

# Chapter 5

## Applications of Stable Isotopes for Regional to National-Scale Water Quality and Environmental Monitoring Programs

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### 5.1 Introduction

Isotope studies conducted over large spatial and/or temporal scales can provide powerful insights into natural ecosystem functions and the effects of anthropogenic disturbances. Large-scale field campaigns require considerable monetary and personnel resources, and it is therefore advantageous to combine isotope studies with existing monitoring programs. This approach leverages existing field sampling resources to provide large sets of isotope samples, and the isotope data can, in turn, provide valuable information for the monitoring programs. Isotope studies can also be useful during the planning stages of large-scale monitoring programs, because high-resolution isotope sampling can provide strong indications of locations that will be critical to monitoring efforts. For example, locations exhibiting unusually high rates of biogeochemical cycling or elevated pollution levels usually have distinctive isotopic compositions that are suggestive or diagnostic of the reactions and pollution sources. Furthermore, combining isotope measurements with other physical and chemical analyses may reveal important inputs or processes that could not be identified with concentration analyses alone.

In this chapter, we will discuss how isotope measurements have been successfully integrated into several regional and national-scale monitoring programs, and provide suggestions for using this approach. We will show how data from these studies have revealed spatial and temporal patterns in the stable isotopes of nutrients, organic matter, and water using isotope contour maps (isoscapes). These broad isotope patterns can be used to indicate sources, track important biogeochemical processes, and assess ecosystem health. This chapter will focus on developing and interpreting watershed and river isoscapes.

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## 5.2 Isotopes and Monitoring Programs

The different components of the world – atmosphere, hydrosphere, and biosphere – are constantly changing in response to both natural and anthropogenic processes. These changes, at the local, regional, national, and global scales, can have significant repercussions on the inhabitants, the environment, and the economy. Hence, there is an increasing need for cross-disciplinary integrated science to provide the information necessary to make regulatory decisions. The main purpose of many monitoring programs is to determine the status of a resource and to detect changes in that resource. One example is the USGS National Stream Quality Accounting Network (NASQAN). The basic premise of this and many river-based water quality monitoring programs is that rivers reflect the landscape through which they flow. More precisely, the chemistry of a water sample collected at one location reflects a complex combination of transport, mixing, biogeochemical processes, and human activities in the watershed upstream of the sampling point. Hence, by measuring the amounts and types of chemicals and sediments at sites in state and national-scale networks, these monitoring programs seek to provide the data needed to characterize the watersheds, to determine sources of these materials, and to assess the effects of various human and natural influences on the observed measurements. The National Atmospheric Deposition Program (NADP) is another example of a status-and-trends network, but focused on precipitation rather than rivers.

Other environmental monitoring programs are implemented for more site-specific reasons, usually related to deteriorations in ecosystem health that can have severe economic consequences. Examples include eutrophication, acidification of stream and lakes, and toxic spills. Accurate identification of sources and a thorough understanding of processes are needed for effective regulation and mitigation.

### 5.2.1 *Tracers of Hot Spots and Hot Moments in Watersheds*

High resolution isotope studies can be very useful for designing large-scale monitoring programs because isotopes can often be used to identify sites of critical importance within a given system. In recent years there has been increased understanding of the role that small spatial areas or short time periods can play in determining conditions throughout the larger system. According to the original definition in McClain et al. (2003), hot spots are patches that show disproportionately high reaction rates relative to the surrounding matrix, and hot moments are short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods. However, these terms are commonly used for places and times where some type of disturbance, often anthropogenic, has resulted in abrupt changes in composition.

Since reaction rates at hot spots may be many times larger than reaction rates in other parts of the system, these locations need to be identified and included in monitoring programs in order to better characterize ecosystem function. However, identifying hot

spots may be difficult, and fixed-site monitoring locations are often chosen without consideration of the possible existence of hot spots. How do we find these critical hot spots? Although remote sensing methods (Chapter 3: Wang et al. 2009). Can identify certain types of hot spots, perhaps the easiest and cheapest approach for looking for hot spots in a river is to conduct a downstream synoptic (transect) sampling of the river, dragging some kind of fast-responding instrument to measure such parameters as temperature, conductivity, nitrate concentration, etc. Given the low cost of such sensors, synoptic cruises can provide critical siting information for subsequent monitoring at a small cost relative to the cost of typical monitoring networks. Illustrations in Vaccaro and Maloy (2006) provide good examples of the usefulness of this kind of approach.

Another approach is to collect discrete samples for more comprehensive characterization of hot spots and hot moments. Isotopes can be more effective at identifying hot spots and hot moments than concentrations alone because isotopic ratios may change even when concentrations don't, thereby allowing identification of hot spots and moments that otherwise would not be apparent. Furthermore, many processes that cause hot spots and hot moments leave distinguishable isotopic signatures, especially in  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ .

There are a wide variety of stable isotopic tools that are useful for studies related to (1) nutrient and organic matter sources, particularly investigations focused on anthropogenic disturbances, (2) biogeochemical processes in aquatic environments, and (3) ecosystem function or health. These isotope tools, and examples of their applications to environmental studies, are listed in Table 5.1.

### 5.2.2 *Sampling Strategies Used by Monitoring Programs*

Most state and national river monitoring programs (e.g., the USGS NASQAN program) have emphasized the importance of sampling at fixed sites, at fixed-time (or discharge-weighted) intervals for estimation of hydrological and solute budgets. Unfortunately, sites and sampling intervals that are appropriate for water and solute budgets may inadequately assess the variability in important biogeochemical and anthropogenic processes and inputs that can occur at distributed positions along a river reach. Studies of ecosystem health (e.g., EMAP, EPA's Environmental Monitoring and Assessment Program), on the other hand, are usually conducted using synoptics, where sample locations are chosen using statistics-based distributions of sites; this sampling design improves the chance of having a sampling site detect any hot spots present. These kinds of synoptics are usually duplicated (but using a different grid of sites) during different seasons or years, to improve assessments of controlling variables.

Another useful approach is to conduct longitudinal transects of chemistry and hydrology along a stream reach. These longitudinal transects may be truly Lagrangian (i.e., following a specific parcel of water downstream), pseudo-Lagrangian (sites are sampled in downstream order but not within a single water parcel), or synoptic (sites are sampled at roughly the same time, within a designated time-scale – which could be a day, week, or season).

**Table 5.1** Description of several useful stable isotope tracers and what information they provide for water quality and environmental monitoring programs

Tracer type	Interpretive value
Water $\delta^{18}\text{O}$ and $\delta^2\text{H}$	Ideal conservative tracer of water sources and mixing; useful for quantifying flow contributions from different tributaries and groundwater; sensitive indicator of evaporation
Nitrate $\delta^{18}\text{O}$ , $\delta^{15}\text{N}$ , and $\Delta^{17}\text{O}$	Quantify nitrate from different sources (fertilizer, wastewater, wetlands, atmospheric deposition, etc.); role in the production of algae and degree of recycling; evidence for denitrification, assimilation, and nitrification
Particulate organic matter (POM) $\delta^{15}\text{N}$ , $\delta^{13}\text{C}$ , and $\delta^{34}\text{S}$	Information on sources of POM; information about the source of the C, N, and S – and the biogeochemical reactions that cycle the elements – even after incorporation into algal biomass; quantify algal vs terrestrial contributions to biomass
Dissolved organic matter (DOM) $\delta^{15}\text{N}$ , $\delta^{13}\text{C}$ , and $\delta^{34}\text{S}$	Information on sources of DOM; information about the source of the C, N, and S – and the biogeochemical reactions that cycle the elements – even after incorporation into biomass; quantify algal vs terrestrial contributions to biomass; evidence for degradation of organic matter
Dissolved inorganic carbon (DIC) $\delta^{13}\text{C}$	Information on sources of DIC, evidence for in situ algal productivity, evidence for degradation of organic matter, degree of gas exchange with atmosphere, nitrification
Dissolved oxygen (DO) gas $\delta^{18}\text{O}$	Information about the ratio of productivity to respiration in the water column, source of the $\text{O}_2$ , degree of gas exchange with atmosphere, biological oxygen demand (BOD) mechanism
Sulfate $\delta^{34}\text{S}$ , $\delta^{18}\text{O}$ , and $\Delta^{17}\text{O}$	Quantify sulfate from different sources (soil, wastewater, wetlands, atmosphere, etc.), source of algae, and extent recycling
Phosphate $\delta^{18}\text{O}$	Quantify phosphate from different sources; information about the extent of algal production, recycling of material within the river reach, and P limitation
Biota (algae, invertebrates, fish) $\delta^{15}\text{N}$ , $\delta^{13}\text{C}$ , $\delta^{34}\text{S}$ , $\delta^2\text{H}$ , and $\delta^{18}\text{O}$	Information on geographic origin of biota; information about the source of the C, N, and S – and the biogeochemical reactions that cycle the elements – even after incorporation into biomass; quantify algal vs terrestrial contributions to biomass; trophic structure; food chain base

One main benefit of doing preliminary synoptics of a river is to locate potential hot spots/moments of human or other disturbances before selecting river sampling sites for routine monitoring. Another benefit of regional synoptics and longitudinal transects is spatial data density (compared to the normal fixed-site networks). Such datasets are obvious candidates for plotting using Google Earth, LiDAR, or other base maps with different colored symbols for different compositions. Such isoscapes are easy to prepare and can be valuable tools for assessing possible linkages between the locations of hot spots and landscape features such as waste lagoons or tile drains (Vaccaro and Maloy 2006). Communicating the results of isotope measurements to local stakeholders can be challenging, and strong graphical presentation techniques

can provide a bridge between scientists, stakeholders, and regulators, conveying isotope results in ways that are accessible to everyone involved. In particular, this kind of detailed information and effective graphic can be extremely useful in getting local stakeholders interested in the inputs and/or processes that are causing the changes in the river near their own homes and farms.

### ***5.2.3 Benefits of Piggybacking Isotopic Sampling on Monitoring Programs***

There are many benefits to the scientist of including isotope studies as part of national and state monitoring programs. One main benefit is the savings in cost. A large percent of the expense of a monitoring program is the manpower required for collecting the water-quality samples. For minimal additional time and manpower at the field site, additional water can be collected at the same time for eventual isotope analyses, and such samples archived pending future funding and interest.

Large monitoring programs are often willing to collect splits of samples for other scientists at the same time they are collecting samples for their own purposes, and then archive the samples until the accumulated set is sent to the isotope laboratory. Examples include the water, nitrate, and POM (particulate organic matter) isotope samples collected at NASQAN sites (Kendall and Coplen 2001; Battaglin et al. 2001; Kendall et al. 2001); and periphyton, mosquitofish, and sediment composites collected at EPA REMAP (Regional EMAP) sites in Florida (Kendall et al. 1997). Sometimes it is possible to retrieve valuable samples that would otherwise be discarded by the programs. For example, the study of temporal and spatial variability in the POM sources at major US rivers (Kendall et al. 2001) originated with our learning that the NASQAN program filtered water samples for pesticide analyses with glass fiber filters, and then discarded the filters. We approached the head of the program and requested that the field workers instead save the filters, archive them frozen until a year's worth of samples were collected, and then ship them to the USGS Menlo Park isotope lab (Kendall et al. 2001).

Some national programs archive several years worth of extra sample material, and will provide splits of samples upon request. For example, splits of NADP rain samples were obtained and analyzed for water isotopes (e.g., Welker 2000) and nitrate isotopes (e.g., Elliott et al. 2007; Kendall et al. 2007), and the data have been presented as isoscapes. EPA's CASTNET (Clean Air Status and Trends Network) program archives dry deposition samples; samples for sites in the NE USA were obtained, analyzed for nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , and isoscapes presented (Elliott et al. *in press*).

Other major benefits of piggybacking on large monitoring programs include the fact that these samples are commonly collected using more rigorous protocols than individual scientists are likely to afford. For example, samples collected at NASQAN sites are depth and width-integrated, whereas almost all river samples collected by other programs and individual scientists are near-shore grab samples. Also, these programs typically analyze the samples for a very comprehensive list of constituents, and rapidly make the data available to the public. Hence, they provide large amounts

of chemical and hydrological data about the same samples and sites as your sample splits that you don't have to pay for. And because your isotope data are on the samples collected by the monitoring program, your data and science add value to the programs and enhance the usefulness of the monitoring programs to society. Funding agencies (e.g., NSF) commonly favor research that piggybacks on major monitoring programs because it leverages scarce resources.

There are several less obvious benefits of the large sets of data made possible by measuring isotope ratios of samples collected by monitoring programs. One is that large-scale patterns may become apparent which otherwise would have been obscured by minor sources of variability in studies at smaller temporal or spatial scales, or with fewer samples. Another benefit is that the number of large-scale isotope studies is still relatively limited, and many research groups focus only on their own sample collection programs. Hence, your results are likely to be considered novel and easily publishable. Also, the large-scale sets of samples made possible by national monitoring programs (e.g., EMAP, NASQAN, NADP) are obvious candidates for use in detecting and assessing environmental changes.

Table 5.2 lists our recommended sampling scheme for piggybacking isotope measurements onto monitoring programs concerned with nutrient-related issues. Each time that chemistry samples are collected, we suggest that you consider collecting and archiving splits of samples for isotopic analysis. These abbreviated instructions are based on the analytical methods used in our lab; other labs may have other requirements. A good set of collection guidelines are posted at: <http://isotopes.usgs.gov/Instructions.htm>.

The list in Table 5.2 includes only a subset of the isotope tools described in Table 5.1. The shorter list was prepared based on our experience with many riverine studies. We find that the first three sample types in the list are especially easy to collect, prepare, and archive – and have always proved useful for nutrient-related studies, especially rivers with low dissolved oxygen problems. POM samples, in particular, provide “good bang for the buck” in that they are very easy and cheap to collect and archive, cheap to analyze for isotopes, and provide semi-quantitative information

**Table 5.2** Suggestions for collection and archiving isotope samples for river nutrient studies

Isotope	Recommendations
Nitrate $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ , $\Delta^{17}\text{O}$	Collect 20–50 mL, filter (0.2 $\mu\text{m}$ ), and freeze. Alternatively, samples can be preserved by adding reagent-grade NaOH or KOH to pH greater than 10–11.
POM $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , $\delta^{34}\text{S}$	Collect 1–2 L of water. Filter through a flat, pre-combusted, 0.7 $\mu\text{m}$ glass fiber filter, and freeze the filters.
Water $\delta^{18}\text{O}$ , $\delta^2\text{H}$	Collect and archive 10–25 mL of water at room temperature. The filtrate from the POM samples can be used for water samples.
DOC $\delta^{13}\text{C}$	Collect, and filter (0.2 $\mu\text{m}$ ) 40 mL into well-cleaned glass bottles containing 50 $\mu\text{L}$ of 85% reagent grade phosphoric acid. Store chilled.
Sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$	Collect, filter (0.7 $\mu\text{m}$ ), and archive 10–100 mL at room temperature. The filtrate from the POM samples can be used for sulfate samples.
DOM $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , $\delta^{34}\text{S}$	Collect 100–1,000 mL, filter (0.2 $\mu\text{m}$ ), and freeze and/or acidify to pH ~ 2. The filtrate from the POM samples can be used for DOM samples.

about the percent of the POM that is algal-derived, sources of nutrients to the water column, and biogeochemical processes – all critical information for nutrient-impacted rivers. Since large amounts of water have to be filtered at monitoring sites for other chemical samples anyway, and if a flat filter is used instead of a cartridge filter, the POM isotopes samples are essentially a “free” byproduct of the filtration process.

### 5.3 Causes of Spatial and Temporal Isotope Patterns in Watersheds

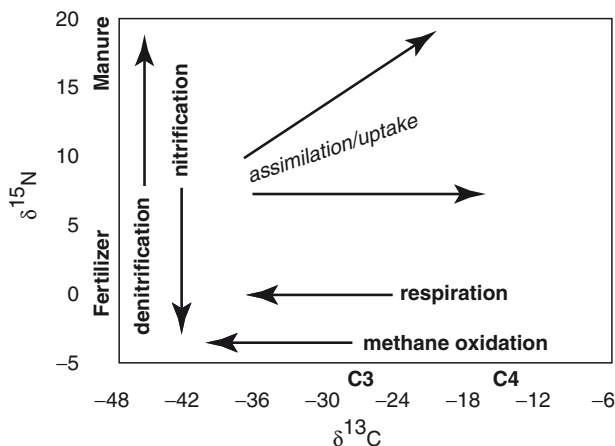
Isotopes are a potentially powerful complement to monitoring and assessment programs aimed at quantifying and mitigating alterations to ecosystems from human activities because different physical and biogeochemical processes in landscapes often create distinctive isotopic signatures. In particular, isotopic techniques have proved useful for tracing sources and sinks of various pollutants in large river basins, wetlands, and airsheds. This section presents an overview of the causes of spatial patterns in  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$  in watersheds, primarily in rivers. For more information about tracing sources of organic matter and nitrate, see Finlay and Kendall (2007) and Kendall et al. (2007), respectively. The fundamental processes controlling the distributions of water isotopes are not summarized here because they are thoroughly covered in several chapters in this book and others (e.g., Kendall and McDonnell 1998).

Figure 5.1 shows how several main biogeochemical processes in the water column affect the  $\delta^{13}\text{C}$  of DIC and the  $\delta^{15}\text{N}$  of nitrate, and subsequently the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of algae growing in the water column. For example, assimilation (uptake) of C and N by growing algae causes progressive increases in the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of the residual dissolved species, and in the newly grown algae. Hence, a large algal bloom in a river is likely to create an isotopic hot spot, observable in both the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of dissolved species and of algae. Since several recent publications have found that a large percent of the seston (POM) in large rivers in the USA is derived from primary productivity in the water column (e.g., Kendall et al. 2001; Kratzer et al. 2004; Volkmar and Dahlgren 2006), an easy way to look for such hot spots is collect and analyze POM samples for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  as proxies for algae.

#### 5.3.1 Longitudinal Spatial Patterns in $\delta^{13}\text{C}$

The relative contributions of organic carbon from terrestrial and aquatic sources vary systematically in rivers, depending on river size (Vannote et al. 1980). Terrestrial sources dominate in small streams because shading by overhanging trees limits algal photosynthesis. As streams widen, algal contributions progressively increase and usually dominate unless turbidity reduces light penetration and hence limits in-stream productivity. Downstream changes in biogeochemical processes can also produce





**Fig. 5.1** Conceptual model showing the main biogeochemical processes that control the  $\delta^{13}\text{C}$  of DIC and the  $\delta^{15}\text{N}$  of nitrate, and consequently the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of aquatic plants and POM in the water column. The arrows indicate the usual effect of an increased amount of the specified process on  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . For example, increased amounts of nitrate formed by nitrification probably cause decreases in  $\delta^{15}\text{N}$  (but usually minimal effect on  $\delta^{13}\text{C}$ ); increased amounts of respiration probably cause decreases in the  $\delta^{13}\text{C}$ . The approximate  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of important C and N sources are also shown (e.g., for C3 and C4 plants and nitrate from fertilizer and manure, respectively)

longitudinal changes in the  $\delta^{13}\text{C}$  of DIC, algae, and biota. Important biogeochemical factors include longitudinal patterns in DIC concentrations; changes in isotope fractionation due to declining DIC and increasing algal growth rates; and higher DIC- $\delta^{13}\text{C}$  due to uptake of DIC, exchange with atmospheric  $\text{CO}_2$ , and degassing.

Longitudinal gradients in DIC- $\delta^{13}\text{C}$  and consequently algal  $\delta^{13}\text{C}$  in streams can also be produced by the physical and anthropogenic factors in the watershed. Examples of important physical factors include changes in water velocity due to successive pools and riffles (Finlay et al. 2002), springs or groundwater upwelling zones (Finlay 2004), variable percentages of water in the stream derived from groundwater vs soil water with watershed scale (Bullen and Kendall 1998), and junctions with other water bodies (e.g., rivers, lakes, impoundments, estuaries) that contribute nutrients and cause algal blooms. Mixing of river and wetlands waters with marine water in estuaries will also produce a strong longitudinal gradient in  $\delta^{13}\text{C}$  because marine DIC typically has a higher  $\delta^{13}\text{C}$  value than DIC in rivers.

### 5.3.2 Anthropogenic and Other Spatial and Temporal Effects on $\delta^{15}\text{N}$

The  $\delta^{15}\text{N}$  of plants reflects the  $\delta^{15}\text{N}$  of available elemental sources in the atmosphere, soil, and aquatic environment as well as a whole host of environmental conditions. There is considerable literature on using the  $\delta^{15}\text{N}$  of algae, terrestrial



plants, and animals as “proxies” for the isotopic compositions of nitrate and/or ammonium (especially related to sewage) – and hence for sources and land uses that are specific to the N source. This use of isotopes to explain spatial distributions of sources and/or biogeochemical processes is sometimes called “isotope biomonitoring”. Some good examples include: Harrington et al. (1998), Koerner et al. (1999), Hebert and Wassenaar (2001), Saurer et al. (2004), Anderson and Cabana (2005, 2006), and Kohzu et al. (2008).

Longitudinal changes in  $\text{NO}_3$  concentrations and  $\delta^{15}\text{N}$ , due to changes in sources or cycling of  $\text{NO}_3$ , often result in similar spatial patterns in algal  $\delta^{15}\text{N}$ . Potential causes of longitudinal gradients or abrupt changes in  $\delta^{15}\text{N}$  of  $\text{NO}_3$  and POM in streams include anthropogenic effects (e.g. fertilizer, animal waste, emissions from power plants), proximity to the ocean (e.g., marine-derived nutrients), redox chemistry (e.g., denitrification, nitrification of ammonium), and uptake of nitrate by algae. In particular, the  $\delta^{15}\text{N}$  of nitrate, algae, POM, and biota can be affected by inputs of water from waste water treatment plants (WWTPs) in urban areas, or confined animal feeding operations (CAFOs) and agricultural runoff in farming areas.

### 5.3.3 *Anthropogenic and Other Spatial Effects on $\delta^{34}\text{S}$*

There is much less known about spatial distributions in the  $\delta^{34}\text{S}$  of riverine sulfate and biota. Three main potential causes of spatial gradients in  $\delta^{34}\text{S}$  in streams and wetlands are proximity to the ocean, bedrock geology, and redox chemistry. Agricultural inputs such as S fumigants and fertilizers (Bates et al. 2002, Hinckley et al. 2008) may also be important in agricultural rivers.  $\delta^{34}\text{S}$  values are an effective tracer of organic matter at the land–ocean margin (Connolly et al. 2003) because  $^{34}\text{S}$ -enriched sulfate can be transported up to hundreds of kilometers inland. For example, the  $\delta^{34}\text{S}$  of marine sulfate and vegetation near the ocean is  $\sim +20\text{‰}$  but decreases to  $+6\text{‰}$  over  $\sim 100$  km (Wadleigh et al. 1996; Wadleigh and Blake 1999). Geology may influence  $\delta^{34}\text{S}$  where rivers cross geologic units with large concentrations of sulfide minerals. Oxidation of the sulfide minerals can decrease the  $\delta^{34}\text{S}$  of riverine sulfate, and presumably aquatic plants, as observed in the McKenzie River system (Hitchon and Krouse 1972). Last, reducing conditions typical of wetlands, bogs, and the deep waters of some lakes lead to low  $\delta^{34}\text{S}$  values because sulfate reduction produces  $\text{H}_2\text{S}$  with low  $\delta^{34}\text{S}$ , which may be assimilated into plants (Nriagu et al. 1991).

## 5.4 Isotopes, Isolation, Isotropy, and Isoscapes

Whether or not a particular set of spatially (or temporally) distributed data can be validly presented as a contoured isotope map (isoscape) involves a number of considerations (see Wunder 2009 this volume). Among the important factors to consider are how isolated the sampling sites are (in time and space), whether the

sites are connected by some mechanism, and the degree of geographic anisotropy. In other words, how isotropic (similar in all directions) are the landscape and data, in terms of sources and processes. Spatial patterns of isotopic compositions in some environments (e.g., lakes and airmasses) are relatively easy to present as contour maps because the media are well connected and “relatively isotropic”. Isotropic, in this context, means that the media mix similarly in all directions. Hence, the data define a myriad of compositional gradients in various directions and the compositions of adjacent samples are generally related by some process and/or by the mixing of sources, supporting the use of gridding and contouring algorithms.

Rivers are characterized by linear connections of water, water-column constituents, and biota because of the unidirectional (downstream) flow of water. Other examples of linearly connected systems include roads, atmospheric rivers, and perhaps migration paths. There are two main kinds of river datasets, each with their own special challenges for preparing valid isoscapes. The first type of dataset is comprised of many isolated sites in hydrologically separate watersheds (e.g., the normal fixed-site networks of most river monitoring programs). Construction of isoscapes using such datasets makes implicit assumptions about the connectivity of these isolated rivers that may not be supported by the data, or supported equivalently for the isotopic compositions of different constituents (e.g., the water  $\delta^{18}\text{O}$  values may be spatially connected but nitrate  $\delta^{15}\text{N}$  values probably aren't). The second type of dataset is comprised of several linearly connected sites along a single river reach (e.g., from samples collected along a downstream transect).

One main complication for modeling riverine data is the heterogeneity of watersheds. The isotopic compositions of nitrate, algae, and other constituents from different isolated rivers – or successive downstream sites along a single river – can be affected by a wide range of sources and processes that occur at unpredictable locations along the river reach (Section 5.3). Examples of sources include groundwater, overland flow, and tributaries; examples of processes within the river include algal uptake, nitrification, and evaporation. However, the main challenge to preparing isoscapes for longitudinal river data is that transport is unidirectional – that the effects of spatially distributed sources to the river and processes within the river only mix downstream. In a strict sense, the validity of gradational (or contoured) presentations of the data depends on whether downstream changes in isotopic composition are due mainly to source-mixing during transport or fractionating processes.

Since the river water only flows downstream, mixing of sources (e.g., the input of water from a tributary or groundwater into the main river channel) can only influence sites downstream of the source locations. Therefore – to give an example relevant to the discussion below – the  $\delta^{15}\text{N}$  value of POM or  $\text{NO}_3$  at one location cannot influence the  $\delta^{15}\text{N}$  values of upstream sites and, hence, should not be used to interpolate the values of intermediate upstream locations. In contrast, if a main control on the POM- $\delta^{15}\text{N}$  values is some process (e.g., uptake of nitrate by algae) that produces a predictable downstream trend in  $\delta^{15}\text{N}$  values (e.g.,  $\delta^{15}\text{N}$  decreases as more algae with low- $\delta^{15}\text{N}$  grows in the river, or  $\delta^{15}\text{N}$  increases because algal uptake is significantly reducing nitrate concentration and thus increasing the  $\delta^{15}\text{N}$

of the residual nitrate), then downstream changes in POM- $\delta^{15}\text{N}$  values would be expected to be gradational. However, in many river studies, the temporal and spatial changes in sources and processes are unknown (and were probably major reason for the study). Hence, contour plots developed using simple interpolation protocols can be an appropriate and useful means for investigating processes and sources, and developing hypotheses.

## 5.5 Developing Isoscapes from Riverine Data

This section focuses on how to prepare isoscapes for riverine data, using examples from several studies generated while piggybacking isotope sampling on routine monitoring programs. As discussed in [Section 5.2](#), water quality monitoring programs are of two general types: fixed-site studies with isolated samples on separate rivers, and longitudinal synoptics with multiple, linearly-connected samples on the same reach of river. The section is intended to (1) illustrate the wide range of useful applications of isotopes for monitoring programs at local to regional to national scales, and (2) provide a basis for discussions of the relative merits of different approaches for preparing isoscapes and evaluating the spatial and temporal variability

### 5.5.1 *Isoscapes of Regional to National-Scale Riverine Studies*

Preparation of regional to national-scale isoscapes of average  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of a large set of generally unconnected rivers, each sampled at a single integrator location (i.e., the normal “fixed-site” protocol of large monitoring programs), presents a number of challenges. These challenges and several empirical approaches for dealing with them are discussed in great detail in Kendall and Coplen (2001), and will be briefly summarized here to illustrate some of the issues to consider when preparing isoscapes of datasets with potential connectivity and heterogeneity problems.

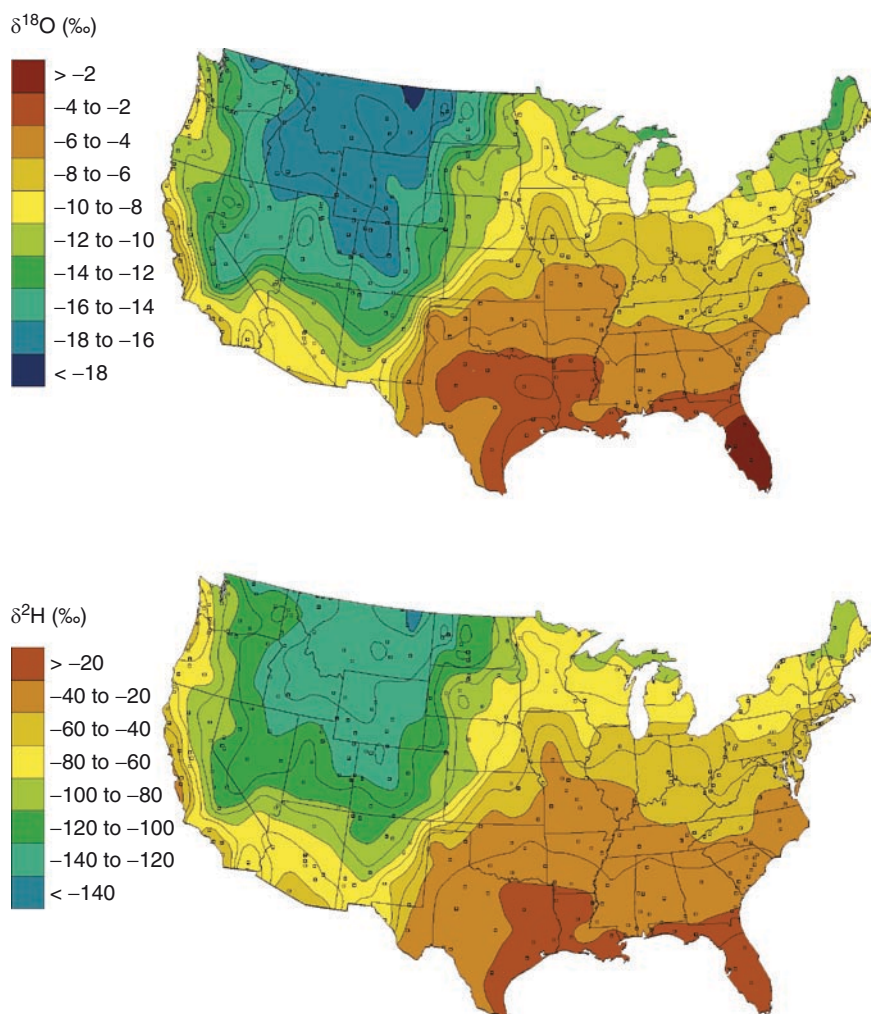
The Kendall and Coplen (2001) study piggybacked on USGS water quality monitoring programs whereby depth and width-integrated samples were collected from 391 selected sites within the NASQAN and Hydrologic Benchmark Network (HBN) programs, and sent to the USGS stable isotope lab in Reston VA for analysis (Coplen and Kendall 2000). Each site was sampled bimonthly to quarterly (depending on site and season – the networks generally use discharge-based sampling protocols) for 2.5 to 3 years intervals during the years 1984–1987, with an average of 12 samples per site (range 2–35 samples). Drainage areas ranged in size from 6 km<sup>2</sup> to almost 3 million km<sup>2</sup> (i.e., the Mississippi River at Arkansas City). Thus, this was a very heterogeneous isotope dataset compared to the precipitation studies discussed by Bowen 2009 (this volume), where all samples are volume-weighted monthly samples.

One major issue that had to be resolved was whether the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of this diverse collection of rivers were sufficiently similar to ambient rain that interpolating  $\delta$  values from unconnected watersheds was valid. These plots were the first detailed map of meteoric (or meteoric-derived) waters in the USA, and the first detailed and rigorous maps of river  $\delta$  values ever attempted. These rivers had unknown contributions from local groundwater, lake water, and irrigation returnflow, and some had dams and other human disturbances. Furthermore, evaporative effects might have caused the isotopic compositions of rivers in arid regions to be less “connected” to each other and to precipitation than in more humid environments. Hence, it was not known whether the river isotope patterns would be spatially coherent.

However, comparison of the river  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values with the sparse precipitation isotope data available at the time – plus evaluation of the correlations of the river  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values with temperature, precipitation amount, latitude, etc. – showed that the river data showed patterns very similar to precipitation (Fig. 5.2), providing support for contouring data from samples in geographically unconnected watersheds (Kendall and Coplen 2001). Other challenges included (1) whether the “instantaneous” river sample data should be discharge-weighted before averaging; (2) should sites with small and non-representative datasets, or ones where the  $\delta$  values were unlikely to resemble those of the original precipitation, be excluded to eliminate artifacts; and (3) what should be the size-cutoff for “too large” drainage areas.

Ultimately, only the simplest and most defensible site selection criterion, drainage area, was used for excluding data for the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  plots because thorough investigation of various possible criteria showed that only exclusion of basins  $>130,000\text{ km}^2$  (27 sites) made any significant difference in the positions of the contour lines. Several conclusions can be drawn from the insensitivity of the contours to the various site selection criteria evaluated: (1) the kriging parameters were chosen appropriately to minimize artifacts caused by anomalous single-site compositions, (2) there were sufficient sampling points to make an adequate assessment of major spatial patterns, and (3) that the spatial patterns were coherent and robust. This study concluded that water isotopes can be successfully contoured between river basins because the river samples mainly derive their isotope patterns from large-scale atmospheric processes.

Other kinds of isotope data (e.g.,  $\text{NO}_3$ , DIC,  $\text{SO}_4$ , POM, DOM isotopes) from regional to national-scale river studies are less likely to show the same kind of continuity (connectivity) between watersheds or basins as water isotopes. Two main factors are responsible for the lower expectations for spatial continuity of such “biogeochemical” isotopes, as opposed to “hydrological” isotopes like O and H: (1) major C, N, and S sources of dissolved inorganic species and organic matter are generally local, with variable relations to sources in adjacent watersheds; and, (2) variation in biogeochemical processes within and between watersheds probably has a stronger effect on isotopic compositions than does geographic proximity. However, while the C, N, and S isotope ratios of riverine materials are generally only minimally connected via the atmosphere, compared to the O and H isotopes of riverine materials, we anticipate that future large-scale river studies will deliver some surprises with regard to the role of anthropogenic



**Fig. 5.2** Spatial distributions of discharge-weighted average water- $\delta^{18}\text{O}$  values for ~400 USGS NASQAN river sites, sampled 1984–1987; almost 5,000 samples were analyzed (Modified from Kendall and Coplen 2001). Fig. 5.2, see Appendix 1, Color Section

processes in controlling large-scale spatial patterns in isotopic compositions in geographically isolated rivers.

Human activities over the last century have had major effects on regional to global scale C budgets (via increased  $\text{CO}_2$  emissions), N budgets (via anthropogenic  $\text{NO}_x$  emissions and fertilizers), and S budgets (via  $\text{SO}_x$  emissions). Many of the coherent spatial isoscapes of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$  values of biological materials in terrestrial and marine environments presented in the various chapters in the book are a consequence of the impact of human activities on biota isotopes.

Hence, it is not too hard to imagine that the connectivity of diverse river sites via the atmosphere or via persistent land-based human activities (agriculture, urbanization) may ultimately supercede the effects of local differences in elemental sources, human activities, hydrology, and aquatic processes in controlling the distributions of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$  of constituents in rivers. Coherent spatial patterns in  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$  in riverine systems are probably more likely for large sets of data collected at the regional to global scale, or for datasets that compare isotope values collected over decades to centuries.

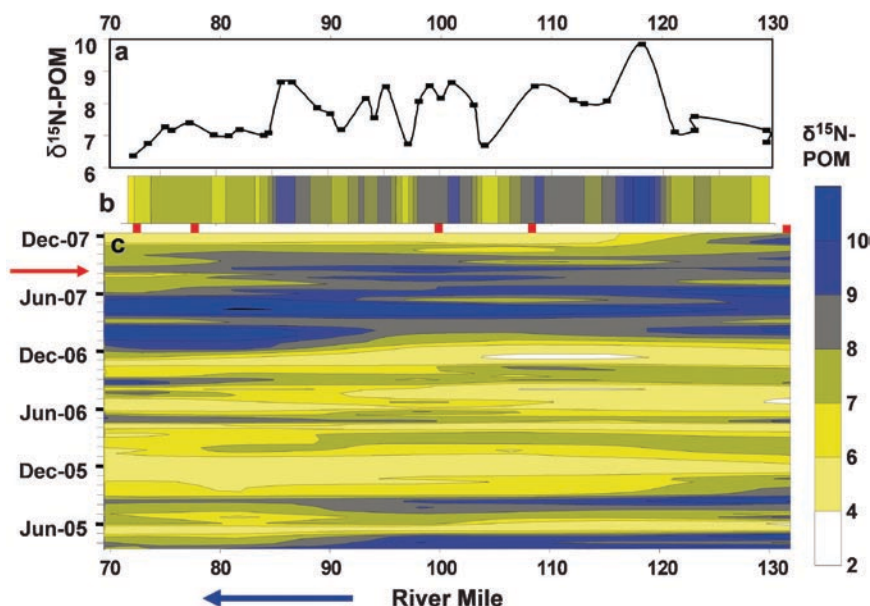
### 5.5.2 *Isoscapes for Longitudinal Riverine Studies*

The rest of this section will be devoted to a discussion of several types of river-delta-estuary isoscapes prepared using data from the San Joaquin River (SJR), its delta, and the northern San Francisco Bay. This study was a direct result of recommendations from a group of local stakeholders that there was a need for more detailed information about sources of nutrients and organic matter in the SJR basin (that might be contributing to low dissolved oxygen levels downstream) than could be accomplished with a few river synoptics or with data from the single USGS NASQAN site on the SJR (at Vernalis). Consequently, the state of California (CA) funded a 3 year fixed-site study that included the collection of land-based grab samples and physical data from six mainstem sites and 15 tributaries draining into the SJR, at weekly to twice-monthly intervals (Stringfellow et al. 2008). With funding from the state, we piggybacked on this river monitoring program and obtained splits of all samples for isotope analyses (Table 5.2). In order to follow the nutrients and organic matter through the entire estuary, we also piggybacked on routine fixed-site water quality programs in the Delta (conducted by the CA DWR, Department of Water Resources) and in the northern San Francisco Bay (conducted by the USGS). For these two programs, our piggybacking was literal – we rode along on the routine cruises and collected boat-based grab samples ourselves at ~30 sites.

#### 5.5.2.1 *Example: San Joaquin River POM Isoscapes*

Unlike most other regional datasets discussed in this book, the spatial data from river synoptic studies are narrow (i.e., they define a very thin geographic band on a map), whereas the temporal data are broad (i.e., twice-weekly to monthly data collected over 2–3 years in the SJR). Bivariate plots of  $\delta$  values vs locations are the obvious way to present the spatial changes in rivers. For example, Fig. 5.3a shows the spatial changes in  $\delta^{15}\text{N}$  of POM at 35 mainstem sites on the SJR, for boat-based samples collected during a 5-day downstream synoptic in August 2007. Samples from all significant tributaries (~30 sites) along this reach of river were also collected and analyzed, but the data were omitted from Fig. 5.3a for the sake of clarity.





**Fig. 5.3** Comparison of three different approaches for plotting  $\delta^{15}\text{N}$  data for riverine POM samples from a 60 mile reach of the San Joaquin River. The lower the river mile number, the further downstream the location. The spatial distributions of  $\delta^{15}\text{N}$  values from a boat synoptic in August 2007 are presented in two manners: (a) as a typical bivariate plot ( $\delta^{15}\text{N}$  vs river mile), and (b) as gradational changes in color within a thin “band” representing the river channel. The spatial and temporal distributions of  $\delta^{15}\text{N}$  values from five fixed-location monitoring sites (locations shown with red bars at the top of Fig. 5.3c) sampled ~75 times March 2005–December 2007 are shown in (c). The date of the August 2007 synoptic is shown with a red arrow to the left of the panel. Fig. 5.3, see Appendix 1, Color Section

There are several other ways to present the data in Fig. 5.3a as gradational changes in  $\delta^{15}\text{N}$ . Figure 5.3b, which shows the spatial relations as a band of color, was easy to prepare. Similar “band” or “ribbon” plots using other isotope data from the same sites and dates (e.g., the corresponding water  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , nitrate  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ , DOC  $\delta^{13}\text{C}$ , and POM  $\delta^{13}\text{C}$  and C:N data) could be stacked vertically, to facilitate comparisons. Both types of plots convey the main points about downstream trends approximately equally well: that  $\delta^{15}\text{N}$  values are initially low, they increase to their maximum values at about river mile (RM) 118, and then oscillate between low and moderately high values downstream until about RM 84, when the values then gradually decrease to values lower than the initial  $\delta^{15}\text{N}$  values.

The spatial trends for this single transect can be compared with the isoscape prepared from data from six “fixed-sites” (only five shown) sampled during 75 transects March 2005 to December 2007 (Fig. 5.3c). This isoscape shows the temporal and spatial distributions of POM- $\delta^{15}\text{N}$  using data for ~400 samples collected weekly to twice-monthly. The POM is predominantly (>75%) algal in origin, with lower percentages during the winter because of larger contributions of terrestrial-derived material from major tributaries draining the Sierra Nevada Mountains, and



higher percentages during the summer due to larger contributions of algae from upstream tributaries and in-stream productivity. The year 2007 was much drier than 2006, and resulted in significantly higher  $\delta^{15}\text{N}$  values.

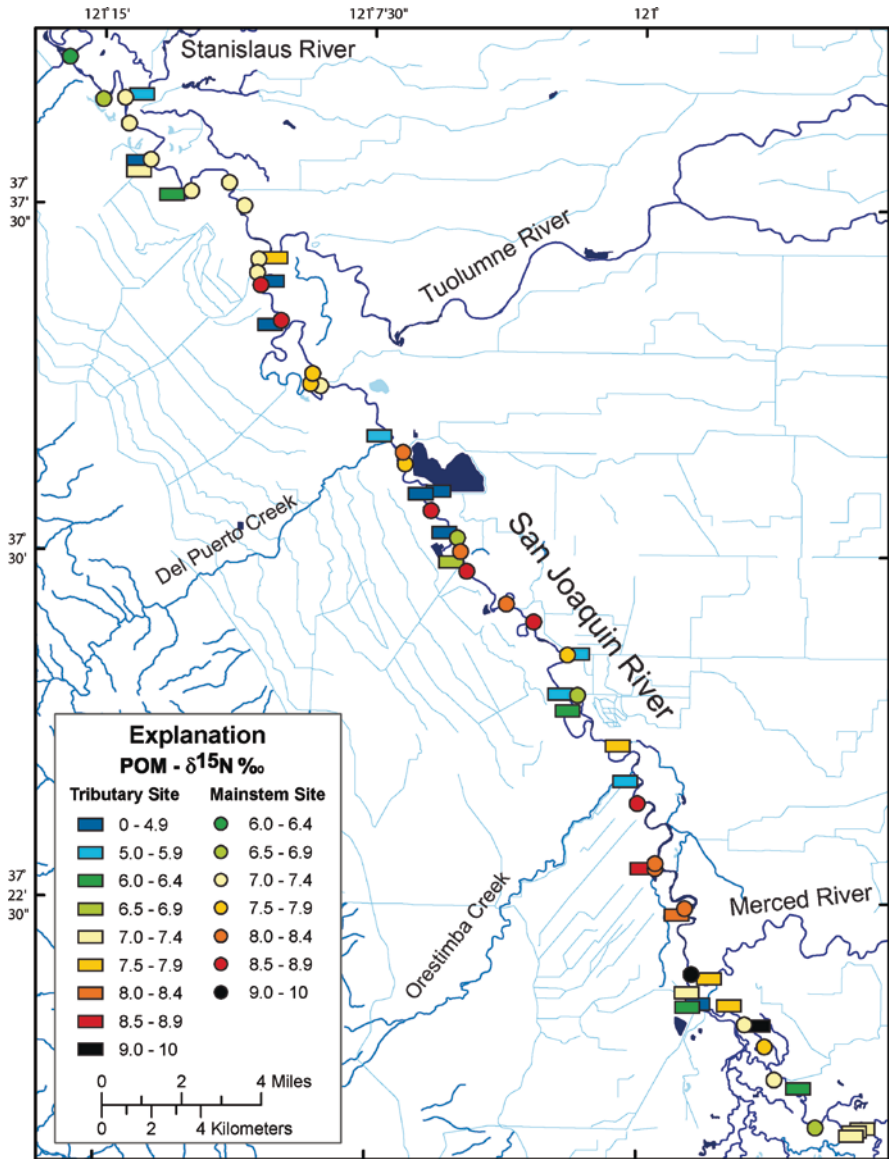
In general, POM- $\delta^{15}\text{N}$  values during July–September 2007 on Fig. 5.3c showed similar ranges of values to those of Fig. 5.3b, with a slight decrease in values starting downstream of ~RM 90. However, the main difference between the perspectives to be gained from the two isoscapes is that Fig. 5.3c suggests a consistency in the  $\delta^{15}\text{N}$  values downstream whereas Fig. 5.3b clearly shows that some mechanism is causing rapid oscillations. In short, based on this single comparison of intensively sampled synoptic vs fixed-site data, sampling at only six sites captured the main spatial trend (decreasing  $\delta^{15}\text{N}$  values after RM 118) but failed to capture the oscillatory nature of POM- $\delta^{15}\text{N}$  values in the river along this reach. Given that >30 tributaries along this reach had measurable flow during August, it is not unreasonable to suppose that POM inputs from the tributaries might be the cause of some of the oscillations.

Plotting the data from Fig. 5.3a on some sort of base map as a series of different colored dots (e.g., Fig. 5.4), or as a thin ribbon with gradational changes in color, is much more effective in illustrating linkages of the isoscape to physical landscape features. For example, if a sudden change in POM- $\delta^{15}\text{N}$  in the river is noted just downstream of a tributary marked on the map, then one can hypothesize that inputs from the tributary helped cause the change. Linking changes at mainstem sites to inputs from the tributaries can be facilitated by also plotting the isotopic compositions of the tributaries on the map. Plotting the data on a LiDAR or Google Earth map might be even more effective.

On Fig. 5.4, POM- $\delta^{15}\text{N}$  values of tributary samples (grab samples collected slightly upstream of their confluences with the SJR) are plotted as colored rectangles using the same color choices as for mainstem sites. Many of the rectangles appear to be located at about the same location as the mainstem site. However, the mainstem samples were always collected just upstream of a significant tributary, so that the mainstem compositions were not unduly affected by unmixed point sources.

Rectangles were chosen for tributary symbols because they were not equant (like the mainstem symbols) and, by placing them on either side of the river, their shapes effectively indicate whether the tributary enters the river on the east or west side. There are distinct differences in sediments and land uses on different sides of the SJR, so knowing the geographic source of the tributary is important for the interpretation of the data.

It is interesting to note that the tributary samples almost always have lower POM- $\delta^{15}\text{N}$  values than mainstem samples immediately upstream. Hence, if POM loads from the tributaries were high enough (which they rarely are, except for the major tributaries: the Merced, Tuolumne, and the Stanislaus, labeled on Fig. 5.4), these inputs could cause sudden decreases in the mainstem POM- $\delta^{15}\text{N}$  values. Careful inspection of Fig. 5.3 shows that mainstem  $\delta^{15}\text{N}$  values drop slightly near the confluences with Tuolumne River (RM 84) and the Stanislaus (RM 75), perhaps because of dilution by low- $\delta^{15}\text{N}$  POM from these rivers. However, the mainstem  $\delta^{15}\text{N}$  values increase sharply near the confluence of the Merced River (RM 118),



**Fig. 5.4** Spatial distribution of POM- $\delta^{15}\text{N}$  values in the San Joaquin River collected during a synoptic in August 2007, plotted as a series of colored dots on a base map; these are the same data shown in Fig. 5.3a and b.  $\delta^{15}\text{N}$  values for samples collected at the mouths of tributaries are plotted as *colored rectangles*. The positions of the rectangles relative to the San Joaquin River show whether the tributaries drain into the river from the E or W side. Fig. 5.4, see Appendix 1, Color Section

and stay high for several miles downstream. Since the POM from the Merced has significantly lower  $\delta^{15}\text{N}$  values than downstream mainstem sites, addition of POM from the Merced cannot explain the high mainstem  $\delta^{15}\text{N}$  values. Based on field observations and lab measurements, the likely cause of the high  $\delta^{15}\text{N}$  values of POM (which, as always during the summer and fall, is almost entirely algal in origin) is an intense algal bloom caused by the input of clear water from the Merced into the high nutrient San Joaquin River (Kendall et al. 2008, unpublished).

Per discussions earlier, if mixing with POM from tributaries is the main cause of downstream changes in the  $\delta^{15}\text{N}$  of POM, then contour plots Fig. 5.3b and c can be misleading because data from below the tributary were used to calculate compositions upstream of the tributary. Isoscapes like Fig. 5.4, that don't make implicit and possibly unwarranted assumptions about the connectivity of the isotopic compositions, are a very effective means for evaluating the causes of spatial changes observed during longitudinal synoptics of rivers, in specific for changes due to inputs from tributaries.

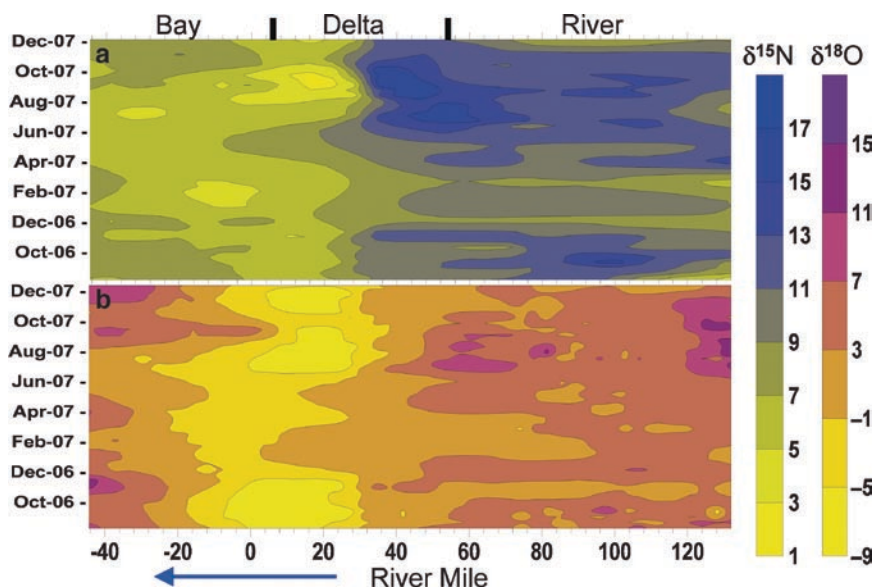
### 5.5.2.2 Example: Nitrate Isoscapes Along the River-Estuary Continuum

Figure 5.5 shows the spatial and temporal distributions of the nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values from ~18 months of samples collected from ~35 sites distributed along the entire 170 miles of the river-estuary system, which extends from the current headwaters of the San Joaquin River in agricultural return waters in the Central Valley, through the delta of the San Joaquin and Sacramento Rivers, and across the northern San Francisco Bay to where the estuary drains into the Pacific Ocean. These transects show large ranges in nitrate  $\delta^{15}\text{N}$  (~16‰) and  $\delta^{18}\text{O}$  (~25‰). A detailed interpretation of these fascinating isoscapes is beyond the scope of this chapter, but a few observations are merited.

The nitrate  $\delta^{15}\text{N}$  values upstream of ~RM 56 show spatial and temporal patterns roughly similar to those of POM- $\delta^{15}\text{N}$  (Fig. 5.3c). One prominent feature is the abrupt decrease in nitrate  $\delta^{15}\text{N}$  at ~RM 30, which is probably a result of tidal and pumping-induced mixing with water from the Sacramento River within the delta. The hot spots of high  $\delta^{15}\text{N}$  values around RM 40 reflect excess nutrients derived from a nearby WWTP, the resulting massive algal blooms, and the consequent isotope fractionations caused by assimilation and nitrification. Downstream of this location,  $\delta^{15}\text{N}$  values eventually increase because of mixing with higher- $\delta^{15}\text{N}$  marine-dominated waters (Kendall et al. 2008, unpublished).

The spatial patterns in nitrate  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  are very different (Fig. 5.5). First, spatial and temporal changes in  $\delta^{15}\text{N}$  appear gradual and smooth, whereas  $\delta^{18}\text{O}$  values appear temporally and spatially erratic, with frequent small oscillations in value. Some of the difference may be a result of two to three time higher analytical uncertainty of  $\delta^{18}\text{O}$  compared to  $\delta^{15}\text{N}$ .  $\delta^{18}\text{O}$  values decrease abruptly at about ~RM 30, at the same place as the  $\delta^{15}\text{N}$  values decrease, and probably for the same reason: mixing.

The lack of correlation of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  patterns suggests that these isotopes are “decoupled”. Wankel et al. (2006) studied spatial changes in nitrate isotopes in the Bay, observed decoupled responses of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values, and explained the decoupling as the effect of N cycling (especially nitrification) in the Bay.



**Fig. 5.5** Spatial and temporal distributions of nitrate  $\delta^{15}\text{N}$  values (a) and nitrate  $\delta^{18}\text{O}$  values (b) from 170 miles of river, extending from the headwaters of the San Joaquin River in agricultural return waters in the Central Valley, through the delta of the San Joaquin and Sacramento Rivers, and across the northern San Francisco Bay to where the estuary drains into the Pacific Ocean. The river miles are measured from where the river converges with the larger Sacramento River (=0). This plot reflects data from ~1,200 samples collected August 2006–December 2007). Fig. 5.5, see Appendix 1, Color Section

Nitrate samples derived from many of the tributaries to the SJR are also labeled with the distinctive isotopic signatures of nitrification, as are many samples collected near the Stockton WWTP (Kendall et al. 2008, unpublished). Therefore, nitrate derived from nitrification of ammonium is a major contributor to nitrate in the SJR, and there appears to be significant amounts of nitrate derived from nitrification in the delta associated with Sacramento River water.

Space limitations preclude further discussion of the use of isotopes as indicators of ecosystem processes, functions, and health in aquatic environments. This topic is discussed in several recent books focused on ecological applications of isotopes: Fry (2006), Michener and Lajtha (2007), Hobson and Wassenaar (2008), and Nagata and Miyajima (2008; in Japanese, with some figures labeled in English).

## 5.6 Conclusions

The incorporation of stable isotope techniques into regional and national water quality and environmental monitoring programs provides many benefits to both the programs and the investigators. Isotopes are a potentially powerful complement to monitoring and assessment programs aimed at quantifying and mitigating alterations

to ecosystems from human activities for many reasons. Locations exhibiting unusually high rates of biogeochemical cycling or elevated pollution levels usually have distinctive isotopic compositions that are suggestive or diagnostic of the reactions and pollution sources. Isotopes can be more effective at identifying hot spots and hot moments than concentrations alone because isotopic ratios may change even when concentrations don't. Hence, isotopes facilitate the identification of hot spots and moments that otherwise would not be apparent, thereby providing a valuable addition to standard chemical and hydrological mass balance methods.

Watersheds are characterized by spatial gradients, patchiness at all scales (Vannote et al. 1980), and temporal variability. In many studies at large scales, isotope hydrologists and biogeochemists have found that stable isotope data – collected at the appropriate temporal and spatial scale – usefully integrate the natural patterns of this organized world. With the increasing automation of isotope techniques, it is becoming ever easier to acquire the large sets of isotope data that make it easy to see the environmental patterns beyond the noise. Isoscapes provide a useful means for illustrating the nature of the temporal and spatial variations in isotopic composition at the landscape scale, and for generating hypotheses about causes of the patterns. Hence, isoscapes are effective tools for identifying large-scale environmental patterns and changes which may be critical to understanding ecosystem function and regulating existing or future anthropogenic impacts. They can also provide invaluable information about the sources of various contaminants impacting human use of water supplies in the basin.

Isotope techniques are especially valuable for tracing sources of nitrate and organic matter in rivers, as illustrated by several examples of how isotope measurements have been successfully integrated into regional and national-scale monitoring programs. To the investigator, perhaps the main advantage of piggybacking onto large-scale monitoring programs to obtain splits of samples is that the large sets of samples made possible by national monitoring programs are obvious candidates for use in detecting and assessing environmental changes. Other benefits include leveraging of resources by the savings in collection costs, that samples are commonly collected using more rigorous protocols than individual scientists are likely to afford, and that the program provides a comprehensive set of environmental data associated with the samples at no additional cost. This chapter provides suggestions of which isotope tools are especially useful for nutrient-related studies, guidelines on how to collect and archive samples for isotopic analysis, examples of their applications to environmental studies, and a discussion of how to prepare isoscapes using data from river synoptics and networks.

The development of isoscapes for different kinds of riverine isotope data poses several challenges, among which are the linear and unidirectional flow of water, the heterogeneity of sources and processes within rivers and watersheds, and the lack of geographic connectivity of isolated sampling sites in large regional studies. River datasets can be complicated because river-related data have explicit spatial and temporal relations. Even in cases where the spatial relations among river sampling points might remain constant (as in fixed-site monitoring programs), the temporal relations do not (e.g., temporal changes in flow and nutrient levels from different

point sources). There is a need for guidelines for how to incorporate spatial and temporal isotope data for river studies (for different isotopes, site types, and tributaries) into a GIS context, so that the combined dataset can be used for spatial/temporal modeling of water and constituent budgets, and the development and testing of remediation strategies.

Large-scale regional and national monitoring programs present an excellent opportunity for the development of new isotope studies aimed at examining broad patterns that are usually obscured by spatial and/or temporal variability in smaller-scale studies. Although this chapter focused on the integration of isotope techniques into large-scale river and watershed studies, there are many other opportunities for isotope researchers and isoscapes to bring new insights into other types of large-scale monitoring programs, including those focused on atmospheric deposition (e.g., NADP) and ecosystem health (e.g., EMAP). As more studies demonstrate the value of isotopes in large-scale monitoring programs, we hope to see these analyses eventually incorporated into routine monitoring plans.

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