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What Goes Up Must Come Down: Integrating Air and Water Quality Monitoring for Nutrients

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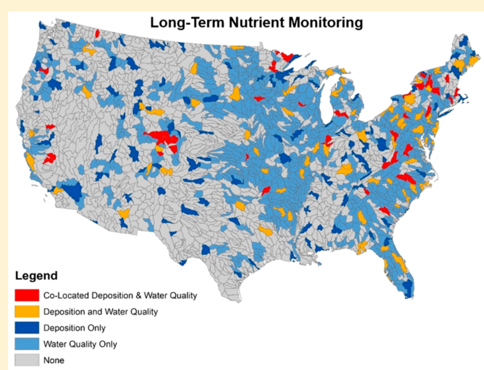
ABSTRACT: Excess nitrogen and phosphorus ("nutrients") loadings continue to affect ecosystem function and human health across the U.S. Our ability to connect atmospheric inputs of nutrients to aquatic end points remains limited due to uncoupled air and water quality monitoring. Where connections exist, the information provides insights about source apportionment, trends, risk to sensitive ecosystems, and efficacy of pollution reduction efforts. We examine several issues driving the need for better integrated monitoring, including: coastal eutrophication, urban hotspots of deposition, a shift from oxidized to reduced nitrogen deposition, and the disappearance of pristine lakes. Successful coordination requires consistent data reporting; collocating deposition and water quality monitoring; improving phosphorus deposition measurements; and filling coverage gaps in urban corridors, agricultural areas, undeveloped watersheds, and coastal zones.



1. INTRODUCTION

Robust environmental monitoring is fundamental to understanding our environment and assessing the efficacy of environmental policies.[1] For many chemical elements of economic and environmental relevance (e.g., nitrogen, phosphorus, sulfur, mercury), air and water chemistry are intrinsically connected. While important progress has been made over the past 20 years,[2] most monitoring in the U.S. still does not connect atmospheric inputs to surface water quality. Where connected, information from integrated air and surface water quality monitoring has contributed to the basis, justification, and efficacy assessment of the Clean Air Act Amendments of 1990.[3] Integrated monitoring

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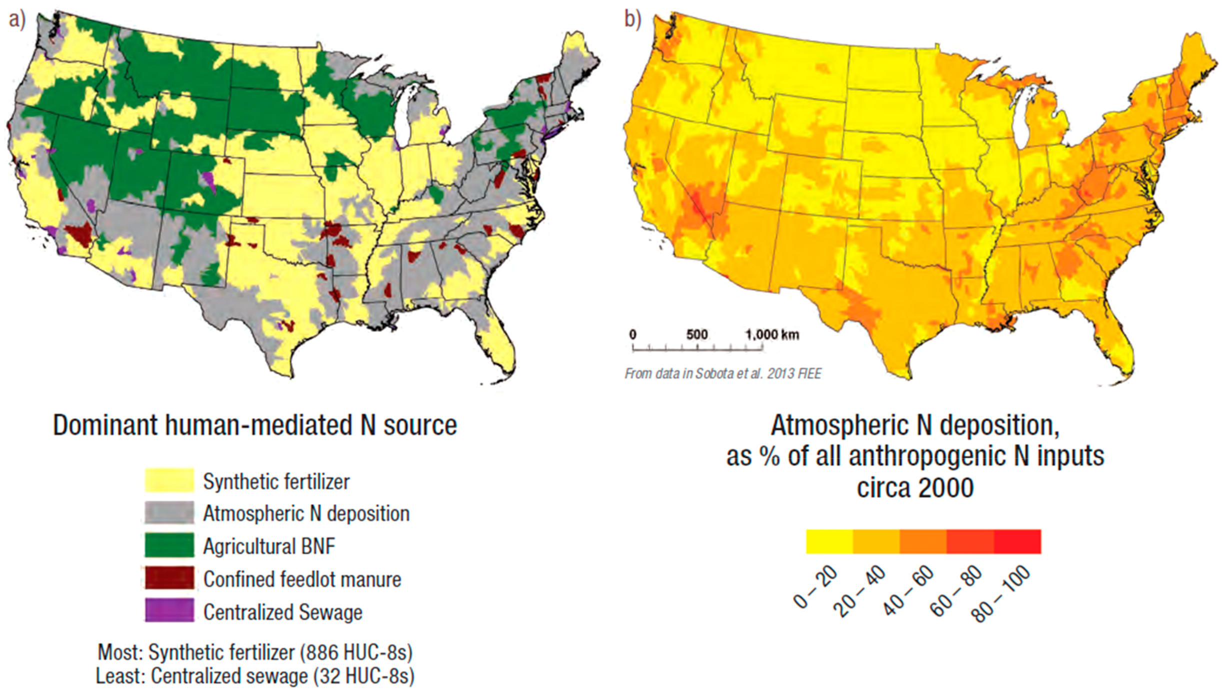

Figure 1. (a) Dominant anthropogenic sources of nitrogen to surface water for HUC 8 (Hydrologic Unit Code) watersheds. BNF denotes biological nitrogen fixation. (b) Atmospheric nitrogen deposition expressed as a percentage (0 to 100%) of all anthropogenic nitrogen inputs. Source: Compton et al.[20]

at inland sites has helped us understand how decreasing atmospheric nitrogen deposition reduces estuarine nutrient enrichment.[4] These efforts have allowed us to determine sources, trends, and whether pollution reduction decisions have been effective and fiscally responsible.[5]

Excess nitrogen and phosphorus ("nutrients") is one of today's most challenging and costly water quality issues.[6] The challenge arises from balancing trade-offs between human needs, such as food and energy production, with harm to human and ecosystem health, such as drinking water contamination[7] or harmful algal blooms and hypoxia.[8] Excess nitrogen damages in the U.S. exceed $100 billion annually.[9] Despite ongoing source reductions, nutrient enrichment of aquatic ecosystems is difficult to mitigate. The persistent hypoxic zone in the Gulf of Mexico was the size of New Jersey in 2017, the largest in the 15-year record.[10] The U.S. Environmental Protection Agency's Science Advisory Board recently concluded a national strategy integrating air and water monitoring is needed to understand sources, transport, and fate of excess nutrients.[11]

Atmospheric deposition dominates nitrogen inputs to surface waters over much of the conterminous U.S.[12] (Figure 1). Atmospheric deposition physically delivers nitrogen and phosphorus to land and water surfaces by wet (e.g., rain, snow) and dry (e.g., gases and particulates) processes. Even in watersheds with large nutrient sources from agriculture or sewage, atmospheric sources can play an important role depending on land use and timing of runoff.[13,14] It is thus important to quantify atmospheric inputs in order to assess reduction efforts, such as agricultural best practices, water treatment upgrades, and power plant emission caps.[4,15] Fewer than 2% of long-term water quality sites are colocated with nitrogen deposition monitoring in the U.S. (Figure 2). Phosphorus is monitored in deposition and water simultaneously at even fewer sites. Recent work reveals the importance of urban atmospheres as a significant potential source of phosphorus to runoff.[16]

Experience from the Acid Rain Program can inform efforts to integrate air and water monitoring at large geographic scales. In the 1970s, studies began documenting widespread acidification of U.S. lakes, streams, and soils.[17,18] Deposition and surface water quality monitoring were coordinated under the Acid Rain Program during the 1990s and 2000s. These sites provided data to assess whether emission reductions from vehicles and the power sector reduced acidic deposition and improved water quality.[3] The number of U.S. lakes and streams at risk for ecological harm from acidity dropped from 24% in 2000 to 9% in 2015,[19] estimates that were made possible by merging deposition and water quality monitoring data.

2. EXISTING U.S. ATMOSPHERIC DEPOSITION AND SURFACE WATER QUALITY MONITORING

The primary monitoring network for assessing wet deposition nationally, the National Atmospheric Deposition Program (NADP), was established in 1978. Currently, there are 271 NADP sites that analyze sulfate, nitrate, ammonium, base cations, pH, and orthophosphate (as a tracer for contamination) in precipitation. The Clean Air Status and Trends Network (CASTNET) provides continuous, long-term data on dry deposition at 95 sites. Most NADP and CASTNET sites are in rural areas to capture regionally representative samples. More than 100 organizations participate in NADP, conducting their sampling with nationally consistent methods. The data are primarily used for testing air quality models, providing inputs to watershed models, estimating critical loads of acidity and nitrogen, and developing ecosystem budgets for nitrogen and other elements. NADP and CASTNET monitoring methods do not capture organic forms of nitrogen, which are known to contribute significantly to total nitrogen deposition.[21] Better understanding of dry deposition processes and the role of organic nitrogen in deposition budgets are important research needs and are addressed elsewhere.[22−24]

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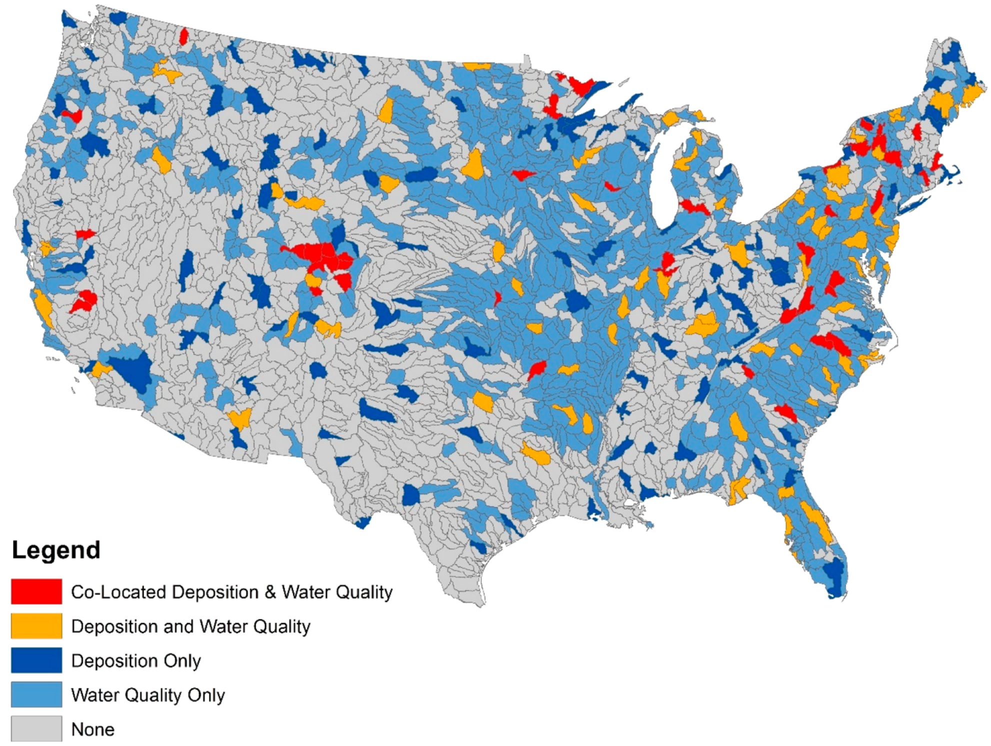

Figure 2. Long-term atmospheric deposition and surface water quality nutrient monitoring locations summarized at a HUC-8 level. Depicted are watersheds with no long-term monitoring sites (gray); only water quality (light blue); only atmospheric deposition (dark blue); both deposition and water quality (yellow); or colocated deposition and water quality monitoring separated by less than 10 km (red).

Surface water quality monitoring in the U.S. began in the late 1800s. Today, over 600 government agencies, academic institutions, and citizen organizations collect water quality data.[25] Water quality constituents associated with deposition include reduced and oxidized nitrogen, pH, alkalinity, sulfate, calcium, phosphorus, mercury, and aluminum. Nutrient data are collected to characterize status and trends, determine whether targets are being met, and investigate factors affecting water quality. Monitoring locations may be randomly located across a region to provide a statistically representative estimate; or selected to represent certain human activities, environmental settings, or hydrologic conditions to provide an understanding of how, when, and why water quality is changing.

At the 2% of locations where deposition and water quality monitoring co-occur, (Figure 2), key insights into processing affecting the coupling between deposition and water quality have been documented. For example, long-term colocated monitoring occurs on USDA Forest Service Experimental Forests, such as Coweeta Hydrologic Laboratory and Hubbard Brook Experimental Forests. Multidecade forest cutting experiments at Coweeta and Hubbard Brook have shown land management can decouple the relationship between atmospheric deposition and stream chemistry until forest regrowth occurs (Hubbard Brook), or for decades following cutting if an atmospheric nitrogen-fixing tree dominates the subsequent forest (Coweeta) (Figure 3).[26−30]

Much as it is in the U.S., we know of only limited integrated monitoring in the international community. In Europe, the International Cooperative Program on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM) monitors the effects of air pollutants on ecosystems at 41 sites.[31] The Acid Deposition Monitoring Network in East Asia (EANET) is primarily a regional wet deposition network, where 13 countries and 57 sites have recorded wet deposition since 2001 (including nitrate, ammonium, and phosphate as of 2016) following similar methods to the NADP. EANET organizes quarterly colocated measurements of surface water quality at a subset of sites. There are a few other sites in Asia where long-term measurements of surface water chemistry are integrated with measurements of deposition.[32] We are unaware of integrated monitoring networks in South or Central America or Africa. Countries face many of the same scientific and environmental management challenges for nutrients. As such, the motivations for integrated monitoring described here for the U.S. apply elsewhere.

3. PRIORITY KNOWLEDGE GAPS DRIVING NEED FOR MONITORING COORDINATION

What is the Atmospheric Contribution to Nutrient Enrichment in Coastal Waters? Excess nutrients in coastal waters can manifest as toxic algal blooms, low oxygen zones, loss of fisheries habitat, and fish kills and can even shift coastal wetlands from sinks to sources of carbon.[33] It is a rampant problem across the U.S.,[34] Europe,[35] and China.[36] Atmospheric inputs of nutrients to coastal ecosystems vary widely, ranging from <5% to >60% for nitrogen.[37] Due to a lack of long-term data, empirical estimates exist only for a few eastern U.S. estuaries. There are approximately 30 operating NADP NTN sites and only six CASTNET sites within 25 miles of coastal waters, with none occurring on the West Coast. Currently, there is no national estuarine water quality monitoring program for nutrients. Of the 138 U.S. estuaries,[38] many ecologically- and economically important estuaries have infrequent or no monitoring. The U.S. Geological Survey National Water Quality Network for Rivers and Streams (see https://cida.usgs.gov/quality/rivers/coastal) has 19 sampling stations located on major rivers, which deliver 65−70% of freshwater flowing to the coasts, but over 100 U.S. estuaries are still without riverine monitoring.

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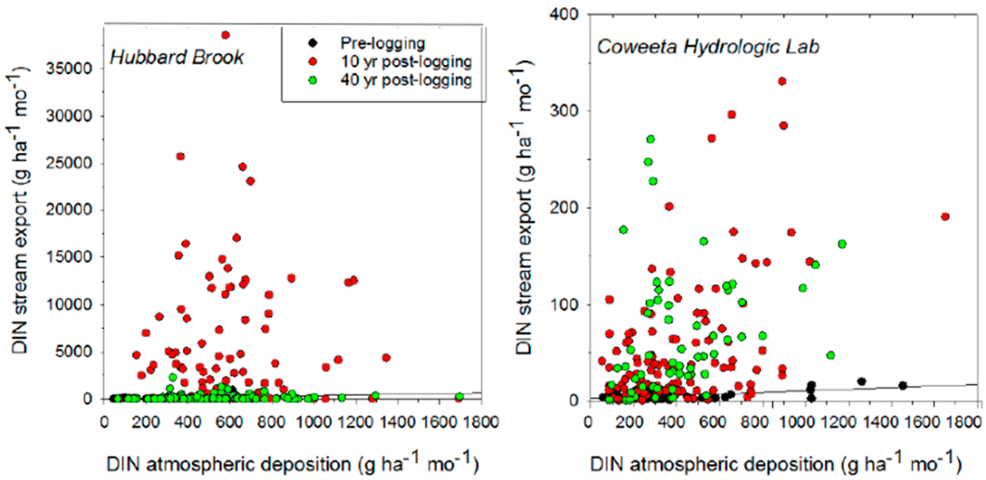

Figure 3. Scatterplots of dissolved inorganic nitrogen (DIN) stream export versus atmospheric deposition at Hubbard Brook and Coweeta before clear-cut logging (black), and 10 (red) and 40 years (green) after clearcutting. At both sites, clearcutting decoupled the linear prelogging relationship between deposition and export. The linear coupling eventually recovered at Hubbard Brook, but not at Coweeta due to forest composition and mortality.

In addition to monitoring upstream sources entering coastal waters, coastal zone monitoring is important, especially for small-to-medium watersheds that can exist entirely within the coastal plain. Deposition to the surface of coastal waters can uniquely impact biology. Most nitrogen deposited to land and transported by rivers will be converted to nitrate or organic nitrogen on its way to the ocean.[39] Conversely, direct deposition to coastal waters bypasses the biogeochemical processing of the watershed and can be a significant input of ammonia. A shift in the speciation of nitrogen inputs can result in harmful algal blooms.[39] Increasing the number, and coordination, of both wet and dry atmospheric deposition and water quality monitoring sites in coastal zones will help mitigate harmful impacts, preserve healthy coastal ecosystems, and fill data gaps for nutrient fluxes in coastal zones.

What Is the Atmospheric Contribution to Nutrients in Urban Stormwater Runoff? Elevated deposition has been documented in numerous urban areas, including cities in the U.S.,[40−42] Europe,[43−45] and Asia.[46,47] Elevated inputs to urban areas can contribute up to 50% of total nitrogen inputs to downstream waters, such as the Chesapeake Bay,[48] estimates that are only possible by examining rates of atmospheric deposition with water quality simultaneously. Sources of nitrogen can vary dramatically over the hydrograph, with wastewater sources dominating during base flow and atmospheric deposition increasing during stormflow.[14] In most urban areas with deposition measurements, they are not coupled to measurements of nutrient loading from other sources to nearby waterways or water quality. This lack of coordination impedes the quantification of atmospheric deposition's contribution to total nutrient inputs and the evaluation of policies or management options to reduce nutrient loads. Improved coordination in urban areas would enable better decision making related to point and nonpoint sources of nutrients.

How Is a Shift in Nitrogen Speciation Impacting Water Quality? The U.S. is experiencing a continental-scale shift in the speciation of inorganic nitrogen deposition from oxidized species (nitrogen oxides) to reduced species (ammonia and ammonium).[49] Europe[50] and China[51,52] are also experiencing long-term trends in the speciation of inorganic nitrogen deposition, but differ in magnitude and composition from the U.S. Oxidized species are primarily associated with emissions from vehicles and electrical power generation, while reduced species are associated with agricultural activities. U.S. nitrogen oxide emissions declined 67% from 1995 to 2009,[3] driven by declining emissions from the transportation and energy sectors. Emissions from food production are projected to increase over coming decades,[53] which may continue the increasing proportion of nitrogen deposition from reduced nitrogen species. This change can alter algal community composition and abundance, with some harmful algae preferring reduced nitrogen.[54,55] Algal dynamics are already being altered in western U.S. mountainous lakes, and the problem could become worse with increasing atmospheric inputs of reduced nitrogen.[56]

Recent studies combining ground-based[57] and satellite observations[58] of reduced forms of nitrogen concentrations and deposition show large spatial and temporal variability within and downwind of agricultural areas, patterns that are not well resolved by current monitoring. Additional NADP Ammonia Monitoring Network (AMoN) and NTN wet deposition sites are needed to fill geographical gaps to characterize reduced nitrogen deposition and trends better, and to improve atmospheric and biogeochemical models that link terrestrial and aquatic nitrogen inputs. Coordinating any expanded monitoring of reduced nitrogen deposition with water monitoring would facilitate decision-making regarding source apportionment, management, and mitigation of affects in aquatic ecosystems.

Are Atmospheric Phosphorus Inputs Degrading Pristine Lakes? Phosphorus concentrations in lakes are increasing across the U.S. without a clear explanation.[59] An alarming feature of the trend is the decrease in the number of naturally low-nutrient concentration lakes from 24.9% in 2007 to 6.7% in 2012.[59] Increasing phosphorus concentration in lakes could be driven by increasing atmospheric deposition of phosphorus.[60] The pH of rainfall has been recovering to less acidic levels since the 1990 Clean Air Act Amendment, which may also be increasing phosphorus solubility in soils.[61]

The current lack of understanding about the extent, or mechanism, for phosphorus deposition to impact surface water quality underscores the need to enhance monitoring coordination. Historically, measuring phosphorus in wet deposition was not a priority given its low concentration in precipitation.

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For example, in North America, NADP NTN analyzes for orthophosphate (PO_4^{3-}) in precipitation, but due to protocol limitations, measurable concentrations are observed infrequently and detection is primarily an indication of sample contamination from birds. This is a critical limitation given that trends are strongest in lakes and streams with low phosphorus concentrations. Improved methods are needed for: measuring total, ortho-, organic, and particulate-form phosphorus; and measuring phosphorus in wet and dry deposition. An examination of studies conducted between the mid- to late-1990s through 2007 identified only 23 sites worldwide that made measurements of annual wet deposition of dissolved phosphorus for some of this period. Among atmospheric deposition networks worldwide, only one small network (nine sites), the NADP Atmospheric Integrated Research Monitoring Network (AIRMON) in the eastern U.S., measured it routinely.[62] Routine network measurements of both wet and dry phosphorus deposition are needed on all continents and oceans in order to quantify the role of atmospheric deposition in the biogeochemical cycling of phosphorus. Routine comeasurements of comparable phosphorus species in deposition with those measured in lakes and streams will require more coordinated monitoring strategies than are currently in place.

Box 1. What "critical loads" teach us about the challenges of data integration

A critical load (CL) is a threshold for deposition below which specified ecological changes do not occur in an ecosystem.[68] CLs are calculated based on several analytes in water samples. The CL of waterbody is "exceeded" if deposition of a pollutant is too high. CLs inform U.S. air pollution policies, water resource management, and impact assessments for both acidification and nitrogen enrichment.

There are many challenges in calculating CLs, particularly at regional-to-national scales. Lynch, Phelan, Pardo, and McDonnell[19] could only calculate CLs for approximately 13 000 streams and lakes, despite +290 million water quality measurements in our national water quality databases.[66] CLs for acidity require nitrate (NO_3^-), sulfate (SO_4^{-2}), and base cations measurements. Differences in procedures, methods, and reporting can exclude data from assimilation. Another challenge is having all the needed water quality measurements for the same waterbody. In many cases, water samples may only be analyzed for certain analytes (e.g., nitrogen) and not others (e.g., base cations). The new documentation format WQX used by the Water Quality Portal[67] provides greater order to unit and naming conventions, fostering better use of water quality data and allowing for better integration with other environmental data, including atmospheric deposition.

4. ENHANCING INTEGRATION

Reinvigorating the call for monitoring coordination (e.g., refs 63 and 64) is timely because the computational tools to facilitate integration have never been better and the need—both in terms of filling knowledge gaps and leveraging declining resources—has never been greater. Strategies presented here are informed by today's problems. We encourage a flexible approach to integration that emphasizes coordination and consistency, and maximizes efficient use of monitoring resources.

Support Consistent Reporting of Surface Water Quality Data and Metadata. An important aspect of integrating air and water data is consistency of reporting and metadata. Box 1 provides an example of the obstacles posed by fragmented and inconsistent data documentation, and the challenges in data assimilation. Additional detail about the challenges specific to water data can be found in Sprague et al.[65] We encourage open, online access, sufficient and consistent documentation, and comparable methods for sample collection, analysis, and quality control. The efforts of more than 1700 U.S. volunteer water monitoring organizations should be included. Consistent and sustained funding—for air and water monitoring—is fundamental.

Online infrastructure is needed to support coordination of water data. Launched in 2002, the National Environmental Methods Index (www.nemi.gov) serves as a central clearinghouse for measurement methods and helps users compare methodologies. The Water Quality Portal (www.waterqualitydata.us) provides a single point-of-access to the largest combined water quality data set for groundwater, stream and river, and coastal sites,[66] with a consistent metadata documentation format (Water Quality Exchange - WQX).[67] These are major steps toward improving compatibility of water and air data.

The NADP offers a working model for a federated network of water organizations. Important principles transfer from the NADP model to the coordination of water monitoring for efficient use of increasingly limited resources, such as collaboration among agencies, cost sharing, and centralized online data access.

Enhance Integration at Existing Monitoring Sites. Coordination of monitoring networks among organizations is a daunting task, but could be made more tractable by beginning with a pilot effort focused on a specific, small objective. One such objective might be coordinating surface quality water sites colocated with NADP NTN deposition sites, for the purpose of evaluating deposition effects on water quality. A core set of analytes could be identified, either by stakeholders or NADP NTN, and sampled at these sites. A standing committee analogous to the NADP NTN operations committee could facilitate coordination among organizations and establish minimum standards for collection, analyses, and documentation at colocated sites. Clear procedures for adding new sites to the pilot could ease an eventual transition to an expanded, long-term integration of monitoring with the goal of achieving sufficient coverage to relate air and water quality.

In planning pilots, it will be important to consider that atmospheric nitrogen loading to watersheds often, but not always, parallels stream nitrate concentrations.[4,69,70] Both short- and long-term environmental processes can cause temporal lags between streamwater quality and deposition. Fast-growing young forests tend to accumulate nitrogen in biomass, releasing very little to the surface waters, whereas slower-growing older forests often release nitrogen as their ability to store it diminishes (e.g., nitrogen saturation). Other factors such as snowpack, groundwater storage and flow, and in-lake retention can also attenuate the signal of deposition.

The next few years present a critical opportunity to encourage coordination between nutrient water and deposition monitoring. Total deposition samplers for phosphorus are being piloted at 10−15 NADP sites in the western U.S. beginning in late 2017.[71] New in situ sensor technology for measuring nutrients in water is increasingly available at lower prices,[72] although care should be exercised not to trade lower up-front costs for higher maintenance and data quality assurance costs. Opportunities for coordination are ripe while organizations are piloting and deploying new technology. We encourage focusing on water quality sites that also measure streamflow. Flow is needed to

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compare streams of different sizes, quantify exports, and complete nutrient and material budgets. With the frequency of extreme events projected to increase,[73] in situ sensors and colocated monitoring of deposition, surface water quality, and key watershed processes are needed now more than ever.

Fill Monitoring Gaps. There are large regions of the U.S. without long-term deposition or water quality monitoring for nutrients (Figure 2). The most important coverage gaps are

1. **Coastal zones**. Coordinated air and water monitoring is needed in the Atlantic, Pacific, and Gulf of Mexico. A unique challenge to coastal areas is the need to monitor deposition over open water and in tidal zones, which can be substantially different than deposition inland. Deployment strategies may include buoy systems, use of oil production platforms, or collaboration with local fishers.
2. **Cities**. NADP has recently established sites in Boston, New York, Denver, and the Washington, D.C. area. Additional sites are especially needed in urban corridors with heavy car traffic near waterbodies, such as Charleston and New Orleans. Multiple locations across a single city are ideal because of the heterogeneity of pollution within cities. Where possible, pairing studies of atmospheric deposition in cities to nearby rural areas provides a reference point to quantify potential urban hotspots.
3. **Agricultural areas**. Better deposition and water quality monitoring coverage is needed within and downwind of confined animal feeding operations and intense fertilizer application in the Midwest and southeastern U.S, including spatially dense monitoring of atmospheric ammonia concentrations for estimating dry deposition. Fusion of satellite ammonia observations with chemical transport modeling could inform expanded monitoring locations. We note groundwater discharge can also be an important pathway of nutrients in these settings.[74]
4. **Undeveloped watersheds**. The greatest needs are in the western U.S. and high-elevation areas. Power sources and site maintenance can be logistically challenging in these environments.

Investment in expanded coordination of new deposition and water quality monitoring locations has benefits for addressing nutrient enrichment, but also builds critical architecture to assess, inform, and respond to emerging and future environmental issues quickly. This could include contamination from other cross-media pollutants such as mercury or organic forms of nitrogen, effects of climate change, effects of large forest fires, or unforeseen consequences of large shifts in major economic sectors such as transportation electrification. The cost of new monitoring is small compared to the potential benefit. Citing an example from the Acid Rain Program, which simultaneously monitored atmospheric deposition and surface water chemistry, "Taken together, the total cost of these critical atmospheric deposition and surface water monitoring programs represents less than 0.4% of the implementation costs of Title IV [of the Clean Air Act Amendments] and less than 0.01% of the estimated benefits".[1]

Coordinating atmospheric deposition and surface water quality monitoring will help fill important scientific, management, and policy-relevant knowledge gaps. Monitoring that connects deposition and water quality enables better ecosystem management, evaluation of pollution reduction efforts, and detection and response to unanticipated environmental changes. Investment now in key activities that couple air and water monitoring is not just relevant for nutrients, but has cobenefits for sulfur, mercury, and other pollutants.

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Notes

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