to answer the questions of the study with the desired certainty. One tool you should find useful to facilitate planning data collection activities in a systematic way is the data quality objectives process. The outcome of the process is a set of qualitative and quantitative statements called data quality objectives that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for

establishing the quality and quantity of data needed to support decisions.

Quality assurance refers to activities that ensure that the quality of the results of the work done meets the needs determined up front in the project. All projects that receive federal funding need to submit Quality Assurance Project Plans (QAPPs); most other funders will require one as well. The QAPP covers quality assurance activities related to all stages of a project, including planning, management, and oversight of the project, and collection and management of the data. This plan will usually have to be submitted after the project has been approved, but before funds are released and field work begins.

An outline of a QAPP is included in a box on the next page. For more information on developing quality assurance programs, data quality objectives, and QAPPs, you can look at EPA's quality system Web site ([www.epa.gov/quality](http://www.epa.gov/quality)). This site includes reference documents, training opportunities, example documents, and links to other references and examples. In addition, you can get examples by asking other managers who have done atmospheric deposition projects if they are willing to share their QAPPs.

#### Hypothetical Example of the Simple Pass-Through Method

Assume that the best estimate of total inorganic nitrogen deposition in the literature is between 6 and 14 kg/ha/yr on a 354-square-mile watershed. The average deposition rate is 10 kg/ha/yr. According to county records, the watershed is 1% urban, 67% forested, 30% farmland, and 2% wetland. The pass-through rates from the literature are 75% for urban, 10% for forests, 40% for farmland (annual average), and 10%\* for wetlands. The watershed is 90,624 ha, of which 906 ha are urban, 60,718 ha are forested, 27,187 ha are farmland, and 1,812 ha are wetland. The loads are

- 6,795 kg/yr from the urban areas (906 ha x 10 kg/ha/yr x 0.75 pass-through)
- 60,718 kg/yr from the forested areas (60,718 ha x 10 kg/ha/yr x 0.1 pass-through)
- 109,148 kg/yr from the farmland areas (27,287 ha x 10 kg/ha/yr x 0.4 pass-through)
- 1,812 kg/yr from the wetland area\* (1,812 ha x 10 kg/ha/yr x 0.1 pass-through)

The total indirect load from the watershed is 193,026 kg/yr. An additional correction factor is needed to estimate in-stream losses. They depend on the rate of water flow and, for biologically available pollutants, the season. After the indirect loads are corrected for in-stream losses (approximately 50% could be a ballpark estimate), they can be added to the direct deposition load for the total atmospheric load. Given the uncertainty of pass-through estimates, it can be useful to run through this exercise twice, once with high pass-through estimates and once with low ones.

\*These estimates were made up as a best guess—they are not real literature values! (See top box on page 38.)

### What Does a QAPP Look Like?

Below is a working outline for a QAPP for a nitrogen deposition monitoring project.

- I. Data Quality Objectives
- II. Ambient Air Nitrogen Species and Particle Size Distribution
- III. Wet Deposition Monitoring
- IV. Dry Deposition Monitoring
- V. Measurement of Ambient Air Species
- VI. Modeling Nitrogen Dry Deposition
- VII. Modeling Nitrogen Oxide Transport, Dispersion, Transformation, and Deposition
- VIII. Estimating Uncertainty
- IX. Quality Assurance/Quality Control

It is very important not to cut corners when it comes to quality assurance/quality control (QA/QC). This means using field and lab blanks, duplicate samples, split samples, spiked samples, audits, and other QA/QC techniques to ensure high quality data. Basically, there is no point spending tens of thousands of dollars on fancy equipment if there is no QA/QC analysis to tell you how accurate the results are. Without knowing the accuracy of those numbers, the data are wide open to criticism from all sides; and management decisions will be very hard to make and to implement. Plan on spending 25 to 30% of your budget on QA/QC activities.

For data collection and analysis, you will need to consider quality control with respect to how the samples are collected, transported, stored, and analyzed. When choosing a sampling methodology, you need to consider the detection limits of the methods and ensure that the sample volume is sufficient. For example, dioxins/furans are found at low levels in the ambient air. Consequently, the sample volume needed to get detectable amounts is high. In addition, maintenance and operation of both field and laboratory equipment are important to quality control. Various quality control techniques are going to be essential for you to have a data set that is usable. These could include field and laboratory blank samples, duplicate samples, split samples, spiked samples, a tracking system that clearly delineates who is responsible for the samples at what points in the process, and training for staff.

You also need to remember other potential uncertainties in addition to those directly related to

measurement and analysis of samples. Many of these have been touched on in other sections of this handbook. One example is the representativeness of the sites and time periods you sample relative to what you are trying to measure. Another example is the uncertainty of assuming deposition velocities derived from the scientific literature to estimate dry deposition. If you are estimating the contribution of air deposition relative to other pathways for pollutants entering the waterbody, there is the uncertainty of the estimates for those other pathways.

Quality assurance is the key that makes the whole package work. If you don't know the error and uncertainty associated with the data collected in your study, or that the data are of a sufficiently good quality to support the management decisions and actions, then the data are not much more than a collection of numbers. This quote from a researcher working on atmospheric deposition of nitrogen says it best:

Wet deposition estimates depend on capturing every rain event and retrieving uncontaminated, undegraded samples. NO SMALL FEAT! The dry deposition models rely on empirical algorithms with relatively large uncertainties, not to mention the uncertainties associated with the input data. Literature contains estimates of these uncertainties and should quickly disabuse anyone of the [idea that] accuracy...can be obtained in their nitrogen [or other pollutant] deposition estimates.

This is not to scare you off; just to insert a note of caution about the potential difficulties of getting accurate data. Plan on spending a significant portion of your budget (e.g., 25 to 30%) on quality assurance/quality control activities.

### How Much Data Can I Get for \$15,000, \$50,000, or \$400,000 a Year?

This section provides an idea of what kind of data you might get under three different budget scenarios. It is intended to give you a feeling for the costs of monitoring, as well as some suggestions for

low budgets. The budget categories apply to each pollutant (i.e., you cannot get everything in the box at the right for \$15,000, just one pollutant). There are some exceptions to this, however, particularly in regard to metals. Once the equipment is in place to sample for one metal, analyzing for several additional ones would probably be possible within the \$15,000 budget. In most cases, however, the budget applies to only one pollutant and a rather basic approach with limited data analysis.

Keep in mind that these are estimates only; costs may be significantly higher (or, with lots of in-kind support, lower) in some situations. The majority of the scientists and managers who have conducted atmospheric deposition studies stress the importance of partnering, borrowing, leveraging, and any other legal means to make the money stretch farther. The cost for the data analysis and interpretation is extra. If you spend \$15,000 on data collection and sample analysis, expect to spend another \$5,000 or more for data analysis; if you spend \$50,000 on data collection, expect to spend another \$10,000 or more on data analysis; and if you spend \$400,000 on data collection, expect to spend as much as \$100,000 more on data analysis. That said, here are some experts' opinions of the best data to collect in each price range.

These budget categories for monitoring can also be thought of as goals you can reach over time. In other words, start with the \$15,000 version, then add a small piece every year; and after four years you will be doing the \$50,000 monitoring scenario.

Remember, these suggestions are **guidelines only**. The goal is to design a monitoring strategy that answers as many of the questions you have as possible given the resources you have.

### **\$15,000/Pollutant/Year**

All experts agree that only the bare minimum amount of sampling for a single pollutant could be done for \$15,000/year. In some cases, such as for PAHs and other semivolatile compounds, no sample analysis can be done.

In that case, some experts suggest collecting the samples anyway and analyzing them when sufficient

### **\$15,000/Pollutant**

**Nitrate or ammonia:** Look for wet and dry values reported at nearby sites or model runs in the literature. The inventories used in the model runs should be checked against local knowledge of sources, and land use data should be collected from USGS or the Soil Conservation Service (SCS). Could set up an NADP wet-only site.

**Mercury:** Collect 50 to 80 event-specific precipitation samples over the year at a single site (probably with low-cost labor such as a student or intern). Analysis for each wet total mercury sample costs approximately \$100. Samples should be split, with half saved for future analysis. Dry deposition cannot be measured with this budget; use rates found in the literature or the 1:1 wet to dry ratio (the ratio method only works if the climate is not extremely dry and there are no sources of divalent mercury close by).

**PAHs:** No significant monitoring possible. Look for wet and dry values reported at nearby sites or model runs in the literature, or collect the samples and store them for future analysis.

**PCBs:** Same as PAHs.

**Dioxins/furans:** Use a single ambient air sampler to collect two-month integrated samples and estimate deposition and revolatilization rates for the most common congeners.

**Cadmium and other heavy metals:** Measure either wet or dry deposition (wet in buckets and dry using a filterpack). Get a crude estimate by multiplying a wet-to-dry ratio assumption. Samples generally are very cheap to analyze (about \$20/sample) once collected. Very easy to collocate with sites for other pollutants, like mercury (if available).

**Current-use pesticides:** Target monitoring to the portion of the year when use is highest (in areas where year-round agriculture is practiced, measure year-round). You cannot, of course, extrapolate deposition rates from the highest-use times to the entire year; this only provides data on what the worst-case scenarios are. It will probably be possible to measure only one compound on a short-term, event basis.

**Historic-use pesticides:** Do a paper study of atmospheric deposition rates (wet and dry) and water column measurements to estimate revolatilization rates. It will probably be possible only to measure one compound on a short-term, event basis.

funds become available. If samples are collected, but not analyzed immediately, **make sure they are stored properly!** This often (but not always) means deep-freeze or refrigeration. Find storage protocols appropriate for the pollutants you want to measure from researchers and follow them. This is to make sure the samples can be analyzed accurately later.

Another tactic is to take a large number of samples and only analyze a few that you suspect will give good results. The advisory group will help you figure out what samples those are. Then the data from these initial analyses can be used to leverage funds to get the rest of the samples analyzed and, if necessary, continue the monitoring program.

In addition to representative sample analysis and getting all the in-kind donations possible, explore the opportunities to piggyback on existing sites. Much of the start-up costs for sampling consist of securing a site, getting power brought in, and buying a rain gauge and other meteorological equipment. If there is an existing air quality monitoring site with some or all of that already done, it will make beginning a sampling project much easier. Some pollutants, especially metals, can often be measured very cheaply and easily by adding a filter to, or analyzing additional samples collected from, monitoring equipment already in place. Note, however, that some researchers have tried analyzing sub-samples for organics or metals from a standard wet deposition collector being used for nitrogen, and have not gotten useful results because sampling and handling protocols necessary for the organics and metals were not followed. So, when considering shortcuts, look to see what success (or lack thereof) others have had.

Regardless of how many samples are collected and analyzed, it is critical to interpret the data. That is, once the samples have been analyzed in a lab, the data must be analyzed to figure out what they are telling you. You will get better interpretation if someone with experience analyzing atmospheric deposition data analyzes your data. Data interpretation usually costs between 25 and 30% of the total project cost. So an additional \$5,000 or more would be budgeted, either in the first or second year of the project for data analysis. It cannot be overemphasized how critical this part of the project is; without it, all the effort into sampling and laboratory work just results in a pile of numbers. For robust data that can be used in decisionmaking, the interpretation must be done well.

### **\$50,000/Pollutant/Year**

For \$50,000 it is possible to have at least one monitoring site for almost any pollutant. For organic pollutants such as PAHs, PCBs, dioxins/furans, and historic-use pesticides, it is unlikely that you could have a replicate sampler for quality control purposes for this budget without borrowing one. You have to consider your data quality needs when deciding what sampling to do on this budget. For nitrogen it will be possible to have two or even three sites, depending on whether dry deposition will be measured. To conserve costs, it may still be worthwhile to set up several sites and selectively analyze samples. The results may be used to prove the need for more resources. If initial results do not indicate a substantial amount of deposition, store all the samples anyway and analyze them within a few years to make sure there are not spikes in deposition or other events that the selective sample analysis did not reveal.

#### **\$50,000/Pollutant**

**Nitrogen or ammonia:** Put out at least two sites (or locate one site in relation to existing sites) and measure both wet and dry deposition. Annular denuders or filterpacks are preferred for dry deposition analysis.

**Mercury:** Add more sites, analyze samples for reactive mercury ( $\text{Hg}^{2+}$ ) or wet deposition samples for methylmercury, as well as total mercury. Pass-through estimates are probably too expensive unless most of the research and/or modeling has already been done.

**PAHs:** A few samples integrated over short time scales and during different times of the year.

**PCBs:** Use a single ambient air sampler to collect integrated samples and estimate deposition and revolatilization rates from literature values.

**Dioxins/furans:** Add additional sites, measure precipitation samples, as well as ambient air samples.

**Cadmium and other heavy metals:** Add more sites, take wet and dry measurements to refine wet:dry ratio.

**Current-use pesticides:** Measure more often (measure more events or measure regularly), measure more compounds.

**Historic-use pesticides:** Measure more often and measure more compounds.

It is critical to save enough resources to get the data analyzed. In fact, since you probably generate more data under this scenario, it is even more important. It will still cost between 25 and 30% of the amount spent monitoring to get the data analyzed, so budget an additional \$14,000 or more to get data from these types of studies analyzed.

### **\$400,000/Pollutant/Year**

The theme for this scenario is “put out more sites that cover more pollutants or species (or flavors) of pollutants.” At this point, you could afford to monitor for any pollutant and you could afford to do it in quite a few locations. Those locations should be chosen based on the question(s) you need to answer, but given these resources, sites could be located both to provide regional deposition rates and to measure deposition from specific hotspots.

You could also decide to dedicate some of the resources toward modeling. This could be either developing a good watershed transport model or using air deposition or source attribution models to begin thinking about management options.

Another type of study that might be done in a research mode is an airplane study. Airplane studies measure the spatial heterogeneity of deposition rates. They typically are done by researchers to better understand atmospheric chemistry. Therefore, such studies are not likely to be cost-effective for meeting the needs of watershed managers. Basically, many different kinds of samplers are loaded on an airplane with an air intake designed to minimize taking up exhaust from the engines. The samplers are then run to collect huge amounts of data on pollutants and meteorology at different heights. The samples must be taken while at least one on-ground dry deposition sampler is making continuous measurements. The samples taken from the airplane are then compared to samples collected at the ground sampler(s). This information on how pollutants interact in different layers of the atmosphere is used to refine deposition estimates. Airplane studies also show what kind of spatial variability there is in the dry deposition estimates coming from the sampling sites. An airplane study can cost at least \$100,000 for

### **\$400,000/Pollutant**

**Nitrogen or ammonia:** Add more sites, measure dry deposition and organic nitrogen at several.

**Mercury:** Add more sites, measure speciation (total, elemental, methylmercury) at several. Can measure dry deposition as well.

**PAHs, PCBs:** Add more sites, measure different species. Measuring common species that were not already measured (there are 10,000+ different PAHs and 200+ PCBs) will help identify sources. Measure water column, as well as air deposition, to get volatilization and microlayer effects.

**Dioxins/furans:** Measure at more wet and dry sites, measure more frequently, analyze particle-phase and vapor-phase samples separately, and analyze sediment core samples.

**Cadmium and other heavy metals:** Same as for \$50,000 scenario.

**Current-use pesticides:** Add more sites; measure all compounds of interest; measure water column, as well as air deposition, to get volatilization.

**Historic-use pesticides:** Measure more often and measure more compounds.

approximately 50 hours of flying time, plus data analysis.

Once again, whether or not an airplane study is done, it is important to save 25 to 30% of the total project budget to properly analyze the data.

### **How Much Monitoring is Enough**

There is no such thing as “enough data” to most researchers. Long-term data sets are so rare and so valuable that it is almost impossible for any researcher to say that enough monitoring has taken place. However, you are in the business of managing resources, not doing research on them, so you will get to the point where enough is enough. If possible, try to turn your site over to someone else who will keep it going rather than stopping monitoring altogether.

The length of time you should monitor depends on what questions you are trying to answer. A single year of deposition monitoring is often used to determine what proportion of the total pollutant load comes from atmospheric deposition. This is not optimal because deposition rates vary some from year to year depending on emission rates and,

more importantly, changes in meteorology. Therefore, deposition rates during a drought year, or during a year in which your site was hit by three hurricanes, may not be representative of what generally happens at the site. This doesn't mean you can't use one year's worth of deposition data. It just means that if you do, the uncertainty of your estimate is larger than if you use averaged deposition rates for three or five years.

Because of this variability in deposition rates from year to year, it is recommended that a site be active for at least five years. NADP requires new sites to commit to operating the site for five years as well. This is long enough both to get a good grasp on the "real" average annual deposition rate and to know if

rates from year five really are the same or different than rates from year one. Therefore, to know if you are receiving more deposition or less than in the past, you have to make a significant commitment to monitoring. This is especially relevant when the purpose of monitoring is to quantify changes as a result of particular management actions. In other words, monitoring for a year or two to determine if there is a problem, then doing something about it is great. It is even better, however, to continue monitoring to assess how successful that management action was. Assessment not only strengthens the argument for controlling atmospheric sources in your watershed; it helps other watersheds in similar situations build the case for the management actions they need to take.

## VIII. What You Need to Know About Air Deposition Modeling

The first thing to know is that you will not have to do the modeling. While you may be the site operator for a monitoring site(s) and collect the samples, and may in a few cases analyze them, modeling is technical enough that it requires individuals with significant training to do well. The downside of this is that it tends to be more expensive. The upside is that you only need to know enough to be a good interpreter; you don't have to become a modeler.

Two types of modeling are used to assess atmospheric deposition: deposition models and source attribution models. Sometimes models designed to answer questions about deposition rates can also answer questions about source identification and vice versa. More often, different models or different model runs are used to answer questions about source attribution. It is useful to think of them as two different kinds of models because they are used at different points in the assessment process to answer different questions. This section discusses atmospheric deposition models; models that help answer the question "How much of a pollutant is being deposited on the watershed?" Source identification and attribution models are discussed in Chapter X on **Source Attribution**.

Modeling is an art. On one hand, models are easy to believe because they present easy-to-understand pictures of what we think is going on. On the other hand, because they are by definition simplifications of reality, they are easy to criticize because they always leave something out. The key to developing successful models is to justify what has been simplified or left out based on expert knowledge and sound science.

This section contains information on



- Questions that air deposition modeling can answer
- Basic theory of air deposition models
- Comparison shopping among models and modeling inputs
  - Inventories
  - Meteorological data
  - Models.

### Questions That Air Deposition Modeling Can Answer

It must be stressed that all models rely on the quality of the data and reasonableness of the assumptions that go into making them. There are two keys to good models that must occur together: accurate atmospheric chemistry and transport equations and good input data (inventories and meteorological data). In other words, there is no

point in having a highly accurate model if the input data are not good—the "good" model will still turn out incorrect results. It is possible to get the "right" answer—one that agrees with the monitoring data or that confirms suspected linkages—for the wrong reason. To avoid that trap and accurately answer questions, the limitations and sensitivity of the model must be clearly understood, and the model must be based on

reliable data with known error margins and reasonable assumptions.

Given those caveats, atmospheric deposition models can do the following:

- Summarize current conditions to help to identify management options
- Fill in spatial or temporal holes left by a monitoring program
- Predict future conditions due to growth (e.g., economic development) or regulatory changes
- Estimate what reductions are necessary to reach specific goals (such as a particular nitrogen loading or concentration in an estuary)
- Detect what changes in deposition rates will be significant to ecological or human health.

### Basic Theory of Air Deposition Models

Models are generally classified as **LaGrangian** or **Eulerian**. The difference between them has to do with how calculations are made. LaGrangian models track emission plumes that spread out toward some receptors (an example being an estuary) based on their chemical and physical parameters and the meteorology.

Eulerian models do calculations based on grids. These grids are areas over which inputs are averaged, calculations are performed, and deposition is averaged. For example, a model running with a 36-km grid (36 km on a side) assigns each source to be emitted in a particular grid and calculates atmospheric chemistry, transport, and deposition on those pollutants over a certain amount of time. The model then sends the pollutants to the next grids according to the results of those calculations. The key feature of grid size for model users is that the deposition rate is estimated for the entire grid area. For example, the 36-km grid calculates a single deposition rate for a 1,296-km<sup>2</sup> area. For finer resolution (to see differences on a smaller scale), the model must be run on a smaller grid. This means more calculations, which increase the amount of time it takes to run the model. The first atmospheric deposition models were run with grids of

#### Definitions of Common Terms

**Grid:** A grid is the scale at which an Eulerian model averages emissions, meteorology, atmospheric chemistry, and deposition rates. The smaller the grid size, the higher the resolution of the deposition rates. This does not necessarily mean that the deposition rates are more accurate, just that they are calculated over smaller areas. Grid areas are important when trying to interpret deposition rates. Large grid sizes work better to capture deposition on a rougher scale (such as from one source region to another). To get finer resolution (such as deposition gradients from a particular source), small grids are better. Small grids may cause calculational problems that lead to inaccurate estimates, however, if the input data or equations are not designed to be iterated at that frequency. Small grids may also cause problems if the meteorological data set is based on a larger grid size. Emission sources can be averaged over any grid size, but meteorological data collected at 80-km grids may be too coarse to use in 36-km model grids. Make sure the conditions of the model runs, including grid size, are acceptable to the advisory group before modeling begins.

60 or 80 km/side. Many are now run with 36-km grids, and some can be run on grids as small as 12 km or even 100 m.

It should be pointed out that the term “grid” is somewhat inaccurate. The grids are actually three-dimensional rectangles of air space. The vertical space in these models is made up of “layers” of different thicknesses. The thickness of the layers varies; one may be 1 m thick, another 10 m thick, another 100 m thick, and so on. These layers correspond to different layers in the atmosphere where processes happen differently based on the physical characteristics of air at that height. Simply described, layers are the way models capture the fact that emissions from cars (which are very low to the ground) are subject to different meteorological conditions and travel differently than emissions from 100-m smokestacks. This is because meteorological conditions (such as wind speed and direction) vary with height above the ground. For example, long-range transport of pollutants from China to the west coast of the United States appears to occur only when meteorological conditions push pollutants into high air currents. The number of



layers is one of the factors determining how accurately the model represents the atmospheric chemistry and transport of pollutants.

Eulerian models are good at capturing the complex non-linear chemistry necessary to model ozone, nitrogen, sulfur, and many toxic compounds (e.g., mercury) accurately. LaGrangian models generally work well for those toxic compounds that have fairly linear atmospheric chemistry. Linear atmospheric chemistry means that a compound generally does not react or change from the point at which it is emitted through transport to the point of deposition. An example is cadmium. It is emitted, transported some distance based on wind speed and direction, and deposited based on its size (which is about the same as when it was emitted) and some meteorologic parameters. Non-linear or complex atmospheric chemistry means that a compound undergoes chemical and physical changes in the atmosphere from the time it is emitted to when it is deposited. For example, nitrogen compounds undergo many chemical reactions in the atmosphere, which depend on several factors including sunlight, water vapor, and other chemicals. The nitrogen deposited is likely in a different form from that emitted.

Eulerian models include RADM, REMSAD, and Models3 (see pages 50 through 52 for a discussion of these models). RELMAP and CALPUFF are LaGrangian models, and HYSPLIT is a LaGrangian model that can be run in an Eulerian mode.

### Comparison Shopping Among Models and Modeling Inputs

Shopping among models is not shopping to get the best price, although that may enter into it. Rather, it is wading through the various options to figure out which one has the features that can give you the kind of answer you need. The choice of model should be made with the advisory group and, in most cases, should be made *before* monitoring begins. Sensitivity analyses may be a useful tool to inform you about critical data inputs to the model. Models are one of the “uses” to which the data will be put—as an input, validation, or two pieces of a

larger puzzle. Thus, it is critical to know the uses of the monitoring data before they are collected, so that the sampling is conducted with the proper temporal and spatial resolution and includes all the parameters required by the model. Therefore, the type of modeling the project will include should be identified as soon as possible in the design process. This section provides an overview of several models and modeling inputs and discusses some of the differences among models and among modeling inputs.

### Inventories

Emissions inventories are collections of information on releases of pollutants to the air over a specified time for particular sources or geographic area (e.g., county). Inventories also may have other information about the emissions, such as the form in which the pollutant is emitted (e.g., elemental mercury), the height at which the pollutant is released (e.g., ground level or from a hundred-foot stack), the temperature and velocity of the release, and detailed information about the location of the release points (e.g., latitude and longitude).

Information about the emissions is necessary input to any deposition model. In Eulerian models, each grid in the model contains emissions of all the sources located in that area. In LaGrangian models, the emissions are emitted as a plume from each source. These emissions are then transported, may be transformed, and may be deposited. The fate is dependent on multiple meteorological, chemical, and physical factors.

As simple as an inventory sounds in theory, the reality is quite complicated because there are many types of air pollution sources. One way to broadly classify sources is by point, area, mobile, and biogenic sources. Point sources are larger stationary sources, such as factories and electric power plants. Area sources are smaller stationery sources, such as dry cleaners, degreasing operations, or houses. Mobile sources include cars, trucks, buses, airplanes, and other sources that move. Biogenic sources include trees and vegetation, gas seeps, and microbial activity. An inventory may include

estimates of emissions from all or some of these classes of sources.

Many inventories use codes to classify various types of sources. You may find Standard Industrial Classification (SIC) codes, which were used by the U.S. Census Bureau to identify the primary type of activities an establishment is engaged in. The SIC codes are available at <http://www.census.gov/epcd/www/sic.html>. A new classification system is replacing the SIC codes; it is the North American Industry Classification System (NAICS), which will be standardized across the United States, Mexico, and Canada. Information about the NAICS and how it relates to the SIC codes can be found at <http://www.census.gov/epcd/www/naics.html>.

Other codes commonly appear in EPA and state-developed inventories. Source Classification Codes (SCC) (not to be confused with SIC codes!) describe the type of process that releases emissions. For example, there is an SCC for liquefaction (mercury cell process) at chlor-alkali production facilities. For the National Toxics Inventory (described below), there are also codes that connect the emissions information to a given regulatory category. These are Maximum Achievable Control Technology (MACT) codes. Additional information on SCC and MACT codes, as well as others, can be found at <http://www.epa.gov/ttn/chief/codes/index.html#nei>.

The data in an inventory are likely to be derived from a combination of measurement and estimation techniques. Some large point sources have monitors that continually measure the pollutants at the stack. For the majority of sources, though, emissions are estimated using other methods. These methods include tests of emissions from the source over a short period of time and extrapolated over a longer period, material balances, emission factors, analysis of fuel, emission estimation models, engineering judgment, or a combination thereof. An emission factor is the relationship between the amount of the emissions released and the activity of the producer. For example, emission factors can be reported as emissions per hour of production or

emissions per widget produced. An emission estimation model relates multiple parameters that influence emissions. For example, emissions from cars and trucks are estimated from a combination of factors, including estimates of vehicle miles traveled, fuel type, vehicle model, and types of travel.

If you plan to develop an inventory, several factors will influence your decisions on what sources and other information to include and what emission estimation techniques to use. These factors include the intended use of the inventory; the quality of data needed to achieve the intended use; the availability of information; and the availability of time, money, and personnel.

In most cases, you will want to work with an inventory that has already been developed. You should understand what types of sources are included and, in general, the methods used to estimate emissions and the quality of the estimates. You also may want to look at the local sources to see if the information is consistent with your knowledge of them. Do you know of sources that haven't been included? Is the information in the inventory about a particular source really different from what you'd expect based on your local knowledge? Don't forget that inventories are huge undertakings and also represent a particular time period. You may find that the quality of the data does not match your needs, that you need more up-to-date information, or that an error has occurred. Therefore, you may decide to make adjustments to an existing inventory for your modeling work. It would be helpful to pass on your improved or up-to-date information to your local, state, or tribal agency. They may find it useful in improving their inventories.

Below are descriptions of several national or regional emission inventory efforts. They typically represent emissions over the period of a year (for example, a 1996 inventory would represent emissions over the calendar year 1996). A given year's inventory may be updated periodically to incorporate improved or new information that was not available when the inventory was first published.

**National Emission Inventories Prepared by the EPA.** The U.S. EPA prepares a national emission inventory with input from numerous state and local air agencies. These data are used for air dispersion modeling, regional strategy development, regulation setting, air toxics risk assessments, and tracking trends in emissions over time. The National Emission Trends (NET) database has emissions data for 1985 through 1998 for the pollutants known as “criteria pollutants” (see Air Program Basics in the **Now What** section of this handbook, page 64). These pollutants include nitrogen oxides, ammonia, and lead, among others. The data in the NET for emissions of nitrogen oxides and sulfur oxides for electric utilities is from the acid rain program (<http://www.epa.gov/airmarkets/>).

Emissions data for air toxics are available for 1993 and 1996 in the National Toxics Inventory (NTI) database. These air toxic pollutants include mercury, cadmium, lead, PCB, POM (and PAH), and HCB.

For 1999, the criteria and toxic emissions data are being prepared in an integrated fashion in the National Emission Inventory (NEI), which will take the place of the NET and the NTI. The NEI will be conducted on a three-year basis (e.g., 1999, 2002, 2005). These inventories have information about larger point sources on an individual source basis. For smaller area sources and mobile sources, emissions are aggregated at the county level. More information about these inventories can be found at <http://www.epa.gov/ttn/chief/net/index.html>. Summary data from the NTI and NET can be accessed at <http://www.epa.gov/air/data/sources.html>. More detailed data can be accessed through <http://www.epa.gov/ttn/chief/net/index.html#dwld>.

The more general site, <http://www.epa.gov/ttn/chief>, also includes basic information about inventories in general, emission factors, models and other methodologies for estimating emissions, and continuing efforts to improve the inventories. For example, there are efforts to better speculate emissions of certain pollutants, such as mercury, from electric power plants. There are also links to state sites, which may contain more up-to-date inventory information.

**Toxics Release Inventory (TRI).** The Emergency Planning and Community Right-To-Know Act authorizes the TRI to provide the public with information about potentially hazardous chemicals and their use in their communities. Industrial facilities are required to report annually on releases of toxic chemicals into the air, water, and land, as well as other information. This inventory includes primarily larger industrial point sources. Area sources, mobile sources, and natural sources are not included. The pollutants reported in the TRI include mercury, cadmium, lead, dioxins and furans, PCBs, PAHs, HCB, and several pesticides. Additional information and links to the TRI database can be found at <http://www.epa.gov/triinter/index.htm>.

**Dioxin Inventory as Part of EPA Dioxin Reassessment.** In 1992, the EPA’s Office of Research and Development began an effort to reassess the exposure and health effects associated with dioxin. The effort includes an inventory of dioxin sources in the United States. The inventory and reassessment are in draft form as of the writing of this handbook. Additional information about the inventory and reassessment can be found at <http://www.epa.gov/ncea/dioxin.htm> and <http://www.epa.gov/nceawww1/diox.htm>.

**Great Lakes Regional Air Toxics Inventory.** The air regulatory agencies in the eight Great Lakes states have worked collaboratively to develop an air emissions inventory of toxic pollutants in these states for various years. The results of this inventory are largely the same as in the NTI discussed above, since a primary source of data from the NTI is information submitted by state agencies. More information about this inventory effort can be found at <http://www.glc.org/air/air3.html>.

### ***Meteorological Data***

It is critical to have good meteorological data for atmospheric deposition modeling. From your monitoring sites, you may have some meteorological data, but you probably would not have collected all the data needed for the modeling efforts. You would then look toward the larger meteorological databases that are regional or national in scope.

Models use three types of meteorological data. One type, called episodic meteorological data, is a short (several days to several weeks in length) segment used to represent a longer period of time. Often several of these are run to estimate annual deposition rates. For example, RADM (see page 51) uses four two-week meteorological data segments to calculate annual nitrogen deposition rates. These segments are supposed to be representative of different weather patterns to capture the range of deposition rates that can occur under different atmospheric conditions. The disadvantage is that actual annual results are not provided by the model. Some models use an “average” meteorological year constructed by averaging monthly data over several years. For example, Tampa Bay Estuary Program uses an average year where January’s modeled meteorology is the average of ten Januaries, February’s is the average of ten Februaries, and so on. Some models, such as REMSAD, use an entire 365 days of meteorological data to drive the model. The advantage of this is that it represents actual events that can be easily verified by monitoring data. The disadvantage is that any given run ignores interannual variability.

Which type of meteorological data is used depends mostly on the complexity of the chosen model. It would be difficult and resource-intensive to run a very complex model for a full year. If there is a choice of using an entire year versus a subset or an average year, there are a few things to keep in mind. Yearlong data are good at catching seasonal changes and patterns. Because it is a continuous stream of data, the model captures the slight changes in initial meteorological conditions that can have large impacts on deposition rates. It is also possible to run these models using several different years of meteorological data to capture interannual variability. A 10-year average meteorological data set captures all that variability in one run, and the episodic model does to some extent as well, depending on how well the segments were chosen. This reduces the chance of basing management decisions on abnormal years (making the right decision for drought years, but the wrong decision

in the long term). The downside is that this takes additional time and resources.

One final thing to keep in mind is that meteorological and emissions data may not coincide with each other or with the data from deposition monitors that can validate the model. For example, a model may run the 1990 emissions inventory using 1997 meteorological data. The weakness of these model runs is that it is more difficult to verify them with monitoring data (because no data were ever collected that meet both those assumptions). It is preferable for model evaluation to choose specific years to run when the best meteorological data, emissions inventories, and monitoring data overlap.

### **Models**

The goal of this section is to illustrate what models may be useful for air deposition studies and is not intended to be exhaustive. Some of the air dispersion/transport models described are in the research stages of development or are not generally available for use. Some may require experts to run them for you.

**Regulatory Modeling System for Aerosols and Deposition (REMSAD).** REMSAD models nationwide wet and dry deposition for mercury, nitrogen (nitrate, nitric acid, and ammonia), sulfate particles, cadmium, atrazine, dioxins, acids, and POM. Lead, HCB, and PCBs are planned to be added to REMSAD. Other pollutants could be added with relative ease. The model is usually run for a full 365 days of meteorological data to move emissions from the sources, calculate transport and transformation rates, and deposit them in grids from 12 to 36 km<sup>2</sup>. However, the model can be run for shorter or longer periods. It is capable of simultaneously modeling concentrations of primary and secondary particles. In other words, REMSAD can model deposition of nitrogen and mercury (or other pollutants) at the same time. This provides opportunities for different agencies or organizations to jointly fund one run that can answer several questions for each of them. It is simple enough to run on a high-end desktop PC (although each run may take a week) so it does not require supercom-

puter time. (This is because it has simpler atmospheric chemistry than models that require bigger computers.) The model is non-proprietary so anyone can get it from EPA.

#### **Regional Acid Deposition Model (RADM).**

RADM models deposition to the eastern half of the United States for secondary particles (principally nitrate and sulfate) and acidic deposition (principally nitric acid, nitrate, and sulfate). A newer version, the extended RADM, includes ammonia deposition. The model uses an "episodic meteorology" approach by running a single two-week segment of meteorology for each season to calculate transport, transformation rates, and deposition. RADM has more complicated chemical transformation equations than REMSAD. These equations are intended to give a more accurate representation of the atmospheric processes and deposition rates. RADM uses a 20 to 80 km<sup>2</sup> grid and is generally run on a supercomputer by the model developers.

**Models3/CMAQ.** This modeling system is actually a framework of a graphical user interface, an atmospheric transport model, and data analysis tools. As of 2001, CMAQ (Community Modeling for Air Quality, which includes a deposition component very similar to the RADM model) is available as an independent air quality model. The Models3/CMAQ system is also available and is currently being evaluated. CMAQ models acid precipitation (primarily nitrate, sulfate, and nitric acid), photochemical oxidants (such as NO<sub>x</sub>, VOCs, and ozone), and aerosol chemical and physical properties. The domain size (the area being modeled) can range from 100 to 5,000 km. It can be run at different grid sizes, including grids as small as 12 km<sup>2</sup>. The model can be run from a workstation (no supercomputer is required).

**California Puff Model (CALPUFF).** This modeling system is composed of a diagnostic meteorological processor (CALMET) and a puff dispersion model (CALPUFF). CALMET can accommodate meteorological data from a variety of sources (including processed meteorological data such as might be used to drive Models3/CMAQ, RADM, or REMSAD). Since CALMET performs

a diagnostic wind analysis, the characteristics of the meteorological conditions improve as the data describing the situation improve. For instance, in situations where the terrain influences are severe (as within a system of interconnected deep valleys), CALMET will require detailed terrain height information to provide reasonable results, and its results will improve dramatically when local meteorological observations are available. Furthermore, since diagnostic methods are being used, application of CALMET requires an experienced professional. CALPUFF is designed to identify the impacts of sources on deposition of gases and particulates. It includes a simplified representation of sulfate and nitrate chemistry, which is known to underestimate sulfate formation since it does not address aqueous phase (in cloud) sulfate formation (which is addressed by the other models listed in this section). CALPUFF has been shown to perform well for characterization of pollutant transport and dispersion at distances of 300 km. Recent enhancements to CALPUFF have been made to extend the distances to which it can be applied and to address aqueous-phase sulfate chemistry, but these enhancements have not been fully tested and evaluated at this time. The model is non-proprietary and can be run on a high-end desktop PC (although some runs may take a week or two).

#### **Regional LaGrangian Model of Air Pollution (RELMAP).**

This is one of the older atmospheric deposition models that still sees some use by U.S. EPA and others for estimating deposition rates for unreactive pollutants, like most heavy metals and dioxins. It has been used to analyze sulfur deposition and deposition of mercury, cadmium, lead, and other toxic pollutants. It was the primary model used in the 1997 EPA Mercury Study Report to Congress to assess the long-range atmospheric transport of mercury emitted from anthropogenic sources in the United States. This analysis generated annual average deposition values across the United States. The model is a regional scale model and was developed using various assumptions about wind and precipitation patterns that do not hold true for smaller scales. Therefore,

the geographic area that you want to get results for should be relatively large, and the size of the individual grid elements used by the model to calculate concentrations and depositions should be at least 20 km in size. The model is simple in comparison to newer models now available or under development, because of the linear atmospheric chemistry and basic meteorological processes it uses. It is best for heavy metals and other relatively unreactive anthropogenic compounds like dioxins. The value of RELMAP lies in the fact that it is a straightforward way to get an initial estimate of the deposition rate for pollutants for which a more complex model is not required. For pollutants such as sulfur, nitrogen, mercury, and some reactive organics, where more sophisticated models are available, those models should be considered instead of RELMAP.

**Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT).** HYSPLIT is being used to model the fate and transport of dioxins, atrazine, and mercury and can be configured to model many other pollutants as well. The model is usually run on 365 days of meteorological data, but both shorter and longer periods can be run. HYSPLIT can accept several kinds of meteorological datasets. HYSPLIT can be downloaded or run at

a Web site of the NOAA Air Resource Laboratory (<http://www.arl.noaa.gov/ss/models/hysplit.html>).

A module called TRANSCO has been developed (for dioxins and atrazine to date) to allow the model to output detailed source-receptor information. In other words, HYSPLIT/TRANSCO can estimate the contribution of each source in the emission inventory to the modeled estimate of total deposition for any given receptor (such as a lake or estuary). This model must be run by scientists at NOAA Air Resources Laboratory.

**Modeling Costs.** It is extremely difficult to put a dollar value on what a modeling effort for a particular pollutant in a specific geographical area might require. Some of the cost depends on how much work you need to do to get inputs together and into a format that can be used in the model. The degree of complexity of the pollutant chemistry and the location of interest can have a sizable impact on the resources required. The resources required are also dependent on how much model input data are already available. The following table identifies some of the factors that will influence the cost of modeling. The order of magnitude values are provided for general illustrative purposes and should not be relied upon to establish a budget for a specific modeling effort.

<b>Questions that Influence Deposition Modeling Costs</b>		
<b>Questions</b>	<b>More Expensive</b>	<b>Less Expensive</b>
Do the pollutant(s) involved have simple or complex atmospheric chemistry?	Complex (e.g., nitrogen)	Simple (e.g., cadmium)
What quality of emission inventory is available?	None previously done	Existing (good and complete) inventory
What geographic scale of analysis is sought; i.e., what is the geographical scale of the sources which may potentially contribute significantly to the waterbody?	Continental - Global (e.g., PCBs, HCB, Hg)	Local - Regional (e.g., some PAHs)
How complex is the terrain?	Complex with microscale weather (land-water interactions)	Simple (flat without local weather anomalies)
Does adequate meteorological data exist for the modeling domain? Any unique microscale weather influences?	Coastal environment with microscale meteorology (fog, lake-effect snow); situations where meteorological datasets to drive the modeling do not already exist, and must be created (from databases of weather observations) using meteorological models.	Adequate meteorological data to drive the model already exists, is easily obtainable, and is in a form compatible with the fate and transport model being used. The data must have sufficient temporal, horizontal, and vertical resolution to capture significant meteorological phenomena affecting the fate and transport of the pollutant in the modeling domain.
Has the model being considered been used for this pollutant before?	No prior use with the pollutant	Well utilized for pollutant of concern
Has the pollutant been analyzed successfully by any model before?	No, substantial work must be performed to "figure out" how to model the pollutant.	Yes, a body of work is available in the scientific literature to aid in the adaptation of the model to simulation of the pollutant.
Can this effort be coordinated with existing studies underway?	No other studies are being performed or are planned in the area	Modeling is already being conducted in the region of interest for this pollutant, and analysis for your receptor can be added relatively easily to this study.
<b>Order of Magnitude Potential Costs</b>	<b>\$100,000 to \$500,000</b>	<b>\$10,000 to \$100,000</b>

# IX. Summary of a Well Designed Assessment Strategy

This chapter summarizes the previous sections of this handbook into a stepwise strategy for easy reference. You have already identified water quality or ecological problems in your waterbody to which air deposition may contribute. The intent of the strategy is for you to learn as much as you can initially from existing information and then plan to carefully determine what information you really need before expending large amounts of resources on a monitoring and modeling program. This strategy is not intended as a requirement; assessments can be well designed using other strategies. Yet, the steps presented below are ones that managers and scientists involved in air deposition assessments have found useful and cost effective.

**Step 1:** Do a paper study. Look up estimated measured or modeled deposition rates in your watershed from national assessments that have already taken place. A good place to start is the NADP assessment for nitrogen and mercury compounds. The IADN is a good place to look for deposition rates of toxic pollutants in the Great Lakes region. If those analyses do not cover the pollutants of concern, look for deposition rates estimated for other nearby watersheds in the research literature, for ambient air data, or for emissions inventories.

**Step 2:** Perform a rough calculation to estimate the load from atmospheric deposition. Take the estimated deposition rate and convert that to a loading by multiplying the rate by the area of the estuary or body of water. Then add the indirect deposition load to the direct deposition load. If the paper study turns up several widely differing deposition rates, take one at the high end and one at the low end and calculate two estimated loadings.

**Step 3:** Compare the estimated deposition load with other pollutant sources, including point source discharges and nonpoint source discharges such as stormwater or agricultural runoff and erosion. If the estimated deposition load is on the same order of magnitude as or larger than other sources, continue additional investigation of the air deposition component. However, if the estimated deposition load is small or comparatively much smaller than other loadings, you may want to consider using your limited resources to better understand the loadings from point sources and other nonpoint sources rather than launch into additional quantification of the air deposition. This does not mean that there are no environmental impacts from air deposition, only that air deposition monitoring is much more expensive than water monitoring.

Once the paper study has been done, the estimated loadings to the waterbody have been calculated, and the atmospheric loadings are estimated to be a significant portion of the total load, it is time to think about atmospheric deposition monitoring and/or modeling.

## Case Study: Sarasota Bay Pollutant Source Identification Strategy

The Sarasota Bay National Estuary Program recognized that atmospheric deposition of nitrogen might be a significant problem in the Bay when it was identified as between 25 and 30% of the total nitrogen load next door in Tampa Bay. However, there were also good reasons to think atmospheric deposition was not as significant a source as stormwater runoff and point source loadings. So Sarasota Bay NEP conducted a monitoring study to measure atmospheric deposition rates and stormwater loadings to the Bay. The purpose of the study was to determine the most significant source of nitrogen to the Bay. Preliminary results suggest that, although there is substantial atmospheric deposition to Sarasota Bay, the atmospheric pathway is not as significant a source as stormwater loadings. This experience emphasizes the importance of putting the atmospheric load in context with the rest of the pollutant loads so that priorities can be established to use limited resources in the most environmentally effective manner.



**Step 4:** Decide the question(s) the monitoring and/or modeling needs to answer. Do you want to know total annual loads to a body of water? Are there particular seasons or weather events that are more important than others? Do you want to know the effect of atmospheric deposition on the plants and animals in the river, lake, or estuary? Do you want to know how much deposition is coming from local sources or in-state versus out-of-state sources? Do you want to identify the atmospheric deposition coming from a particular source category in your area (e.g., several municipal waste incinerators) or a particular source (e.g., a single coal-fired utility)?

**Step 5:** Look for partners. This may include agencies, universities, researchers, non-profit groups, and anyone else who is already doing any atmospheric work, has any interest in doing atmospheric work, or has resources (money or staff) available to help conduct atmospheric deposition work. Atmospheric deposition monitoring and modeling are time-intensive and expensive and generally require a relatively high level of experience and expertise to do well. Therefore, the key to a successful atmospheric deposition study is to leverage as much support as possible at every stage of the project.

**Step 6:** Form an advisory group. The technical portion of the group will answer questions about the monitoring details—what type of monitoring equipment to use, what protocols to use, what type of modeling is appropriate, what data will be needed to do adequate data analysis and how to get it, and other technical details. The non-technical members will make sure the study is an accepted part of the larger

#### **Case Study: Tampa Bay Advisory Committee**

The Tampa Bay Estuary Program (TBEP) was one of the first to assess nitrogen deposition to a coastal ecosystem. Since TBEP had no experience assessing atmospheric deposition and no atmospheric scientist on staff, the TBEP senior scientist created a national advisory group to help develop the program. The advisory group includes nationally recognized experts in wet and dry deposition methodologies for nitrate and ammonia (and more recently mercury), national atmospheric program managers, experts with technical knowledge of modeling, and local stakeholders, including several counties and Tampa Electric Company. Since TBEP does not do most of the monitoring or modeling work itself, the county and university scientists doing the work also sit on the advisory group. The advisory group meets periodically to answer specific complex questions that require a group discussion and consensus. The advisory group responds to other questions on an as-needed basis through individual telephone calls, conference calls, or written recommendations.

management framework and that the data collected can and will be used for management purposes. The point is to get buy-in as early as possible to avoid “good-data, bad-data” arguments later on.

**Step 7:** Decide on an assessment strategy. This may be monitoring, modeling, or more likely some combination of the two. The advisory group should generally agree with the strategy you choose. If they do not, make sure other scientists do (then put them on your advisory committee). If the strategy is not scientifically defensible, it is not worth doing because the ensuing discussion will revolve around the data, not what to do about the results; and few people will feel comfortable making decisions based on questionable data.

**Step 8:** Find the resources to carry out the strategy. These may be grants, contributions from non-profit groups or industry, or in-kind donations. Save 30% of the total to interpret the results or get an in-kind donation to do it. If resources are tight, analyze only a subset of the samples you collected and store the rest. The stored samples can be analyzed at a later date if warranted by the initial results and additional funds become available.

**Step 9:** Begin the assessment. Remember to use the advisory group to answer questions and get around roadblocks. Begin analyzing data as soon as possible.

**Step 10:** Reassess periodically. When the initial phase of the assessment is done (approximately one year or so), take stock. What has been learned? What still needs to be learned? Have priorities changed? Remember the theory of adaptive management: it is OK (actually it is more than OK, it is a good idea) to change the strategy if it is not working or not meeting the needs for which it was designed.

## X. Source Attribution

If atmospheric deposition is identified as a significant problem, the next step is often to identify the responsible sources. Some sort of source attribution is generally necessary before anything can be done to solve the problem associated with the source. Source attribution is often called “attribution” instead of “identification” because, in many cases, the exact source cannot be identified from the crowd of possibilities. Instead, certain types or categories of sources (e.g., municipal waste combustors within 50 miles or hog farms from six counties) or several combinations of sources in a geographic area are identified as contributors to the total atmospheric deposition load. (Note: A description of systems for classifying industry or source categories can be found in the section on inventories beginning on page 47.) Sometimes the results of this type of analysis lead to the development of laws or agreements to reduce emissions from particular types of sources. For example, Title IV of the 1990 CAAA was passed to regulate certain utilities based on knowledge that the source category as a whole was responsible for a substantial portion of the lake acidification problem in the Adirondacks. Therefore, “source attribution” does not necessarily mean being able to point to the specific smokestack or area source; it may mean narrowing down the options to a collection of sources that all contribute to some portion of the problem.

Source attribution may be the most technically difficult part of solving environmental problems caused by atmospheric deposition. Despite all the concerns about accuracy and the sensitivity of deposition sampling methods, contamination, and quality control, measuring deposition is relatively straightforward. Source identification, in contrast, involves some sort of tracking of the pollutant from the source to the area where it is being deposited. This is complicated by the fact that many sources emit the same pollutants. Furthermore, the pollutants are dispersed and do not necessarily travel in a straight line, and they may be transformed in the atmosphere before being deposited. Therefore, you should expect to work with individuals trained and experienced in the methods used for source attribution.



This section contains information on

- Identifying sources
- Designing a source attribution strategy.

### Identifying Sources

#### **Back-Trajectory Analysis**

Back-trajectory analysis is an analysis of meteorological data, specifically air transport, to estimate the location of an air parcel earlier in its history. An air-parcel trajectory is the path of a parcel of air as it is transported by the wind. A backward trajectory follows the parcel of air backward in time. For a given deposition sample, a back-trajectory analysis would help answer the question: “Where did the air that carried the pollutant to my sampler come from?” For example, the analysis might indicate

that three hours earlier the air parcel carrying the pollutant had been six miles to the west of the sampler, and nine hours earlier, it had been nine miles northwest of the sampler. This analysis alone cannot tell you which types of sources or individual sources emitted the pollutants because you don’t know how far along the trajectory (i.e., how far back in time) the pollutant originally was emitted into the air parcel. You also do not know from the trajectory alone what portion, if any, of the pollutant was deposited to the ground by precipitation or dry deposition processes before reaching the sampler. Further, just as forward

trajectories are only estimates of where a pollutant will be in the future because of dispersion, the same applies for back trajectories. For instance, a pollutant source that is located near, but not directly along, a back trajectory may be contributing to the pollutant measured at the sampler.

In spite of its limitations, back-trajectory analysis can provide useful information for pollutants for which there is not an inventory of emissions sources. The direction of transport of the air parcels bringing pollutants to the site can provide clues about potential sources. It can be used as a screening tool, even if you have an emissions inventory. A comparison of the trajectory patterns with data from emissions inventories would help you determine which sources should be examined with additional analyses. Note, however, that if the pollutant has been through the grasshopper effect (defined on page 5), then the back-trajectory analysis would indicate the area of the last point at which the pollutant was re-emitted to the air, rather than the original emission source.

There are several conditions for running a back-trajectory analysis. The deposition sample should have been collected over a time period of a day or less. Over a longer period, the weather patterns are usually too variable to reasonably estimate a trajectory associated with the deposition sample. In addition, the meteorological data used should be temporally resolved on a short-term (one-hour or three-hour) basis, rather than a daily basis, to account for precipitation events, variations in wind, etc. If you have wet-deposition samples, then the trajectory should start during the time of the precipitation, which you know if you have hourly, as opposed to daily, precipitation data. Archived, model-generated weather data based upon measured weather data from surface sites and balloons are available on the NOAA Ready Web site at <http://www.arl.noaa.gov/ready.html>. This allows you to run the back trajectory based on these weather data archives, without having to have any meteorological data of your own. However, on-site weather data may be important, if the flow around the site is very complex (e.g., the site is located in an area of

very complex terrain, or the area of interest is very small, say on the order of 50 square miles). In this case, the back trajectories couldn't be run back very far because the wind direction and speed at the site would be different than that in the regions surrounding the site. Remember, to make a meaningful calculation, the back-trajectory model has to have appropriately resolved meteorological data in the entire domain that the air parcel may have come from. The better the meteorological data represent reality, the better the trajectory will be.

Meteorological expertise is also needed to determine what initial height(s) should be used for the analysis. Air parcels in different vertical layers of the atmosphere can experience different trajectories. A ground-level trajectory is problematic due to the effects of varying terrain on the flow of air, and it is unlikely to represent the layer at which the pollutant was carried before it was deposited. Too high of a trajectory would probably not be representative of the path of the pollutant as it was transported to the sampling site. The choice of the initial height should take into consideration meteorological conditions when the deposition sample was taken (e.g., daytime with vertical mixing or nighttime with stable air masses). Multiple runs of the analysis at various heights will provide a range of possible trajectories. Looking at the area bounded by the range provides a better chance of catching the true path of the pollutant.

An additional reason for expertise in meteorology is to determine how far back in time you can run the analysis before the potential errors become so large that it becomes a useless exercise. Typically, you would expect runs that go back 12 to 48 hours.

An approach that can be thought of as "back-trajectory plus" is called cluster analysis. If a lot of monitoring data are suitable for a back-trajectory analysis (for example, daily deposition samples taken over a five-year period), statistical analyses can be done to determine the probability of pollutants coming from various places. First, the meteorological data are statistically analyzed to determine patterns or "clusters" of trajectories. Then, patterns

in deposition can be examined in comparison to the clusters. This provides a more powerful analysis than looking at just a small set of deposition samples. The obvious drawback is the amount of data required.

One advantage of the back-trajectory approach is that it is relatively simple and inexpensive compared to other source attribution analyses. The HYSPLIT model described in the previous modeling chapter (see page 52) can be run in a back-trajectory mode. This model can be downloaded or run at a Web site of the NOAA Air Resources Laboratory (<http://www.arl.noaa.gov/ss/models/hysplit.html>). General information about trajectories and other modeling topics can be found at <http://www.arl.noaa.gov/slides/ready/index.html>.

### **Chemical Mass Balance Technique**

This technique matches deposition to a source category based on the chemical “fingerprint” of the source and the measured deposition. The fingerprint is the unique profile of chemicals that every process emits.

The chemical mass balance technique does not identify which smokestack, area, or mobile source the emissions are coming from, just that it is, for

#### **Example of the Chemical Mass Balance Technique**

A particular incinerator may have an emission stream that has particulate matter of a certain size, dioxins, mercury, cadmium, copper, lead, and antimony. Generally, if the concern from the water quality standpoint is mercury and dioxins, those will be the only compounds measured at the deposition site. But simply measuring the mercury and dioxins does not give much hint of where it is coming from. If the incinerator is suspected, and the emissions fingerprint can be found or measured, there is another option. The site manager can choose to analyze the mercury and dioxins samples for lead and antimony as well, and if they are present they suggest the incinerator may be contributing to deposition at the site. If they are not present, the incinerator is probably not contributing to deposition at the site.

example, a pulp and paper factory and not a chlor-alkali plant. Usually the entire fingerprint does not have to be measured, only some key compounds. For example, researchers on the Chesapeake Bay know they are getting deposition from Philadelphia every time antimony (from a large antimony roaster in Philadelphia) shows up in higher concentrations in the deposition samples. Sometimes fingerprints from multiple sources can be identified at a particular site by “backing out” one signature after another. Some source types have known emissions fingerprints; others are less well known or not known. Your advisory group will help you determine which sources have good data available. If you do not have good data on source types potentially impacting a site, it is not worth doing this type of analysis because you will not be able to match the data you collect with any known sources.

It may be easy to monitor for the key compounds if the deposition sampling is being done with filterpacks, depending on what you are looking for. Additional metals can be measured from filterpacks for very little extra money and can provide invaluable information about potential sources.

The chemical mass balance technique is particularly useful when used in conjunction with back-trajectory analysis. The back-trajectory analysis provides the general path of the air mass that caused the deposition, and the chemical mass balance analysis provides the type of source to look for in that path. The analysis cannot pin down the exact source location (unless there is only one possibility), but it can significantly narrow the range of possibilities and may provide enough information to begin the process of getting reductions from those sources. The chemical mass balance technique is a little more resource- and time-intensive than back-trajectory modeling. While there may not be additional equipment to buy, there are some additional sample analysis costs, and the time to find source fingerprints and match them with the data results.

## Dispersion Modeling

Dispersion modeling involves using an already-developed model or developing a new model to simulate transport and deposition from emission sources to the waterbody of concern. It can be thought of as “forward-trajectory” modeling; instead of going backward from deposition site to the source, dispersion modeling models transport forward from the source to the deposition site. This type of modeling is data-intensive. You’ll need good emissions inventory and meteorological information.

Various approaches can be used. You can do facility-specific model runs with just the emissions from one or a particular set of sources. For example, if you are interested in learning about the contribution of dioxins from local waste combustors, you could do dispersion modeling of the dioxin emissions just from those sources. An alternative approach is to do a baseline run with all the emissions in the inventory, then do additional runs without the emissions from a given source or set of sources. A comparison of the two runs would indicate the contribution from the source or sources in which you are interested. For example, to estimate the contribution of each suspected source of mercury, a model run would be made that includes emissions from all sources. That is the baseline. A second run would be made without emissions from one type of coal-fired utility, then another run would be made with the coal-fired utilities, but without municipal waste combustors, and so on. Your modeling experts will be able to help you choose the most appropriate approach to answer your questions. For example, the first approach is not viable if the model needs a broad inventory of emissions to simulate atmospheric chemistry that could affect deposition rates.

A new idea in dispersion modeling is to use some type of source labeling to identify sources within the model. This can be thought of as “virtual” labeling: labeling all emissions from one source as watermelon jellybeans, all from another source as cherry, from a third source as licorice, and so on. The fraction of watermelon jellybeans deposited at

any location is the fraction of pollution that source (say, incinerators in the Denver metropolitan area) is responsible for. This type of labeling also works much better for compounds that travel in mathematically simple ways. It has not yet been tried for pollutants with non-linear chemistry, such as nitrogen, whose atmospheric chemistry (and therefore transport and deposition) depends on the presence of other nitrogen compounds, sulfur compounds, VOCs, heat, and ozone.

Dispersion modeling must be groundtruthed with actual meteorological, ambient air, and deposition measurements. The grid size must be chosen carefully to give the resolution needed, and the meteorological data must be compatible with that grid size. Smaller grid sizes generally increase the amount of time it takes to run the model and the expense.

Although it is possible to develop a new dispersion model, it is highly recommended that managers use one “off the shelf” that has already been developed and tested. Not only is it cheaper and easier, but the results will be more robust because the model itself has already been tested and peer-reviewed. The chapter **What You Need to Know About Air Deposition Modeling** describes several dispersion models that could be considered. Since these models also can be run to estimate total deposition *rates*, it is important to be clear on what data are used and how the model is being run. This is where building a good working relationship with the modelers from the beginning of the project will pay off; they will make sure the model runs are robust scientifically and answer the questions you need answered.

Dispersion modeling analysis can get expensive, even if an existing model is used. It depends to a large extent on which model is being used (generally, a model you can run yourself is cheaper than one you have to pay someone to run for you) and what form the input data are in. Often a large part of the cost of running a dispersion model is preparing the inventory and meteorological data to feed into the model. It is important to use the best inventory and meteorological data available for the

year(s) in which you are interested. Although a set of several dispersion model runs can cost as much as several hundred thousand dollars, it can cost an order of magnitude less if most of the meteorological and emissions data needed for modeling are already available.

### Isotope Ratios

Elements are present on earth as different isotopes, or weights. A well-known example is a radioactive isotope of carbon, carbon 14. (The most abundant carbon isotope is carbon 12.) Carbon 14 is used to determine the age of a particular material based on its ratio of carbon 14 to carbon 12 ( $^{14}\text{C}/^{12}\text{C}$ ). Isotopic nitrogen ratios use the same characteristic in a slightly different way. Instead of measuring the age of a material based on a decay rate, nitrogen isotope ratios can narrow down the source by matching the  $^{15}\text{N}/^{14}\text{N}$  ratio at the source and in the deposition sample (or other receptor).

Source categories emit different ratios of  $^{15}\text{N}/^{14}\text{N}$ . The ratio is usually presented as the “enrichment” of  $^{15}\text{N}$  versus some measured baseline, which is expressed as “delta 15 N” ( $\delta^{15}\text{N}$ ). A positive  $\delta^{15}\text{N}$  is enrichment of  $^{15}\text{N}$ , a negative  $\delta^{15}\text{N}$  is depletion of  $^{15}\text{N}$ . For example, one study measured the  $\delta^{15}\text{N}$  of fertilizer as approximately 0‰ (parts per thousand; like a percent except out of 1,000 instead of 100), nonpoint runoff from agricultural fields as +6 to +9‰, and effluent from sewage treatment plants +11 to +14‰. Animal waste lagoons are even more enriched in  $^{15}\text{N}$ , ranging from +16 to +27‰ depending on the animal species. In Europe, studies have shown that dissolved ammonium has a  $\delta^{15}\text{N}$  of approximately -12‰. Isotopic ratios for atmospheric sources can also be measured and used in the same way.

The  $\delta^{15}\text{N}$  can be measured at the receptor (a receptor could be the deposition samples, rivers, estuaries, or estuarine plants or animals) to estimate the source of nitrogen. Like the chemical mass balance method, this method only distinguishes classes of sources, not the actual source. For example, deposition measured at a particular site may have a ratio that is similar to that of organic

fertilizer rather than fossil fuel combustion. That would suggest agricultural sources rather than power plants or mobile sources.

Isotope ratios have a distinct advantage over the other methods in that they can be used to measure the percentage of nitrogen from air deposition in receptors other than the deposition sampling site. The  $\delta^{15}\text{N}$  can be measured in runoff, streams, estuaries, or algae. Theoretically, this would make it possible to estimate what role atmospheric deposition had in any particular algae bloom.

There are some uncertainties with using isotopic ratios as tracers. The biggest uncertainty is that what is measured at any given receptor is sometimes a mixture of nitrogen from different sources. A mixture of sources can do one of two things. It can produce a ratio at the receptor site that is not the same as any of the sources. Or, the ratio at the receptor site can be the same as a particular source type (say, +12‰), but actually be the result of a mixture of source types with ratios of +6‰ and +18‰. One way to get around some of this problem is to use more than one isotopic ratio. Oxygen ratios ( $^{18}\text{O}/^{16}\text{O}$ ) are sometimes used in conjunction with nitrogen ratios to narrow down the source type. For example, if the  $\delta^{15}\text{N}$  indicates two source categories as possible sources, the  $\delta^{18}\text{O}$  may point to one of those sources, making it the likely source. Like many of these methods, isotope ratios are best used in conjunction with other methods and not relied upon as the only method to identify sources.

Another potential limitation of the use of isotopic ratio tracers is that, in the atmosphere, one must assume the isotopic composition does not change from the emission source to the point of deposition. Other assumptions about how these ratios are enriched or depleted as nitrogen inputs move within the food chain are also required when carrying these measurements into surface waters.

This method of source identification is being tested in Sarasota Bay NEP and the Neuse River Basin in North Carolina, among other places, but it is not yet well-developed or accepted for use with

nitrogen compounds in the United States. Most American researchers are unfamiliar with the method, and there are few laboratories with the capability to analyze nitrogen compounds for their isotopic signatures. If you do decide to use this technique, make sure that the advisory group is committed to the choice and that the necessary equipment and expertise are available. Both could be resource-intensive.

### Tracers

Artificial tracers can sometimes be inserted into the emissions from a suspected source and tracked through ambient air and deposition monitoring. This is usually done to verify models. While theoretically very simple, the reality is much more difficult. For a tracer to work well, it must behave like the pollutant of concern (travel and deposit in a similar way), be inert (not affect pollutant of concern), be unique and benign in the environment (not emitted by other sources), and be amenable to detection at very low concentrations. These conditions make it difficult to find suitable tracers. The benefit of using a tracer is that, if it does work, it identifies a specific source. Other methods, except dispersion modeling, can only narrow down source areas or categories.

If a suitable tracer can be found, there is still the substantial logistical problem of getting access to the suspected emission site and inserting the tracer into the emission stream. This is not a small problem. It requires having an extremely good working relationship with suspected sources and sometimes getting permission from the state or EPA. Tracers are usually a “one-shot deal” so it is important to get everything right the first time. There must be a suite of monitors available to track the tracer toward the area of interest. This method is (obviously) very sensitive to existing weather conditions, and the weather scenario should be chosen carefully. Once you go to all the work of finding a tracer and getting permission to use it, the whole thing will be useless (or worse) if you insert the tracer during the 20% of the time the wind blows away from your watershed. Therefore, extreme care needs to be used when using tracers. It

can also be costly to hire the necessary experts to conduct the field work associated with tracer studies. Tracers should probably be viewed as the last resort, to be used only if all the other techniques for source identification do not provide the needed information.

### Designing a Source Attribution Strategy

The easiest way to design a source attribution strategy is to start with the simple methods and work your way up to the more complex (and more expensive) ones.

The first thing you should do is find out what sources emit the pollutant(s) in which you are interested. A list of pollutants and their largest sources is in Appendix 1.

Then get a recent inventory for your area and see if it makes sense. It helps to do this with someone who knows inventories, but it also requires someone with a working knowledge of the local area. Inventories may miss sources or have old data that do not take into account changes in land use, production methods at factories, closure of industrial sites, or other obvious things that only someone familiar with the area would know.

The first source attribution tool to try is the back-trajectory analysis. It is free—just download it from the NOAA Web page—and does not require any special training to use. Compare the results with the inventory to see how suspected sources compare to the back-trajectory results. If there are suspected sources in the path of the most contaminated air masses, it is reasonable to suspect those sources are responsible. This is as far as many managers go to identify sources. With this data, many feel comfortable approaching sources and/or states to talk about options to reduce emissions.

If that is not enough information, the chemical mass balance analysis, where source fingerprints are matched with chemical profiles found in deposition samples, can be used to support back-trajectory results for toxics. Isotopic ratios can do the same for nitrogen, yet there can be many uncertainties with their use; and they are best suited for identifying



what portion of nitrogen in the environment comes from atmospheric deposition (as opposed to what atmospheric sources are emitting it).

Dispersion modeling is a higher-end tool to use if more concrete connections are needed. Much of this is done at the federal level on a regional or national scale in support of regional or national regulations, but it is sometimes done at the state

and local level as well. Check to see what types of source-receptor modeling results are or will be available before deciding to do your own.

Tracers are a last resort if none of the other methods work. They are extremely difficult to do well and should only be done if it is certain that results will be useful in the management context.