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Uncertainty of water-quality predictions in ungauged basins (PUBs)

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Abstract The quality of freshwater at any point on the landscape reflects the combined effects of natural and anthropogenic processes along hydrological pathways, for which the process relations may be cyclical (inter-dependent and/or periodic) and cascading. Local, regional, and global differences in human activities (e.g. mining, industry, agriculture, waste treatment and disposal), climate, and streamflow, are considerable, which, in turn, cause varying effects on water quality and quantity. Natural characteristics also greatly control human activities, which then affect the natural composition of water. These cause-and-effect relations produce uncertainty in water-quality estimates, because they are difficult to quantify. For example, although rock type is a primary control on water quality, annual dissolved major-ion yield estimates from empirical relations using rock type, precipitation quantity, population density, and temperature for large rivers in the US, are precise only to one order of magnitude, which in part is due to nonlinear responses of large non-homogeneous areas. Human activities, as reflected by land-use, can likewise be used to qualitatively indicate differences in constituent concentrations, particularly for constituents that are primarily controlled by non-point sources, e.g. nutrients and pesticides. However, the large concentration variations prevent an accurate estimate. For many naturally occurring substances, uncertainty of estimated concentration or yield is larger for constituents primarily derived from point sources than from non-point sources, until the major point sources and related contributions are known. Also, uncertainty of the estimates of average constituent concentration or yield decreases with increasing averaging time, e.g. a predicted annual flux is more precise than an instantaneous or daily flux.

Key words hydrological pathways; prediction; residence time; water pollution; water-quality standards; watersheds; uncertainty

INTRODUCTION

Hydrological and biogeochemical processes determine background freshwater quality. The primary factors controlling the biogeochemistry are climate and the mineralogy and composition of earth materials. For example, the background river concentration and flux of major ions, such as calcium, magnesium, sodium and potassium, are controlled by the hydrological residence time and weathering, which in turn, are controlled by: (1) the seasonal distribution of temperature and moisture due to climate and associated biota; (2) the contribution or cycling of elements from the ocean and particulates derived from the Earth surface through atmospheric deposition; (3) the relative contribution of waters from hydrological pathways to river flow; and (4) the variability and distribution of the composition and mineralogy of soils and bedrock in the associated river basin. Also, within a river basin, concentrations of these ions in stream water vary markedly during hydrological events due to mixing of waters from different hydrological compartments (an end-member mixing problem) with differing residence times and biogeochemical histories. However, the fluxes of most naturally occurring constituents (concentration times, discharge), are primarily controlled by the discharge because short-term discharge is typically more highly variable, i.e. several orders of magnitude, than constituent concentration, which typically varies by less than an order of magnitude. Note that many exceptions exist to this general rule, e.g. pesticide concentrations and sediment-bound contaminants.

Although this is one of the simplest schemes for element cycling, the cycling is complex. The result is that to accurately predict the concentration variation of major ions in a natural ungauged basin, the bedrock geology and hydrological characteristics would have to be known, which in turn, requires some knowledge about the climate and related storm runoff and seasonal temperature variations. Many processes are cyclical in that they are interdependent and/or periodic, and cascading with downstream effects typically being cumulative (Peters & Meybeck, 2000). Unfortunately, we can only theorize about the characteristics of the relations among environmental factors and natural or background water quality because the effects of human activities on water quality are observed everywhere on the surface of the Earth.

Human activities vary markedly and each has some effect on the environment, which ultimately affects water quality, particularly through landscape alteration, the abstraction and processing of particular biological and earth materials, minerals, and chemical elements, the development and dispersal of new compounds, and the disposal of wastes to the air, land, and water. Furthermore, the same broad category of human activity, such as agriculture, has varied effects in time and space on the landscape, partly due to specific variations in culture, socioeconomic conditions, climate, and available technologies. In the case of agriculture, the type and timing and magnitude of fertilizer, livestock manure, pesticide, and herbicide applications, as well as crop type and rotation cycle, will affect water quality. To make existing complex natural cycling even more complex, human interactions with air, land, and water resources have resulted in a progressive increase in the number of human-made chemical compounds released to the environment. Most of these compounds are not monitored routinely, and therefore little is known about their characteristics, occurrence or distribution, and much less is known about their transport, fate, and transformation.

Although the assessment of prediction uncertainty is a scientific endeavour, the rationale for reducing prediction uncertainty is primarily driven by ecological and human health needs. The effort, therefore, devoted to determining controls on ecosystem and human health functions, typically varies depending on the affects of chronic (long-term average) or acute (instantaneous) exposure of the myriad of water-quality constituents on those functions. Consequently, the knowledge also varies depending on the need, the effort expended to understand the relations, and the complexity of the relations.

The objectives of this paper are: (1) to discuss concentration and flux of water-quality constituents with respect to major controlling factors; (2) to show how some of the primary basin characteristics are related to measured water-quality constituent concentration and fluxes; and (3) to provide a schema of the relative importance of climate and basin characteristics with respect to decreasing estimate uncertainty of concentration and fluxes of a small suite of water-quality constituents.

WATER QUALITY

Water quality is an inherent or distinguishing characteristic or property of an aquatic environment and combines measures of concentrations, speciation (dissolved, colloidal, and particulate phases and interactions), and physical states of inorganic and organic substances, plus the composition and state of the biota in the aquatic environment. Water chemistry and biology are typically compared to that of a background or non-impacted state of the aquatic environment to assess the relative status. The measures usually reference impairment with respect to potential uses of the water, harm to biota living in the environment, and potential impacts to human health (Chapman, 1992). Although specific water-quality constituents are generally targeted, it is useful to group constituents by issues that are related to either some general characteristic of water-quality degradation or some human interference. These issues may be further subdivided, particularly with respect to the spatial and temporal scale of the impact (Table 1).

For example, surface-water acidification generally is caused by acidic atmospheric deposition, which in turn is caused by the combustion of fossil fuels; one exception is

Table 1 Water-quality degradation issues of surface waters and the spatial and temporal scales at which the impact of the issue stabilizes.

Issue	Spatial scale	Temporal Scale (years)
Acidification	local to regional	10–>100
Bacterial contamination	local to regional	<1
Channelization and damming	local to regional	10–1000
Channel erosion and siltation	local to regional	10–100
Eutrophication	local to regional	10–100
Excess organic matter	local	<1–>10
Exotic and invasive species	local to regional	10–>1000
Heavy metals	local to regional	10–>1000
Micro-organic pollutants	local	<1–unknown
Nitrate pollution	local to regional	10–>100
Nuisance and toxin-producing species	local	<1–>10
Oil and its derivatives	local	10–>100
Oxygen demand	local	<1–>10
Waterborne diseases	local	<1–>10
Pathogens	local	<1
Pesticides and herbicides	local to regional	<1–unknown
Pharmaceuticals	local	<1–unknown
Radioactive pollution	local to global	1–>1000
Salts and salinization	local to regional	10–1000
Suspended solids	local to regional	10–>1000
Thermal pollution	local	<1

acid mine drainage. Fossil-fuel combustion emits acid precursor gases and aerosols that are atmospherically transported and transformed to acids (enriched in nitric and sulphuric acid), and deposited on vegetation, soils, and water through wet and dry deposition. Surface-water acidification occurs in basins typically having thin soils that are underlain by weathering resistant bedrock such as quartzites, sandstones, and more generally, granitoid rocks. Furthermore, small basins in headwater areas typically have thinner soils than the downstream areas of larger watersheds. Also, surface-water acidification is typically not an issue in areas containing carbonate minerals or where hydrological residence times are long, which is also typical for the downstream areas of larger basins. Hydrological events (rainstorms and snowmelt) cause short-term reductions in the acid neutralizing capacity of soil water and surface water, called episodic acidification. Episodic acidification typically occurs due to changing hydrological pathways through shallow soils where the acid cannot be neutralized, but the associated changes in chemistry during an acid episode, e.g. increased concentrations of aluminium, are deleterious for aquatic biota, e.g. causing fish kills and a disruption in the food web. Although acidic atmospheric deposition may be regional, the effects of chronic acidification are generally restricted to localized headwater regions, but episodic acidification can affect more of a watershed.

The problem for acidification prediction as well as that for many other water-quality constituents/issues is that heterogeneity in concentration and flux may exist in four dimensions (landscape surface (X, Y) and elevation or depth below the surface (Z), and time (t)). For example, the nutrients mobilized from application of a fertilizer may travel in surface runoff directly to a stream during rainstorms or via near-surface quick flow pathways with a longer travel time, and in groundwater from infiltration and groundwater recharge, which will eventually contribute to streamflow. The temporal water quality of the stream will vary markedly depending on the supply rate and the residence time of the nutrients along these pathways, and the extent to which the pollutant transport pathways are interrupted by landscape features with a greater retention capacity for that pollutant (such as woodland, hedgerows, wetlands). The problem is even more complex for pesticides, particularly if they decay into daughter products that cause deleterious effects on the environment or human health.

Concentration

The knowledge of constituent concentrations—either directly through water-quality monitoring, or indirectly through modelling and associated predictions—are important because there is typically a relationship between concentration and the health of aquatic biota and humans who use the water. Furthermore, the concentration of a select suite of constituents is typically used to determine how the water can be used. Establishing a concentration threshold or range is a common technique for regulating water use and waste disposal. In the USA, water bodies are rated by regulatory mandate, and specific concentration “targets” are established for either maintaining or improving water quality. These “targets” (typically for groundwater or surface water) control future landscape/resource development of a basin. With the decline in monitoring programmes and the continuing need to regulate water use and manage basin resources, the prediction of constituent concentrations is required. In Europe, however, with the advent of the Water Framework Directive (implemented December 2000), there has been a move away from this form of pollution monitoring. Instead, European nations are required to classify their water bodies according to their ecological status in one of five categories: high, good, moderate, poor and bad (see Environment Agency, 2002, for details). High ecological status is defined as a reference state with no evident ecological damage. Good ecological status, to which all European waters must be restored within a fixed time period, is defined as no significant ecological change from reference state. Thus the evidence of improvements in chemical pollution status is sought in the response of the biota to water chemistry and physical habitat descriptors. Concentration thresholds are only likely to persist for toxic or dangerous substances and for the discharge of pollutants from known point sources of origin.

The acidification issue is an example of the use of concentration thresholds for assessment through the development of critical loads models, which are widely used in Europe, for acid sensitivity predictions (Henriksen *et al.*, 1992; Hornung *et al.*, 1995; Curtis *et al.*, 2000). Various models, used to predict the sensitivity of surface waters to acidification, employ alkalinity or acid neutralizing capacity thresholds to separate the various sensitivity classes. Also, for many other constituents in the USA, the US Environmental Protection Agency (USEPA) has established quality criteria for water in which each constituent has a rationale for the criterion (USEPA, 1986). For example, the USEPA's criterion for nitrate concentration is 10 mg N L^{-1} for domestic water because water with higher concentrations ingested by infants can be fatal. Therefore, the issue is one of exposure as it relates to human or ecosystem health with long-term average exposures representing a chronic state and an instantaneous exposure representing an acute state. The prediction therefore, is how certain are the concentration estimates as they affect these two states and over what time scale is the estimate appropriate, e.g. averaging time for chronic exposure and instantaneous values for acute exposure.

Flux

Flux estimates of water-quality constituents are important for assessing sources and sinks of constituents in a drainage basin. Because discharge typically varies much more than concentration, an accurate estimate of the hydrological flux is more important than knowing the specific variability of a given constituent concentration. However, for constituent concentrations that vary systematically with discharge, and particularly for those that increase with increasing discharge, such as suspended sediment and many human-made compounds, some estimate of the relation is important because it affects the flux prediction. Briefly, rainfall patterns and amount, basin storage characteristics, and vegetation, largely determine the water partitioning. The basin storage characteristics in turn are controlled by bedrock type and latitude, which affect weathering and geomorphologic processes. For example, snowmelt runoff differs substantially in basins underlain by similar bedrock type, but with different geologic history due to latitude, i.e. glaciated and non-glaciated basins; streamflow gains and losses in basins containing karst vary markedly from basin to basin; evapotranspiration varies depending on vegetation, e.g. cropland, pasture and forest; and channelization affects runoff and development of impervious areas affects evaporation, particularly with respect to rapidly urbanizing landscapes. The primary factors affecting hydrological predictions at various time and spatial scales are discussed elsewhere in many papers being presented at this IAHS PUBs conference, e.g. see Franks, 2007 (this volume).

WATER-QUALITY RELATIONS WITH SOME CONTROLLING FACTORS

Bedrock type is an important variable in predicting concentrations and fluxes of many major inorganic solutes (Gibbs, 1970; Meybeck, 1979; Peters, 1984; Bluth & Kump, 1994; Meybeck, 1994). The uncertainty in the prediction of annual major ion yields from basins ranging in size from 10 to 100 000 km^2 in the USA, using a multiple linear regression model was an order of magnitude (Peters, 1984). The predictors were a percentage of particular rock types in the basin, annual precipitation quantity, population density, and average stream temperature. Precipitation quantity, a surrogate for runoff, and rock type were the most statistically significant predictors. Yields of magnesium, calcium, and bicarbonate ion were 4–10 times higher from limestone basins than from sandstone and granite basins (Peters, 1984). The relatively large uncertainty for these predictions, in part, may be due a non-linear response for large basins, which may have linear relations among parameters for more homogeneous, smaller or intermediate sized tributary basins. Thus the problem is that in large basins the basic modelling unit cannot be the entire basin, but should be separate regions within the basin, which demonstrate distinct and different linear responses to the driving variables. Modelled separately with model estimates then lumped for the entire basin, a greater degree of the variance can be explained (Johnes & Butterfield, 2002).

As mentioned previously, bedrock and soils information are needed to predict the sensitivity of stream water acidification, as shown for a study of streams in Wales (Hornung *et al.*, 1995). Despite reasonable predictions of sensitivity to acidification at a broad regional scale (>10 km^2), a re-evaluation of additional data by Reynolds *et al.* (2001) showed an unexpectedly high degree of spatial heterogeneity in the hydrochemistry of streams derived from supposedly geochemically uniform soils and bedrock. Thus the sensitivity prediction, particularly for high flow extremes, was poor for basin areas less than 10 ha due to fine scale, unmapped variations in bedrock geochemistry and land use. In the UK context, this is important because the simple predictive model has failed at the scale of interest to practical environmental managers such as foresters and farmers.

Agriculture is a major cause of nutrient pollution of groundwater and surface water, which in turn, causes eutrophication (Fig. 1). In addition to nitrate concentrations of US waters being the highest in agricultural areas compared to other land-use types, stream water nitrate concentration of various tributaries in a US basin during high streamflow, which occurred shortly after fertilizer application, was linearly related to the percentage of the drainage area used for agriculture (Fig. 2). Predicting a concentration at a specific time requires information about the timing of source availability, e.g. fertilizer application or flushing of nitrate from soils during snowmelt in

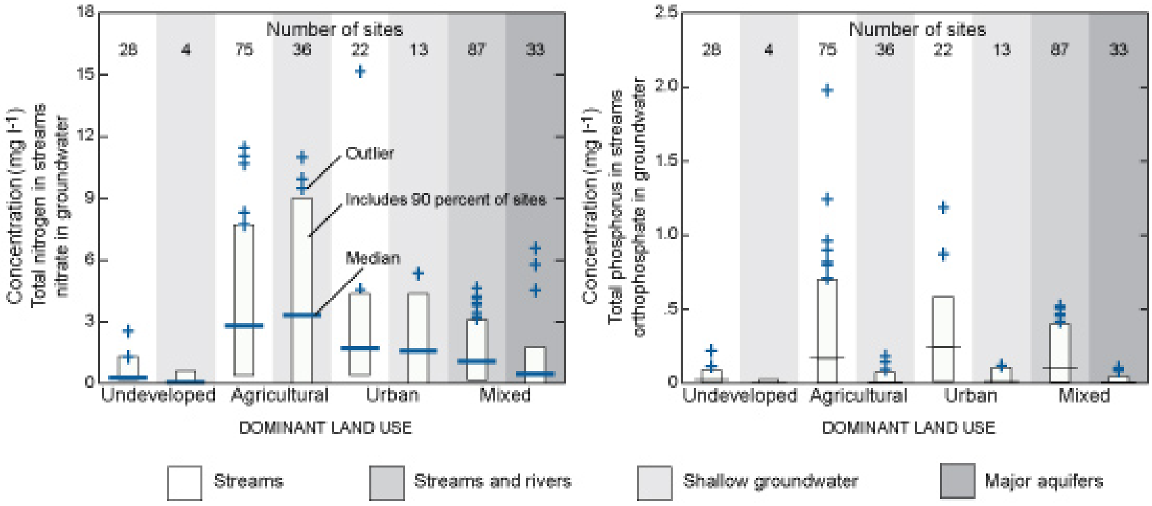

Fig. 1 The relation of total nitrogen in streams and nitrate in groundwater concentrations among streams, shallow groundwater, streams and rivers, groundwater in major aquifers, and dominant land-use categories for basins in the conterminous USA (adapted from USGS, 1999).

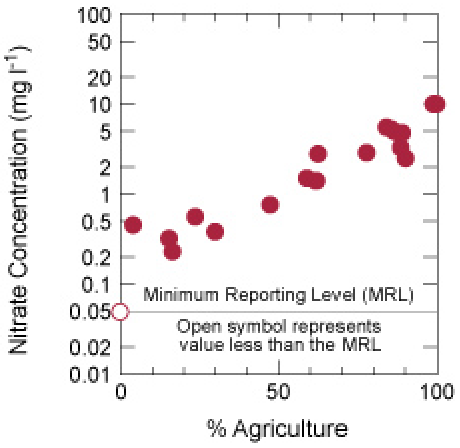

Fig. 2 The relation between stream water nitrate concentration and percentage of agricultural land use in the Willamette Basin, Oregon, during spring high streamflow following fertilizer (adapted from USGS, 1999).

acid sensitive areas, and the relation of the constituent of interest to other factors. For example, phosphorus, a limiting nutrient in most freshwater systems, is typically bound to sediment, which is mobilized during hydrological events (Fig. 3). Even with an association among phosphorus and suspended-sediment concentrations, and land use, additional uncertainty is introduced by a lack of knowledge of when and if the sediment-bound phosphorus subsequently becomes bio-available within the receiving aquatic ecosystem. Waste treatment and disposal plus fertilizer application in urban areas, can also cause relatively high nutrient concentrations in receiving waters (Fig. 1). In a given basin, empirical relations for the predictions of water-quality loads in urban watersheds significantly improve with an estimate of the percentage of the impervious basin area (Tasker & Driver, 1988; Driver & Troutman, 1989).

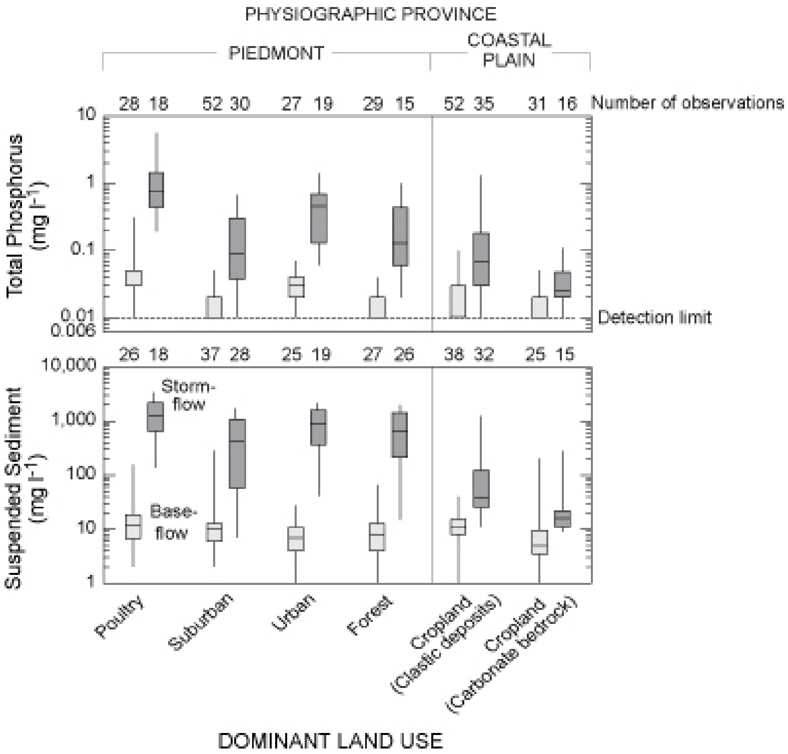

Fig. 3 The relation between total stream water phosphorus and suspended-sediment concentration and dominant land use during storm flow and baseflow in the Apalachicola-Chattahoochee-Flint River, USA (adapted from USGS, 1999).

An example of how uncertainty in prediction can be reduced using selected source and basin characteristics can be seen in the application of a logistic regression model to estimate probabilities of nitrate contamination (>4 mg N L^{-1}) of recently recharged shallow groundwater in the US (Nolan *et al.*, 2002). Although this modelling does not specifically predict concentration, it does address the potential for contamination, albeit above some threshold. The significant predictors in the model were: (1) N fertilizer loading; (2) percentage of cropland-pasture; (3) natural log of human population density; (4) percentage of well-drained soils; (5) depth below land surface to the seasonally high water table; and (6) presence (or absence) of unconsolidated sand and gravel aquifers. Predictors 4–6 relate to the hydrological pathway and time of travel, whereas predictors 1–3 relate to the source of the nitrate. This model, calibrated on 1280 observations, predicted the correct status of nitrate concentration in 75% of the 736 verification observations.

Further subdivision of the agricultural practices may likewise improve future predictions of groundwater nitrate concentrations. McLay *et al.* (2001) assessed groundwater nitrate concentrations at 88 sites in New Zealand. Although the authors documented the dominant land use and the local soils' ability to leach nitrate, there were no discernible trends, and a risk assessment model was only able to explain 50% of the variance in the concentrations, with the permeability of the vadose zone being the most important parameter. McLay *et al.* (2001) observed that non-point source groundwater nitrate contamination reflects intensive agriculture and clear associations were found between concentrations and localized, site-specific factors associated with particular types of agricultural operations such as dairy, drystock, drystock/sheep, market gardens and orchards. The groundwater nitrate concentrations associated with the market gardens typically were the highest and drystock/sheep the lowest.

For another example of the same issue, six empirical and quasi-empirical nitrogen (N) watershed models were evaluated for predicting the riverine export of N from 16 large watersheds (475 to 70 000 km^2) in the northeastern USA (Alexander *et al.*, 2002); all models predicted the export to within 50% of the measured export. One of the models, SPARROW, was calibrated on 374 watersheds ranging in size from 10 to 2.9×10^6 km^2, and provided estimates of the major source contributions to the exported N and the attenuation of N in various parts of the watershed. Furthermore, each model included predictors representing sources, and runoff and basin characteristics, e.g. percentage of land use.

Table 2 Factor and drivers controlling the concentration and flux of constituents in a basin

Constituent Characteristics (properties and processes):

- Inorganic/Organic
  - volatility
  - water solubility
  - high affinity for solids (organic or inorganic)
  - transformation characteristics
- Biological material (type, e.g., parasitic, pathogen, virus, bacterium)
  - transport vector—atmosphere, water, or land
  - life cycle
  - biological characteristics, e.g. # of eggs, feeding habits, light optimum, dissolved oxygen
  - interactions with the environment

Sources, Sinks, and Availability:

- Water type (e.g., groundwater, lake/reservoir, surface water)
- Bedrock and surficial material
- Atmospheric deposition
- Biogeochemical cycling
- Human activities
  - point or non-point (diffuse)
  - temporal variability in application or disposal to the environment
  - spatial variability of application or disposal
- land use (e.g., agriculture, forestry, urbanization)

Transport:

- Climatic drivers (vertical fluxes):
  - precipitation
  - runoff/recharge
  - magnitude and frequency of hydrological events driving stormflow/recharge
  - temperature effects
  - cycles and trends of above (short and long term)
- Hydrological drivers (lateral fluxes):
  - drainage network
  - lakes and reservoirs
  - hydrological characteristics of basin materials (e.g., karst)
  - important hydrological pathways for constituent and related residence times
  - scale effects
- Biological drivers (spatial distribution) – land use:
  - seasonality
  - landscape fragmentation
  - damming

SCHEMA FOR REDUCING WATER-QUALITY ESTIMATE UNCERTAINTY

Because water quality is controlled by: (1) source and availability, (2) transport and transformation, and (3) mixing of spatially and temporally varying components (end-member mixing), a reduction in the prediction uncertainty for an individual constituent can be achieved by systematically assessing a suite of drivers that controls that constituent (Table 2). Each constituent has unique properties that affect cycling. The chemical and physical properties of most natural constituents, and the natural background distribution of sources with respect to atmospheric transport and deposition and geology generally are known. For these constituents, each factor and driver should be evaluated with respect to its relative effect on the constituent that is being predicted. For human-made constituents, for which little is known, we introduce much more uncertainty as their basic characteristics including environmental behaviour must be estimated. However, by systematically reducing the controls on a constituent to a few factors and drivers that dominate, parameters reflecting those factors or drivers can be used to develop models through calibration with data from a surrogate area for estimating the concentration or flux for ungauged basins. It is likely that we will never know with sufficient certainty all the relations between factors and drivers contributing to fine-scale variation in the controls on a particular parameter, i.e. the spatial scale. Our predictions improve at larger scales due to averaging effects (Meybeck, 1994), but the difficulty comes when resource management, and associated policy development, are required at a fine or small scale where uncertainty is large. Although we may adequately predict average conditions (chronic), we may fail to predict biologically important extremes (acute).

Finally, our toolbox has evolved rapidly, particularly in areas of computer technology, remote sensing, smart sensors, and Geographic Information Systems. These tools have improved our ability to predict water quality. Future changes in the toolbox will likely continue to improve our understanding of controls on water quality and the tools needed to predict water quality.

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