

Review

Forensic Assessment of Metal Contaminated Rivers in the 21st Century Using Geochemical and Isotopic Tracers

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Abstract: Documentation of contaminant source and dispersal pathways in riverine environments is essential to mitigate the potentially harmful effects of contaminants on human and ecosystem health, and is required from a legal perspective (particularly where the polluter pays principle is in effect) in assessing site liability. Where multiple natural and/or anthropogenic sources exist, identification of contaminant provenance has proven problematic, and estimated contributions from a specific source are often the subject of judicial debate. The past, current, and future use of geochemical and isotopic tracers in environmental forensic investigations of contaminant provenance, transport, and fate are analyzed herein for sediment-associated trace metals in riverine environments, particularly trace metals derived from mining and refining operations. The utilized methods have evolved significantly over the past four decades. Of primary significance has been the growing integration of geomorphic and stratigraphic techniques with the use of an increasing number of geochemical tracers including stable isotopes. The isotopes of Pb have been particularly well studied, and have been applied to a wide range of environmental media. Advances in analytical chemistry since the early 1990s have allowed for the precise characterization of other non-traditional stable isotopic systems within geological materials. The potential for using these non-traditional isotopes as tracers in river systems has yet to be adequately explored, but a number of these isotopes (e.g., Cd, Cu, Cr, Hg, Sb, and Zn) show considerable promise. Moreover, some of these isotopes (e.g., those of Cu, Cr, and Hg) may provide important insights into biogeochemical cycling processes within aquatic environments. This review suggests that future environmental forensic investigations will be characterized by an interdisciplinary approach that combines the use of multiple geochemical tracers with detailed stratigraphic, geomorphic, and hydrologic data, thereby yielding results that are likely to withstand the scrutiny of judicial review.

Keywords: environmental forensics; geochemical fingerprinting; isotopic tracers; non-traditional isotopes

1. Introduction

Environmental forensics has its roots in forensic geology, a field that can be defined as the use of rocks, sediments, soils, and other geological materials in legal investigations that are likely to end up in the court of law. Forensic geology first gained notoriety in the writings of Sir Arthur Conan Doyle between 1887 and 1893 when the fictional character Sherlock Holmes effectively analyzed geological substances to help solve complex criminal cases [1]. Most of the general principles involved in the present-day application of forensic geology were laid out, however, in the early 1900s when scientists began to use geological and geochemical principles in the investigation of serious crimes. One of the early pioneers in the field was Georg Popp, a German chemist. In 1908, Popp examined three layers of soil adhering to the shoe of a suspect in the Margarethe Filbert homicide [1,2]. Popp found that the composition of the soils did not match those within the agricultural fields where the suspect said he had been. However, one of the layers on the shoe contained red sandstone fragments and other particles which were associated with soils from where the body had been found, and a second layer (containing brick, coal dust, cement and other materials) were comparable to soils from outside a castle where the suspect's gun and clothing had been discovered. Thus, Popp was able to provide evidence that supported the theorized sequence of events associated with the crime [2].

Since the early work of Popp, forensic geology has given rise to a range of forensic geosciences, including environmental forensics, in which a wide range of scientific data from such fields as mineralogy, geochemistry, sedimentology, stratigraphy, geomorphology, soil science, hydrology, and geophysics are brought together to address an environmental issue associated with civil and criminal legal investigations. In essence, multiple forms of geoscientific data must be integrated such that the resulting conclusions can withstand the scrutiny associated with the judicial process. The majority of these cases pertain to the contamination of air, water, sediments, or soils by anthropogenic activities. Perhaps one of the most frequently addressed problems in environmental forensics within riverine environments is to define the source(s) and relative contributions of contaminants to a river from human activities in general, and mining, milling, and refining operations in particular. From a legal perspective, source identification is a critical component of many, if not most, site remediation programs where the polluter pays principle is in effect and the primary responsible parties must be accurately identified. It is not uncommon for millions to tens of millions of dollars to be at stake in terms of remedial costs [3,4]. From a practical perspective, identifying contaminant source(s) is essential to site mitigation, as well as human and environmental health, because remediation strategies are likely to fail if the source(s) of contaminant influx are not identified and addressed.

Although a variety of contaminants can be released from mining and milling operations to river systems, it is fair to say that toxic trace metals and metalloids (e.g., As, Cu, Cd, Hg, Pb, Sb, and Zn) are the most common [5]. Trace metals possess a high affinity for particulate matter in aquatic environments with typically observed (unaltered) pH and Eh conditions, and numerous studies have

shown that trace metals released from a point source of contamination predominantly are dispersed as elements bound to (or sorbed to) riverine sediments [6,7]. Acknowledgement of the importance of sediments as the predominant transporting media, and as a significant trace metal sink along the drainage system, has led investigators to focus in recent years on riverine sediments for the identification of contaminant sources as well as the elucidation of the rates and processes of contaminant transport [4,8].

Within riverine environments, significant portions (10% to more than 60%) of the contaminated sediments released from a point source are deposited and stored along the river valley in channel bed, floodplain, or terrace deposits where they may pose a threat to human or ecosystem health. Environmental forensics is increasingly relying on the use of geochemical fingerprinting and tracing methods to identify the sources of contaminants to these deposits, and to assess the dispersal pathways of sediment-bound contaminants in riverine environments. Following the definitions put forth by Foster and Lees [9] and Hoefs [10], a *fingerprint* is defined here for sediments in river systems as a unique set of physical or chemical properties of the source material that can be used to distinguish it from other sediments within the basin and whose traits are preserved following transport such that its main characteristics are still recognizable. In Popp's case, the red sandstone fragments served as an effective fingerprint for one of the soil layers found on the suspect's shoe. More recent forensic investigations have utilized a wide range of properties for fingerprinting purposes, including sediment color [11,12], grain size [13–17], particle mineralogy [18–20], mineral magnetism [21,22], surface morphology and composition [23–26], and chemical composition as defined by bulk elemental concentrations, concentration ratios, chemical species, and isotopes [15,27–29].

The term *tracer* is often used synonymously with *fingerprint*. A tracer, however, is more strictly defined in this review as a parameter which not only exhibits the characteristics of a fingerprint in that it allows a geological material to be distinguished from other materials in the basin, but can be used to track the movement and cycling of the material through the drainage system. Tracers have been used for several different purposes in riverine environments, including: (1) the identification of contaminant provenance for sediment sampled at a given location; (2) an analysis of the contaminant transport pathways and rates; and (3) an assessment of the biogeochemical cycling of a substance within the aquatic environment. As used for the first two purposes, tracers are often most effective when they exhibit conservative behavior in which its identifiable characteristics are maintained as the sediment is cycled through the riverine environment. In the latter instance, alterations in the nature of the tracer is utilized to assess a specific biogeochemical cycling process, such as microbial or photoreduction. Thus, the nature of the alterations must be well understood.

The use of fingerprints/tracers for contaminant source and transport assessment is complicated by the fact that the origin of the geological materials that we are assessing may have been altered from that found at the source. These alterations involve two primary processes. The first refers to a set of processes through which certain particles are separated from the total (bulk) material found at the source on the basis of particle size, shape, density, *etc.*; thus, the sample under investigation represents only part, or a fraction, of the original material. Fine-grained clay minerals, for instance, may be separated from the original source materials by hydraulic sorting processes during transport, and subsequently deposited in areas devoid of coarse-particles [4]. Isotopic fractionation may also

occur during which physical or chemical processes alter the relative abundance of the source material's isotopes.

The second complicating process is mixing in which sediment weathered and eroded from all of the bedrock and alluvial type areas are co-mingled with contaminated sediment from the source(s) during transport and deposition. The sediments, then, not only reflect the lithology, mineralogy, and geochemistry from the various bedrock types that underlie the basin, but contaminants from all of the sources from which they were introduced to the channel along its course. Contaminant dilution, either through the spreading of the contaminated particles over a larger area, or their amalgamation with "clean" sediments, often accompanies the mixing process. In either case, dilution can prove to be a significant problem in some river systems (see, Miller and Orbock Miller [4] for a more detailed discussion).

Tracers have been utilized to identify both point- and non-point sources of pollution in catchments. Non-point source tracers tend to encompass a wide range of properties (e.g., grain size or mineral magnetics) as the intent is often to identify the source of sediment from a particular soil or land-use type. The tracing of point-source contaminants has historically relied on geochemical parameters, including one or more of the contaminants that is of concern [15,27–35]. The use of the contaminant as a tracer allows for the direct assessment of contaminant provenance along the river, its dispersal rates, and the relative contributions from the identified sources. In many instances, however, trace metals found within the alluvial sediments are derived from multiple natural and anthropogenic sources, and the variations in metal concentrations or chemical forms between the sources may be limited. As a result, trace metal concentration data may prove to be ineffective as a tracer, particularly when the elemental concentrations are near background values. To address the problem, investigators have combined the analysis of multiple elements with multivariate statistical methods (e.g., principle component analysis, cluster analysis, or discriminate analysis) to fingerprint the source [36], an approach widely utilized to determine sediment and nutrient provenance from non-point sources of pollution [37–41]. A significant shortcoming of the approach is that it requires a large number of samples, and its effectiveness depends on the variability inherent within the source materials. Where the variability is larger within a given source than between sources, definitively fingerprinting the contaminant may be difficult even when highly sophisticated statistical analyses are utilized [36].

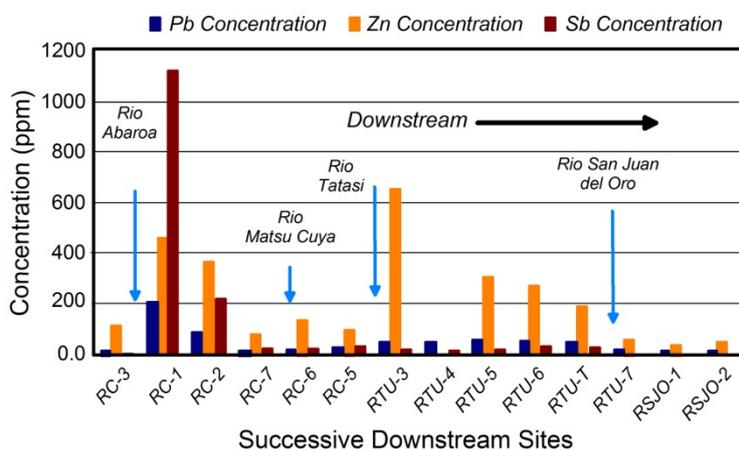
An alternative approach is to utilize stable isotopic data, rather than bulk elemental concentrations or concentration ratios. The potential use of stable isotopes as a tracer has been recognized since at least the 1960s and is based on the ability to characterize a material on subtle differences in the isotopic abundances of a given element [30]. The isotopes of Pb (specifically ^{208}Pb , ^{207}Pb , ^{206}Pb , and ^{204}Pb) have been particularly well studied and applied as a fingerprinting tool [29,42,43]. In fact, it has been argued that Pb isotopic fingerprinting is one of the most popular methods available for determining Pb sources throughout the world [44]. Nonetheless, in an excellent review, Bird [29] notes that Pb isotopes have only recently been applied to identify contaminant sources within river systems and "[i]n comparison to atmospheric and marine environments, the use of Pb isotopes remains relatively under-studied". In addition to Pb, significant advancements since 1990 in analytical instrumentation, particularly the multi-collector, inductively coupled plasma mass spectrometer (MC-ICP-MS) has dramatically increased the potential for using a wide range of non-traditional stable isotopes (e.g., Cd, Cu, Hg, Li, B, Mo, Sb, Zn) as environmental tracers.

The primary objectives of the remaining discussion are to: (1) provide an overview of the methods through which geochemical tracers have been used to unravel the sources, transport mechanics, and relative source contributions of the trace metal contaminants found within alluvial sediments along a river system; and (2) examine the potential use of stable isotopes, including a number of non-traditional isotopes, as an innovative method of directly documenting trace metal provenance and cycling in riverine sedimentary environments. Particular attention will be given to the use of Pb isotopes in environmental forensic investigations. We will then turn our attention to the innovative use of other, non-traditional stable isotopes that may provide a wealth of information on contaminant sources and transport pathways, but have yet to be extensively applied to riverine environments.

2. Identifying Contaminant Sources Using Spatial Patterns in Geochemical Tracers

Historically, geochemical tracing methods have: (1) utilized a contaminant of interest as a tracer; and (2) documented contaminant provenance by examining the spatial variations that occur within the contaminant/tracer along the river system. In general, the method involves documentation of an element's concentration within the source materials and its comparison to concentrations observed at multiple locations along the channel, including areas presumed to be "clean". In the case of a single point source, a distinctive downstream pattern is often observed in which low concentrations upstream of the source abruptly increase to above background values where the contaminated source materials are introduced to the channel. Concentrations then decline semi-systematically downstream from the source (Figure 1). The sampled media may include water, suspended sediment, or sediments from the channel bed or its floodplain. When the focus is on sources that have provided a long-term, semi-continuous supply of contaminants to the river, channel bed sediments are often the media of choice as they tend to show less temporal variations in concentration through time than is found within the water or suspended sediment [4].

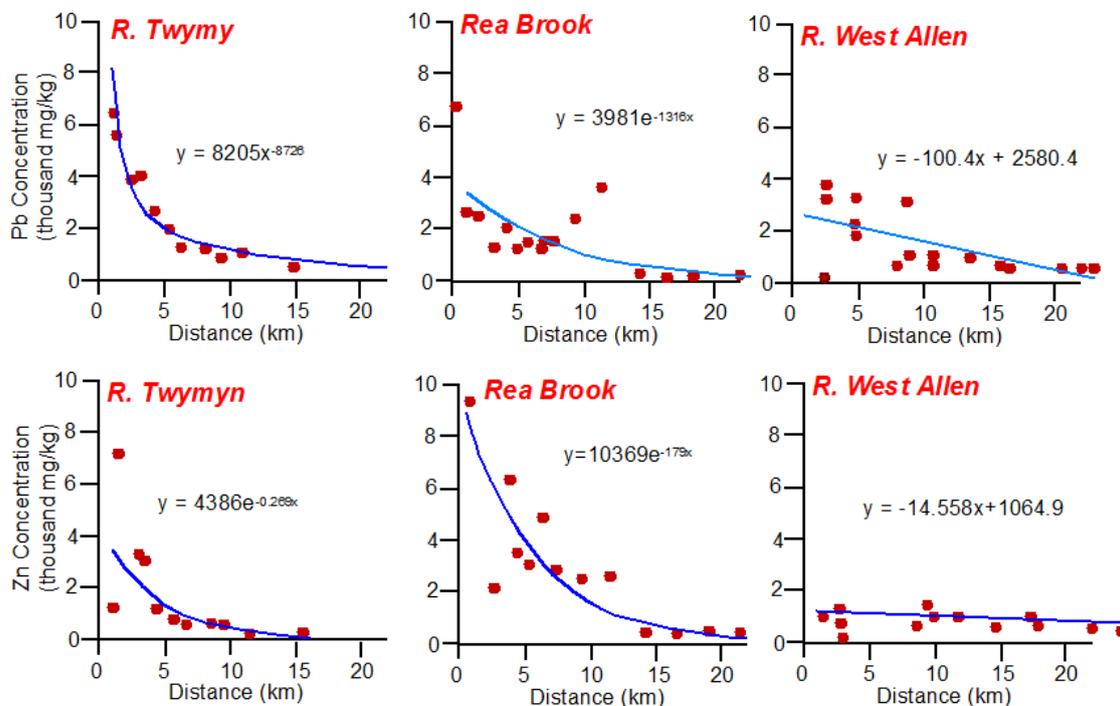
Figure 1. Pb, Zn, and Sb concentrations measured in channel bed sediments of the Rio Chilco-Rio Tupiza drainage system of southern Bolivia. Sb mines are located within the Rio Abaró and Rio Matsu Cuya tributary basins. Polymetallic tin deposits containing limited Sb are located within Rio Tatasi. Point sources of contamination are indicated by abrupt increases in element concentration followed by downstream declines [45].



An example is provided by the Rio Chilco-Rio Tupiza drainage system of southern Bolivia. In this case, Pb, Zn, and Sb concentrations were used as geochemical tracers of mine contamination. Figure 1 shows that sediment from the Rio Abaróa, contaminated by an Sb mine, produced a geochemical trend extending from sampling site RC-3 to RC-5 that is expected from a single point source of contamination. Concentrations abruptly increase at the tributary mouth and then decline downstream. Villarroel *et al.* [45] showed that the downstream declines could be attributed to a combination of hydraulic sorting of sulfide minerals from the mines, dilution, and sediment storage associated with channel bed aggradation. The downstream declines in concentration are abruptly altered at RTU-3 where Zn, and to a much lesser degree, Pb concentrations increase downstream of the Rio Tatasi. Since Sb concentrations did not increase downstream of the Rio Tatasi, the majority of the Pb and Zn at RTU-3 is unlikely to have been derived from the Sb mines. Concentrations of all three trace metals decrease downstream of the mouth of the Rio San Juan del Ore as a result of dilution by the influx of relatively “clean” sediment.

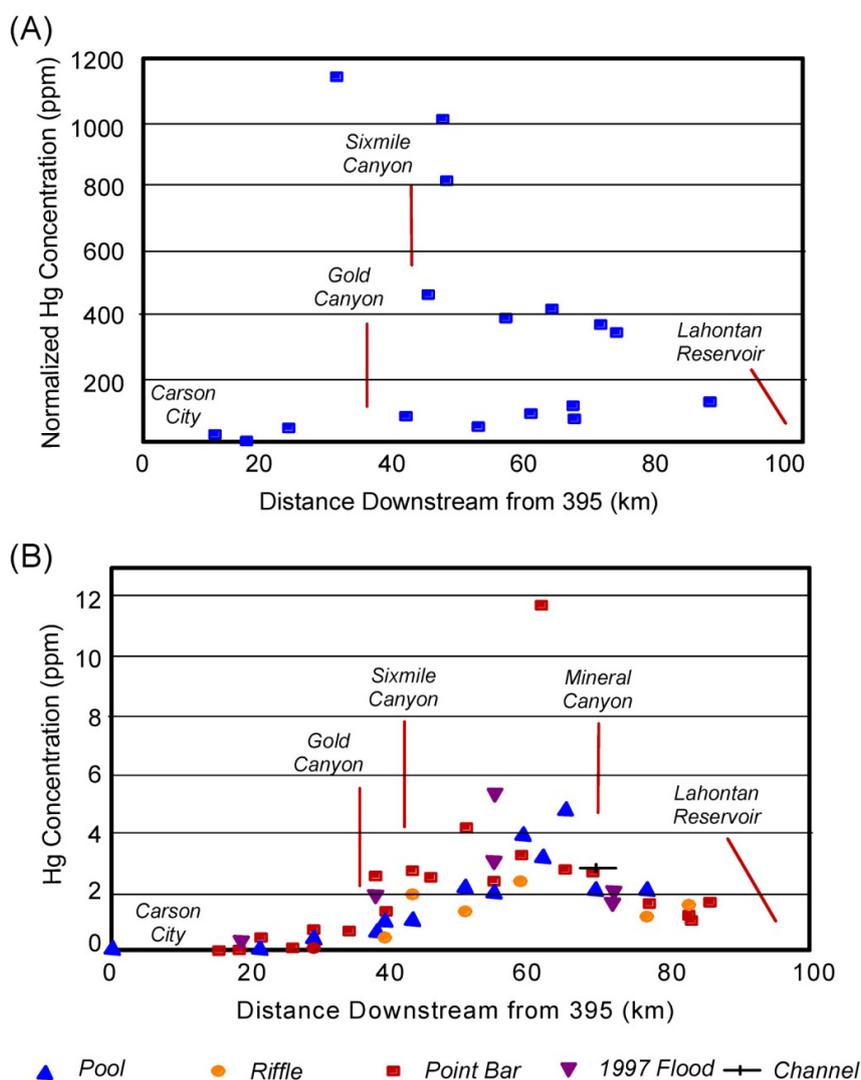
The observed downstream declines in contaminant/tracer concentrations from a point source are generally attributed to a combination of five processes, including: (1) the hydraulic sorting of sediment-borne contaminants on the basis of particle size or density which results in the deposition of larger or denser particles (e.g., sulfide minerals or mercury amalgam grains) close to the source; (2) dilution as sediment-borne contaminants are spread out over a larger area, and/or mixed with “clean” sediment from bank erosion or tributaries; (3) sediment deposition and storage within the channel or floodplain, a process that removes the contaminants from active transport and surface deposits; (4) geochemical processes involving sediment-water interactions, such as sulfide oxidation/reduction, precipitation, and or sorption on to reactive particles; and (5) contaminant uptake by biota, a process that is typically negligible along most rivers. Wolfenden and Lewin [46] illustrated that regression analyses could be used to statistically quantify the downstream changes in tracer concentrations produced by the above dispersal mechanisms. More specifically, the regression models provide a means of describing the concentrations of a contaminant/tracer from a single point source at any location along a river (*i.e.*, between sampling sites), while departures from the trend may indicate the influx of a contaminant from an additional source. Since their seminal work other investigators have applied linear, logarithmic, polynomial, power, and other statistical models to rivers located in wide range of hydrologic and climatic environments (Figure 2) [47–49]. The application of these models has shown that interactions between the various dispersal processes can produce different trends for different trace metals along the same river, even when they originate from the same source, presumably because of differences in transport behaviors. In the case of the Rio Chilco (described above), the downstream declines in Sb differ from those of Pb indicating that the trends are metal specific. Thus, when trace metal concentrations correlate with one another along the channel, it is generally assumed that they are derived from a similar source and are transported by similar mechanisms and rates with the channel.

Figure 2. Downstream trends in Pb and Zn concentrations along the River Twymy, Rea Brook and West Allen in the UK. Solid lines represent the best-fit regression models, and show that concentrations tend to semi-systematically decrease downstream of a point source (figure modified from Lewin and Macklin [48] as shown in Miller and Orbock Miller [4]).



Not all rivers that have historically been subjected to point sources of contamination will exhibit the classic downstream declines in the concentrations of the utilized fingerprints. Perhaps the most common reason that the pattern is absent is that the river can be converted from a system dominated by point sources of elemental influx to one characterized by a line source associated with the erosion of materials from the channel banks. For example, Hg contaminated mill tailings were introduced to the Carson River of west-central Nevada primarily between 1859 and 1890 at several distinct locations. During the late 1800s, sediment enriched in Hg-Ag and Hg-Au amalgam grains were deposited along the valley floor downstream of mill processing facilities. Although there is significant variation in the data, Hg concentrations within the alluvial valley fill that were normalized according to the percent silt and clay within the sample generally declined downstream from the mills (Figure 3a). However, Hg concentrations within the modern channel bed deposits quasi-systematically increase from the original sites of mill tailings influx downstream for approximately 25–30 km before subsequently declining (Figure 3b). Miller *et al.* [50] argued that the observed downstream pattern in Hg concentrations resulted from the progressive erosion of dense Hg-Au and Hg-Ag amalgam grains stored within the valley fill, and their incorporation into the channel bed materials. Subsequent declines downstream were presumably related to dilution caused by the influx of clean sediment from a tributary, and the erosion of uncontaminated, pre-mining deposits from the channel banks which were more extensively exposed downstream. The point, here, is that the absence of the expected downstream trend in concentrations from a suspected point source does not necessarily rule out its potential as a contaminant source.

Figure 3. (A) Downstream variations in Hg concentration normalized for silt and clay percent measured within the alluvial valley fill of the Carson River valley, western Nevada. Increased Hg concentrations occur in response to the influx of Hg from amalgamation processing mills. Variations result from distance from mills of sampling sites, age of stratigraphic units relative to Ag/Au production and Hg influx, hydrologic conditions at time of deposition and other factors; (B) Downstream variations in Hg concentration within channel bed sediments. Concentrations within the modern channel sediments gradually increase as contaminated materials are eroded from the channel banks. The decline in concentration results from the influx of “clean” sediments from tributaries and from the erosion of uncontaminated bank materials (modified from Miller *et al.* [50]).



A number of factors can complicate the use of spatial patterns in geochemical tracers to identify a contaminant source. The most significant include the following:

(1) *Sedimentological Differences in the Sampled Sediments.* Trace metal contaminants are predominantly associated with chemically reactive sediments that are characterized by small particle sizes with high surface areas, a high electrical charge on the particle surface, and high cation exchange capacities [7]. These sediments often consist of clay minerals, Fe and Mn hydroxides and oxides, and organic matter. Sediment composed of quartz, feldspars and carbonates, which tend to be sand sized

(>63 μm) or larger, typically act to dilute the concentrations of contaminants bound to the particles. The net result is that contaminant concentrations can vary as a function of the grain size distribution and composition of the sediments, where samples consisting of larger quantities of sand-sized materials will exhibit lower concentrations. Downstream patterns in concentration, then, may be influenced by changes in the size distribution of the sediments that occurs along the channel or within a particularly sampling location, and mask variations associated with points of contaminant influx.

To compensate for this grain-size effect, it is common to separate the coarse and fine-sediment fractions within the sample, and to analyze only the chemically reactive, fine-grained material, thereby removing the effects of dilution. Alternatively, the bulk sample may be analyzed for the contaminant/tracer and the concentrations normalized according to the amount of fine-grained sediment within the sample. While the latter method provides only an estimate of measured concentrations within the fine sediment, the method is often used because it provides the true concentration in the sediments needed for the calculation of contaminant transport rates, and to assess the potential effects of contaminants on biota. The normalization method, however, generates poor estimates of the concentrations in the fine fraction when there is limited fine-grained material present (<25%–50%) [7]. In addition, Moore *et al.* [51] showed that within many mine contaminated rivers, trace metals are more uniformly distributed within the sediments. Thus, analyzing the fine-material may lead to erroneous results.

Other forms of normalization, such as normalization to a “conservative” element (e.g., Al, Li, Sc, Ti, or Zr) [7,52–54], have also been used to minimize variations associated with sedimentological differences in the samples when the primary goal is to document spatial variations in the contaminant concentrations for the purpose of source identification.

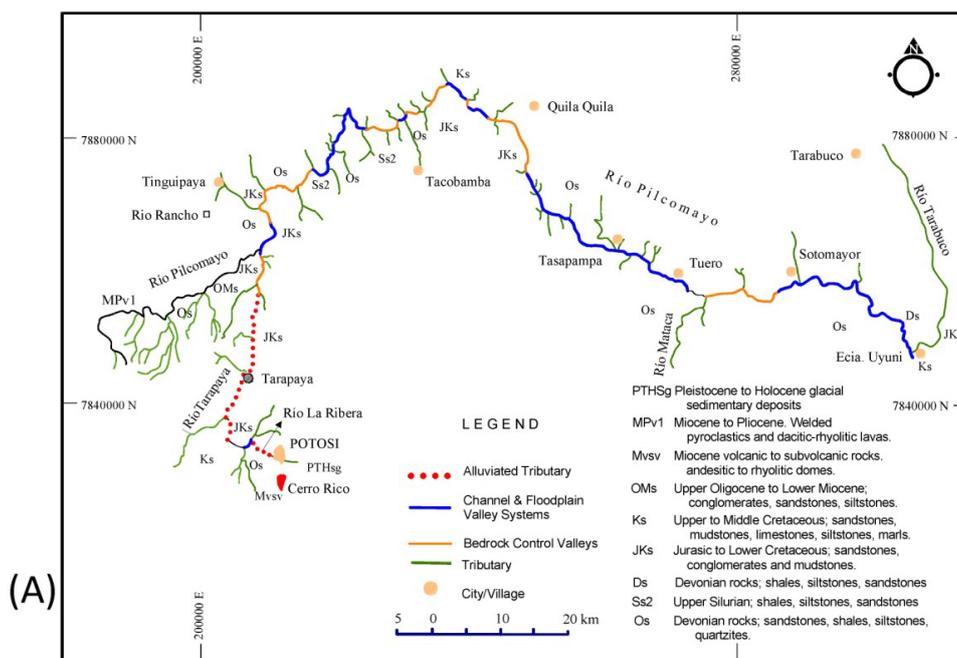
(2) *The Physical Sorting of Contaminants between Channel Bed Features.* Closely related to #1 (above), hydraulic sorting processes, including the selective entrainment and deposition of sediment on the basis of particle size or density, often results in a non-uniform distribution of contaminants between (or even within) morphological features found on the channel bed (e.g., pools, riffles, glides, point bars, *etc.*) [4]. These reach-scale variations in concentration between channel units have the potential to mask downstream trends where differences in concentration along the channel are limited. To compensate for these reach-scale variations it is common to sample specific unit types at each location along the channel, to use composite sampling (where multiple samples are collected from a specific location and combined into a single sample) to reduce field variance, or both.

(3) *Localized Variations in Sediment Transport and Deposition.* Macklin and his colleagues, while studying the River Tyne in the U.K., found that significant variations in trace metal concentrations were present that could not solely be related to the influx of sediment at tributary confluences. Macklin and Lewin [55] found that the underlying control on the observed pattern was the organization of the valley floor into alternating zones characterized by differences in the transport and deposition of sediment and sediment-borne contaminants along the river. The transport dominated zones tended to be steeper and narrower than average, allowing sediment entering the reach to move more quickly through it with only limited storage. In contrast, reaches dominated by deposition (which they referred to as sedimentation zones) possessed wider valley floors and shallower gradients promoting deposition. The result was that most of the Pb and Zn from historic mining operations were deposited within the sedimentation zones, and metal concentrations were relatively high along these

reaches [56,57]. Since their analysis, transport and sedimentation zones have been recognized along other river systems, such as the Rio Pilcomayo [58] (Figure 4).

(4) *Temporal Variations in Sediment Transport.* It is not uncommon for sediment, and any contaminants/tracers that they may be carrying, to move downstream through the system as a series of sediment pulses, or slugs, complicating the pattern predicted by standard regression or mixing models [57,59]. Sediment slugs often result from the injection of sediment into the channel as a result of either natural and human activities that exceed the transport capacity of the river [59–61]. The introduced sediments result in a cycle of channel bed aggradation and degradation which propagate downstream from the point at which it was introduced. Slugs, then, are associated with periods of channel instability that range from minor, localized disturbances to basin-scale perturbations in sediment supply that may lead to a total reconfiguration of the valley floor [59,62].

Figure 4. (A) Map showing the distribution of different process zones located along the Rio Pilcomayo of Bolivia [58]. Bedrock canyons represent sedimentation zones, whereas channel and floodplain valley systems represent sedimentation zones as shown in the aerial photograph (B) [58].



Quantifying Relative Source Contributions

Geographical patterns in geochemical tracers provide only a qualitative understanding of the relative contribution of contaminants to the river from the defined sources. More quantitative estimates may be provided by statistical mixing (or unmixing) models. Although exceptions exist (e.g., [48,63,64]), these models have been most extensively used to determine the relative contribution of contaminants from non-point sources of pollution within river, wetland, and lacustrine environments [32–36]. Nonetheless, the approach may provide highly valuable information regarding the primary source(s) responsible for contaminating a specific river reach, particularly given advances in tracer technologies which are describe below.

The mixing model approach assumes that the sediment located within the channel bed or other depositional environment is a mixture of material from the contaminated sources and all other, uncontaminated sediment transported by the river. It is therefore possible to characterize the suspected contaminant sources, the background materials within the basin, and sediments obtained from along the channel for selected geochemical tracers and statistically compare their tracer characteristics to unravel the relative proportion of sediment that was derived from each source [4,40,64]. In most non-point source studies, multiple tracers are utilized to effectively fingerprint the contaminated materials; thus, the approach represents a multivariate statistical method for source identification. Constraints on the mixing model require that: (1) each source type contributes some sediment to the mixture, and thus the proportions ($x_j, j = 1, 2, \dots, n$), derived from n individual source areas must be non-negative ($0 \leq x_j \leq 1$); and (2) the contributions from all of the source areas must equal unity, *i.e.*:

$$\sum_{j=1}^n X_j = 1 \quad (1)$$

In addition, some differences (error) between the values of the m measured parameters, in the source area, a_{ij} ($i = 1, \dots, m; j = 1, \dots, n$) and the mixture, b_i ($i = 1, \dots, m$) are allowed. The residual error corresponding to the i th parameter can be determined as follows:

$$\varepsilon_i = b_i - \sum_{j=1}^n a_{ij} x_j \quad (2)$$

for $i = 1, 2, \dots, m$, where a_{ij} ($i = 1, 2, 3, \dots, m; j = 1, 2, \dots, n$) are a measurement on the corresponding i th parameter within the j th source area and x_j is the proportion of the j th source component in the sediment mixture. When the number of measured parameters is greater than the number of sediment sources (including contaminant and background materials), the system of equations is over-determined, and a “solution” is obtained using an iterative computational method that minimizes an objective function using a gradient search, thereby obtaining a best fit solution to the entire data set [65]. There are several ways to obtain a best fit, but in previous studies, the objective function, f , has taken the form of the sum of the relative errors [65] where,

$$f(x_1, \dots, x_m) = \sum_{i=1}^m |\varepsilon_i / b_i| \quad (3)$$

or [36],

$$f(x_1, \dots, x_m) = \sum_{i=1}^m (\varepsilon_i / b_i)^2 \quad (4)$$

A criticism of the approach is that there may be a number of solutions that are statistically equivalent, particularly where contributions from a given source approach 0 or 100% (often referred to as the equifinality problem). In other words, similar levels of model performance as measured by a likelihood function can be produced by differing sets of source contributions [66,67]. In addition, uncertainty in the modeling results may be associated with: (1) the inherent variability of the fingerprint within the source materials; (2) the source material sampling density; (3) analytical error; and (4) the changes in sediment characteristics during particle entrainment, transport and deposition which may significantly influence the chemical and physical nature of the sampled deposits, such as grain size and organic matter content [68]. As a result, recent studies have explored methods to reduce and quantify the uncertainty in mixing/unmixing models, including the use of a Bayesian and or Monte Carlo sampling framework [66–70] as well as the inclusion of grain size and organic matter correction factors (e.g., [68]). Validation of these approaches using constructed laboratory mixtures of source materials and synthetic data show the methods hold considerable promise [69].

Attempts to model complex processes generally require simplifying assumptions, and several assumptions are associated with the use of sediment mixing models to assess sediment provenance, including that: (1) the downstream trends in concentration are the product of dilution resulting from the steady-state mixing with tributary and upstream sediment; (2) all of the potential sediment sources are identified and characterized for the geochemical tracers; and (3) the trace metals behave conservatively within the channel (*i.e.*, the geochemical tracers move with the sediment and there is no loss of elemental mass along the channel as a result of geochemical processes). In addition, the approach assumes that the sediment for which the contaminant provenance is being determined is derived directly from the ultimate sediment sources and not its proximal one. It is possible that sediment is eroded from a defined sediment source, transported downvalley and temporally deposited within the channel (or some other site) before being remobilized and transported to its current resting point where it was sampled.

Another assumption for which mixing models have been criticized is that the sediment must be assumed to leave all sources at the same time, and to be transported downstream at an equal rate, so that the sediment arrives at the sampling point simultaneously. Let's take, for example, a sample of sediment from a channel bed accumulated downstream of a contaminant source during a flood event. Assume that the contaminated sediments are derived from a site located a considerable distance from the sampling site, while background sediments are derived from the entire basin, including areas immediately adjacent to the sampling location. Also assume that equal amounts of the sediment from both the contaminant and background sources is deposited at the sampling site as the material is transported through the sampled reach. At the onset of the runoff event sediment from the background sites will reach the sampling location first; thus, the lower portions of the sampling interval will be composed of only background material. As the event continues, material from the contaminant source reaches the site, and equal proportions of the sediment from both sources are deposited. When the mixing model is applied to the sample, it will correctly indicate that a larger relative percent of sediment was derived from the background sources over the depth of material sampled. Thus, sediment

provenance with respect to the deposit has been correctly assessed within the errors inherent in the statistical analysis. However, if the intent is determine the amount of material introduced to the river from the contaminant source relative to background areas, the results will be biased such that the model will underestimate the amount of material derived from the contaminated site. A similar argument applies to differences in transport rates of different sized particles.

A variation in the use of mixing models is to determine the influx of contaminants from individual tributaries rather than distinct contaminant sources. In this case, however, the models do not apply to geochemical tracers, but rather to the changes in elemental concentrations that occur from up- to downstream of a tributary confluence. For example, Church *et al.* [32] applied a pair of geochemical mixing models to determine the relative contributions of Pb, Zn, and other trace metals to the Boulder River, Montana from several mine contaminated tributaries. The mixing model approach recognizes that the channel bed sediment located downstream of a tributary is a mixture of material from the tributary and the upstream reaches of the axial drainage. Thus, the relative percent of a specific trace metal (contaminant) derived from the tributary is a function of the proportion of sediment transported to the axial drainage by the tributary and the concentration of the contaminant associated with the sediment. Mathematically,

$$P_{ct} = (P_{st} \times C_t) / C_d \quad (5)$$

where P_{ct} is the relative percent of the trace metal (contaminant) derived from the tributary, P_{st} is the relative percent (or proportion) of sediment contributed by the tributary, C_d is the concentrations of an element downstream of the tributary confluence, and C_t is the concentration of an element within the tributary sediment. In early studies, the relative percent sediment yield from the tributary (P_{st}) was estimated using proxy data, such as basin area, because quantitative sediment transport (yield) data are unavailable for most rivers. However, the use of proxy data is often plagued by large uncertainties. An alternative, utilized by Church *et al.* [32], is to estimate the percent of sediment derived from a tributary (P_{st}) on the basis of measured elemental concentrations in the alluvial sediments in that:

$$P_{st} = [(C_u - C_d) / (C_u - C_t)] \quad (6)$$

where C_u is the concentration of an element upstream from the tributary confluence, and the other parameters are as defined above. Once the relative sediment influx is determined on the basis of the changes in concentration from up- to downstream of the tributary confluence, the estimated value of P_{st} can be used in Equation (5) to determine the relative contribution of the trace metal by the tributary to the axial drainage.

While the approach provided insights into the relative contributions of sediment from the examined tributaries into the Boulder River, different values of P_{st} were calculated by Church *et al.* [32] for the different elements used in Equation (5). In an attempt to reduce the significance of this problem, Mackin development of a mixing model in which P_{st} was determined using multiple elements and minimization principles from calculus [71]. It is possible that the influx of sediment with very high metal concentrations within a tributary in comparison to the axial channel will result in an over-estimation of sediment delivered by the tributary. To avoid this problem, conservative elements derived from lithogenic sources (rather than anthropogenic sources) (e.g., rare Earth elements) may be used in the

analysis. Thus, this multi-elemental method appears to hold considerable promise for reducing the uncertainties associated with the approach.

3. Use of Geochemical Tracers to Construct Pollution Histories

During the past few decades significant attention has been paid to the potential to construct a history of anthropogenic contamination by analyzing geochemical tracers within alluvial and lacustrine deposits associated with a river system [71–80]. The developed histories can form a significant component of any environmental/geological forensic analysis in that they: (1) provide an understanding of the changes in the chemical health of the river through time where water quality monitoring records are limited or absent; (2) allow short-term monitoring records to be placed into an historical context of the changes in sediment geochemistry over periods ranging from a few years to millennia, and, perhaps of most importance from a forensic perspective; (3) can identify a contaminant source and its relative importance as a contributor of contaminants to the river when a source is no longer present. Chronologies of contaminant influx may also provide highly valuable insights into whether water and sediment quality is recovering either in response to remedial actions or on its own, without any human intervention, after the contaminant source has been mitigated. These integrated stratigraphic-geochemical analyses have most frequently focused on vertically accreted overbank floodplain deposits and lacustrine deposits found within reservoirs located along the river.

3.1. Pollution Histories Based on Overbank Deposits

Catchment scale mass balance calculations have demonstrated that significant portions (ranging from 10% to more than 60%) of the sediment eroded from upland areas and transported to the axial drainage system never reaches the basin mouth [4,81]. The bulk of these sediments, and the contaminants that they carry, are deposited and stored with floodplains located along the river. Of particular interest are overbank deposits that are created when runoff events exceed the channel's bankfull capacity and inundate the floodplain surface. Sediments within the flood waters are semi-continuously deposited across its surface, and as sediments accumulate, younger materials bury older producing a trend in which the age of the sediment varies semi-systematically with depth. Assuming that the deposited sediments reflect the geochemistry of the particulates being transported along the channel, geochemical variations as a function of depth in the overbank deposits reflects changes in contaminant influx to the river. It follows, then, that: (1) the overbank deposits contain a long-term (decadal-scale) record of the variations in sediment and contaminant transport rates; and (2) depth/temporal variations in a geochemical fingerprint/tracer within the overbank deposits can be used to construct a chronology of contaminant loadings from anthropogenic sources [72–80,82,83].

The general approach for developing a chronology of pollution loadings from overbank deposits typically involves the collection of a set of sediment cores from the floodplain which are then stratigraphically described, sampled, and analyzed for selected tracers at uniform or semi-uniform intervals below the floodplain surface. In addition to the analysis of the contaminant tracers, the core materials are typically dated using one more methods, including the use of short-lived radionuclides (e.g., ^{137}Cs , ^{210}Pb , ^{10}Be), radiocarbon dating (^{14}C), or optically stimulated luminescence (see Stokes and Walling [84] for a more detailed discussion of dating methods). When the geochemical

data are combined with an understanding of deposit age, the observed variations in concentration can be linked to a history of anthropogenic activities within the basin to identify the most likely contaminant sources.

The use of overbank deposits to create a chronology of trace metal influx is well illustrated by the work of Macklin and Klimek [72] in upper Vistula basin in southwestern Poland. In this case, they analyzed overbank sediments associated with levees and inset fills confined by a dike constructed near the turn of the 19th century, and within sediments that occurred outside the dike-protected area which were deposited prior 1800. The identified deposits were dated and analyzed for Pb, Zn, and Cd, the latter of which were considered to be effective tracers of mining debris contained within the catchment. The age and geochemical data were then related to one another to create a general history of contamination that could be linked to anthropogenic activities. The results showed that sediment quality progressively declined through time within the upper Vistula basin, particularly after about 1850. Initially, elevated trace metal concentrations occurred at sites located immediately downstream of mining districts within the Przemsza River, a tributary to the Vistula, but became much more widespread, affecting the entire basin during the past 100 years.

Hudson-Edwards *et al.* [85] note that the investigation of pollution histories using overbank floodplain deposits fall into two general categories, those conducted at a relative coarse-scale in which general trends in pre-, peak, and post-metal contamination are determined using geochemical tracers (e.g., [32,81–88]), and analyses performed at a fine-scale during which the sampling interval is measured in centimeters, and the sediments are subdivided into discrete periods on the basis of the degree to which they are contaminated (e.g., [88–91]). In both cases, there are two important assumptions inherent in the development of pollution histories: (1) the observed changes with depth in the geochemical tracers are a reflection of the metal content within the suspended sediment at the time of deposition; and (2) once deposited, the position of the tracers within the sediment is not significantly affected by post-depositional processes. Data regarding the degree to which the overbank deposits, or those found in oxbow lakes and reservoirs for that matter, reflect the transported sediment are surprisingly limited. The available data suggest, however, that the geochemical signal may vary spatially across the floodplain as a function of distance from the channel, the microtopography of the floodplain surface, and the magnitude of flooding, among of number of other variables [4,80,92]. The geochemical signal also may be affected by changes in channel form (e.g., channel straightening), or other sedimentological process that influence the transfer of sediment from the channel to the floodplain [93,94].

Particular attention has recently focused on the role of large floods in controlling the physical and chemical composition of the overbank deposits [75,82,93–95]. Larger floods appear to deposit relatively coarse-grained sediment on the floodplain characterized by lower trace metal concentrations than finer-grained sediments deposited during more frequent, lower magnitude events [75,96,97]. To compensate for these grain size differences, it is common to analyze only the fine-grained sediment fraction, or alternatively to normalize the concentration on the basis of the percent of fine sediment in the sample or to a conservative element. These methods are not always effective. Bábek *et al.* [75] found that short-term, flood-related variations in contaminant concentrations remained, even after normalization to a “conservative” element (Al). However, magnetic susceptibility values were found to correlate with particle grain size. More specifically, fine-grained layers exhibited higher magnetic

susceptibility values in large part because of a higher concentration of paramagnetic clay minerals and phyllosilicates. Thus, Bábek *et al.* [75] were able to use magnetic susceptibility data as a proxy for grain size in order to minimize the effects of flood-related grain size variations on trace metal concentrations [7,63].

With regards to the second assumption, the degree of post-depositional migration of a geochemical tracer can be significant, depending on the reactivity of the tracer and the physio-chemical environment [77,85,92,94]. Hudson-Edwards *et al.* [85], for example, demonstrated using detailed speciation and mineralogical data from the River Tyne in the UK that trace metals often migrate over depths of a few centimeters within the floodplain. The magnitude of migration varied between elements such that the more tightly bound elements (e.g., Pb) exhibited the least mobility. It has also become clear that the degree of mobility can be enhanced by environmental change, such as channel incision which leads to a drop in water table elevations, redox conditions, and the weathering of the existing minerals (e.g., sulfides). Mobilization also tends to be more significant in areas of high water table fluctuation [76]. It follows, then, that the results from fine-resolution data are more likely to be affected by post-depositional processes than those associated with coarser-resolution data sets.

Given the difficulties of creating chronologies of contaminant influx from floodplain deposits, the results are likely to contain uncertainties which are difficult to quantify [75]. Nonetheless, when combined with other data, the results can serve as an important component of any environmental forensic analysis.

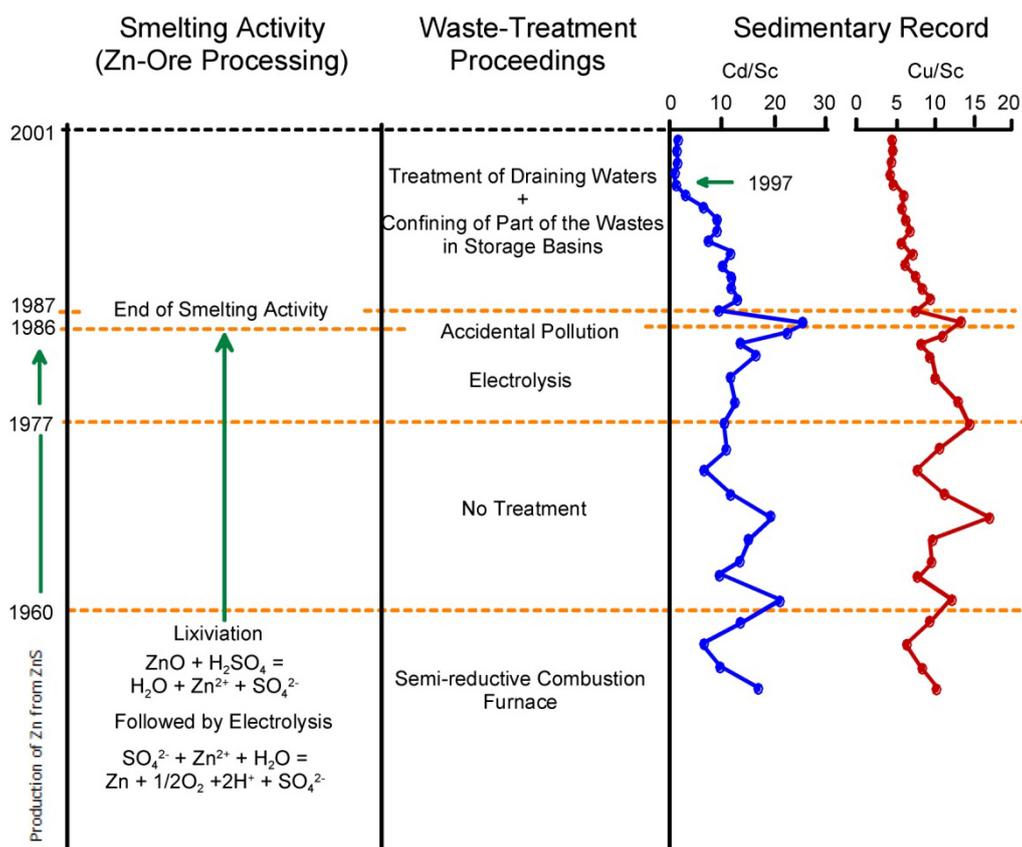
3.2. Pollution Histories Based on Lacustrine Deposits

Overbank floodplain deposits typically exhibit hiatuses and irregularities in deposition that complicate the construction of pollution histories [76,97]. In contrast, reservoirs represent depositional environments that are characterized by high rates of nearly continuous sediment accumulation [98,99]. These high rates of accumulation tend to reduce the potential for post-depositional contaminant migration by early diagenetic processes [100,101], while the continuous deposition of sediment (and the geochemical tracers associated with them) allows for the development of pollution histories of high temporal resolution. As a result, reservoir deposits are frequently targeted to document temporal variations in contaminant influx to a river upstream of the dam (e.g., [71,98,101–103]). Other “lacustrine” deposits such as oxbow lake and estuarine/coastal sediments also have been used [104,105], although the post-depositional migration of trace metals is more problematic in these environments.

The approach to construct a history of contaminant influx using lacustrine sediments is similar to that applied to overbank floodplain deposits. Audry *et al.* [101], for example, constructed a record of trace metal influx to the Lot River, France, a river that has been subjected to contamination by mining and smelting activities since the late 19th century. Sediment age was determined by ^{137}Cs analysis and by extrapolating between depths of known age on the basis of average sedimentation rates. Cd and Cu were selected as geochemical tracers of the smelting wastes, and their concentrations were normalized to Sc, a conservative element, to help differentiate between lithogenic and anthropogenic sources of the two metals. The constructed record showed that prior to ~1975, Cd/Sc and Cu/Sc ratios were highly variable, reflecting high trace metal inputs from smelting activities (Figure 5). From 1975 to 1985, Cd levels increased as smelting activity grew and smelting waste piles within the catchment

expanded. Interestingly, Cu concentrations apparently declined as a result of improvements in processing technologies for metal recovery which tended to be more efficient for Cu than for Cd. An accidental seepage release of trace metal contaminants in 1986 created the peak values in concentration at that time, which were followed by a significant decrease in both Cd and Cu concentrations at the top of the core. This latter decrease was attributed by Audry *et al.* [101] to remediation efforts undertaken after 1987. The concentrations at the top of the core remained well above background values indicating that the remediation efforts only were partially successful.

Figure 5. Vertical (depth) variations in Cd/Sc and Cu/Sc ratios within samples from a dated sediment core extracted from the Cajarc reservoir, located along the Lot River, France. Variations reflect changes in Cu and Cd influx to the river in response to alterations in processing methods and, after 1987, remediation efforts (modified from Audry *et al.* [101]).



As shown for the overbank floodplain deposits, multiple contaminants/geochemical tracers can be analyzed within the lacustrine or coastal cores. It is important to note, however, that not all variations in contaminant/tracer values are necessarily related to changes in the direct influx of anthropogenic contaminants. Miller and Mackin [71], for example, used reservoir sediments from Lake Emory to document temporal changes in trace metal influx to the Little Tennessee River of western North Carolina since dam closure in 1925. They found Cu, Pb, As, and other trace metal and metalloid concentrations with the reservoir deposits frequently exceeded the consensus-based threshold effect concentrations of MacDonald *et al.* [106] for aquatic biota. This consensus-based threshold represents the geometric mean of threshold effect guidelines put forth in multiple studies of aquatic biota and is

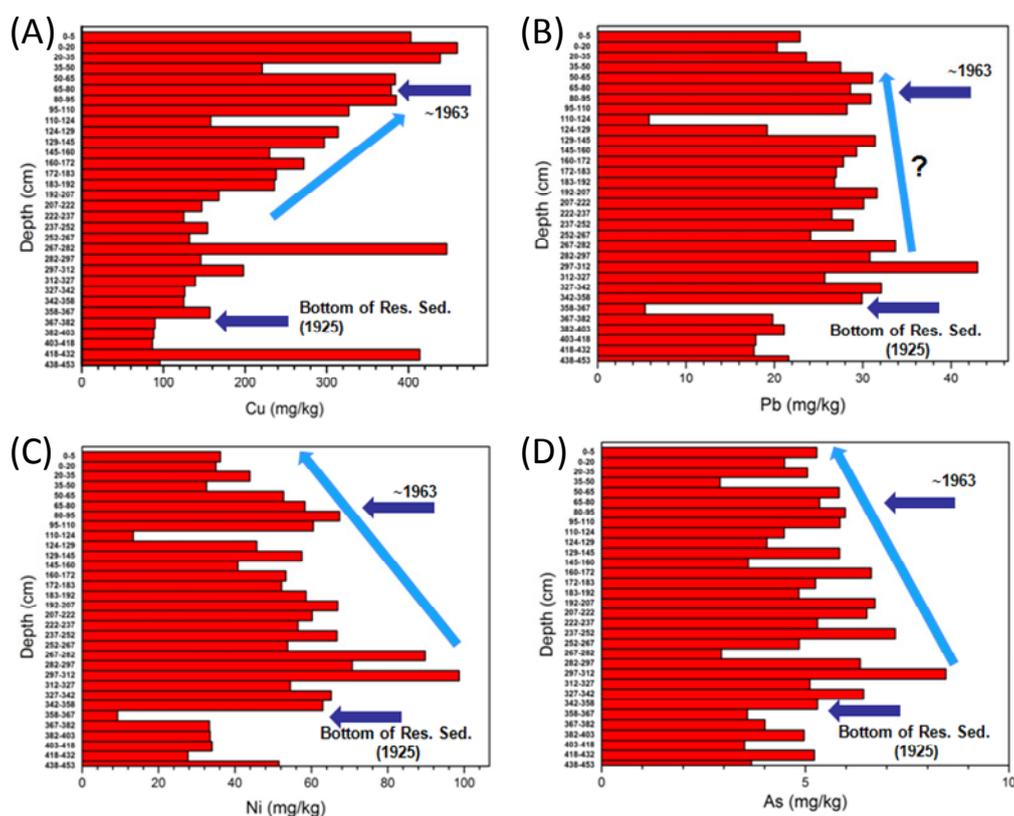
likely to be applicable to a wide range of environments. The data, then, suggest that the metals have the potential to negatively impact aquatic health. In addition, Ni, Cr, and Zn concentrations were found to be relatively high near the bottom of the reservoir deposits, and decrease semi-systematically toward the surface of Lake Emory (Figure 6). The elevated concentrations were coincident with relatively high rates of sediment transport within the river, as demonstrated in Lake Emory by sedimentation rates prior to 1963 that were approximately five times higher than those measured between 1963 and 2010. Using a variety of data, they argued that the trace metals were largely derived from natural sources, specifically the erosion of subsurface soil horizons enriched in trace metals weathering from sulfide mineralized units within the underlying bedrock. The increased loading rates to the river apparently resulted from a period of extensive land-clearing during the late 1800s and early- to mid-1900s that also resulted in the deposition of post-settlement alluvial deposits along the floodplain [107]. The observed decreases in Ni, Cr, and Zn concentrations presumably resulted from improved watershed management practices which limited upland erosion in the basin during the latter part of the 20th century. In contrast to Cr, Ni, and Zn, Cu concentrations within the reservoir semi-systematically increased from the bottom to the top of the reservoir deposits (Figure 6), suggesting that Cu loadings to the channel have increased during the past several decades. The additional Cu was most likely derived from Cu-based pesticides that were extensively used on tomato fields within the watershed.

3.3. Extrapolating Site Data Using Chemostratigraphic Methods

The history of contaminant provenance and transport rates can abruptly change along a river as a function of the mechanisms and rates of sediment-born contaminant dispersal, the space and environments available for sediment deposition, the addition of new contaminant sources, and changes in the contaminant-sediment relations, among a host of other factors. As a result, a question that often arises is how to most effectively correlate the timing of specific contaminant loading events documented for one site with that of another up- or downstream site. The inability to correlate contaminant histories along a channel may introduce significant uncertainties into the extent and duration to which a specific contaminant source has impacted both sediment and water quality in the riverine environment.

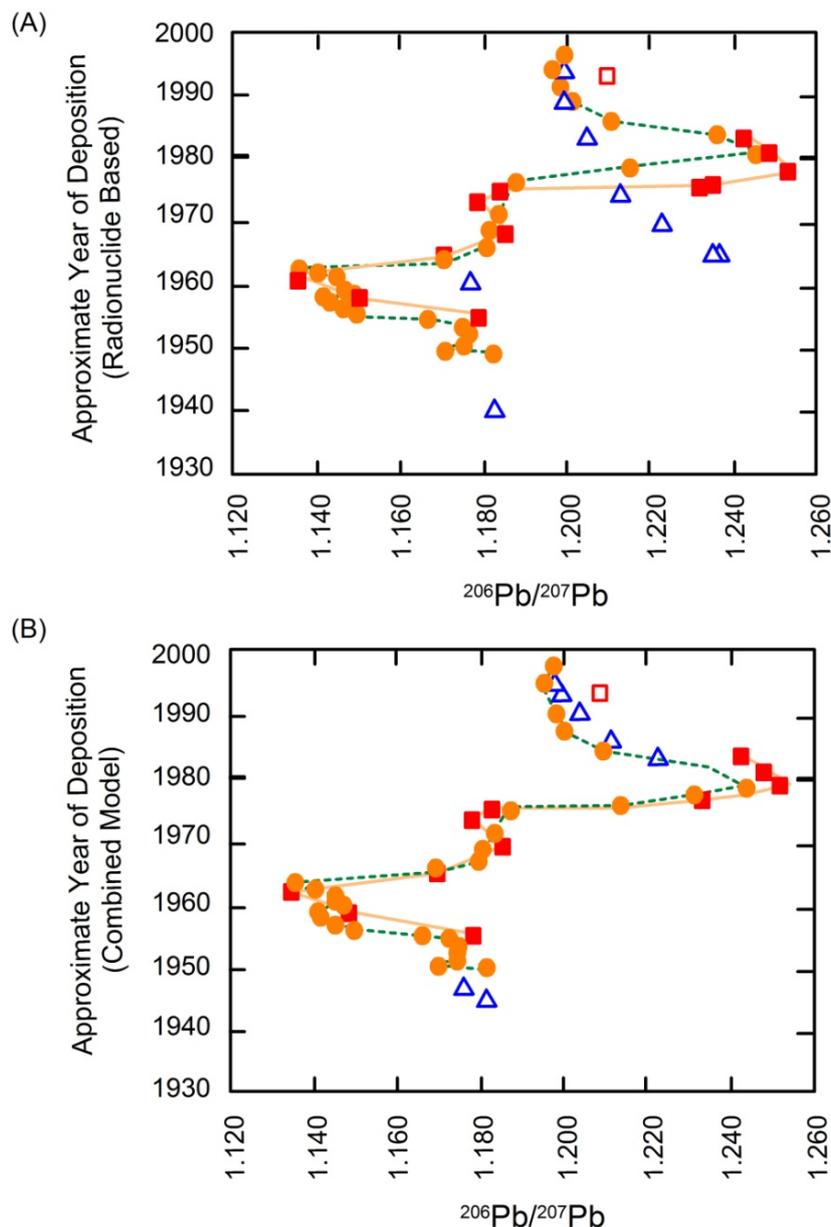
Recent studies have illustrated that geochemical tracers, when combined with the concepts inherent in chemostratigraphy, can provide a powerful tool for correlating stratigraphic units, and the pollution histories based on these units, between sites. *Chemostratigraphy* can be defined as the detailed characterization of the spatial changes in the chemical nature of sedimentary strata, and the identification of sedimentary packages (units) with similar geochemical traits for the purpose of correlating geographically distributed units [108]. Few studies have attempted to apply these methods to recent riverine deposits; rather most chemostratigraphic studies have focused on marine, lacustrine, and lithified strata (e.g., [108–113]). However, the studies that have been conducted to date show that geochemical signatures associated within anthropogenic sources of contamination may be used to effectively correlate otherwise sedimentologically homogenous deposits over large downstream distances [56,114,115]. In addition, if the timing at which a specific geochemical fingerprint was introduced to the river is known, then the fingerprinted materials may be used to constrain the relative and absolute age of the deposits along the drainage system.

Figure 6. Vertical (depth) variations in Cu (A), Pb (B), Ni (C), and As (D) concentrations within samples collected from a sediment core extracted from Lake Emory along the Upper Little Tennessee River, western North Carolina. Pb, Ni, and As concentrations decrease from 1925 to present. High values correlate with the erosion of metal enriched subsoils during land-use change. In contrast, Cu loadings to the river have increased since dam closure in 1925 in response to the use of Cu based pesticides within the watershed (from Miller and Mackin [71]).



The chemostratigraphic approach is based on the identification of recognizable geochemical signatures which can be traced between sites and which allow for unit correlation. The application of chemostratigraphic methods to riverine environments is well illustrated by the work of Chillrud *et al.* [114] for the upper Hudson River in the northeastern U.S. The upper Hudson River was subjected to significant inputs of Cd, Sb, Pb, and Cr during the latter part of the 1900s. Chillrud *et al.* [114] used geochemical tracing methods on sediment cores collected upstream of three dams located a total distance of 24 miles apart to construct a history of contaminant loadings to the river. An important component of the analysis was the chemostratigraphic correlation between the sites on the basis of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (Figure 7). By doing so, they were able to use the age constraints provided by ^{137}Cs data within the upstream core to precisely date the deposits located downstream. This allowed for a detailed analysis of the influx of sediment between the sites from the early 1960s to the late 1970s on the basis of the observed differences in tracer concentrations. They found that 3 to 4 times more sediment entered the river between the upstream- and downstream-most coring sites than was transported from upstream portions of the watershed.

Figure 7. Vertical (temporal) trends in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios within three cores obtained from reservoirs at three different locations along the upper Hudson River. Red squares represents samples from mile post (mp) 188.5 (upstream), orange circles from mp 163.6 (downstream), and open blue triangles from samples collected at mp 169 in 1995 (A). Sediment ages are assigned ages on basis of ^{137}Cs data. Vertical trends in $^{206}\text{Pb}/^{207}\text{Pb}$ are similar between the three sites, but are offset vertically. (B) Temporal trends based on both ^{137}Cs data and chemostratigraphic correlation on the basis of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between the sites so that the in $^{206}\text{Pb}/^{207}\text{Pb}$ trends match (from Chillrud *et al.* [114]).



The point to be made is that while chemostratigraphic methods are cost and effort intensive, they provide a highly underutilized approach for linking together histories of contaminant source contributions constructed for various sites along the river. In doing so, a wealth of information can be extracted from the deposits with regards to the extent and magnitude of contamination associated with each of the identified contaminant sources.

4. Elemental Isotopes as a Geochemical Tracer

As noted in the introduction, a wide range of physical and chemical parameters have been effectively utilized as contaminant tracers in river systems. The bulk concentration of trace metal contaminants, or their related ratios, has been most extensively used as a tracer in riverine environments, particularly when the contaminants are derived from mining, milling, and refining processes. In many instances, however, trace metals found within the alluvial sediments are derived from multiple natural and anthropogenic sources, and fingerprinting contaminated sediment on the basis of bulk elemental concentrations may be ineffective, particularly when the elemental concentrations are near background values. One approach to address the issue has been to use isotopes as a geochemical fingerprint/tracer. Recent studies have demonstrated that selected elements (e.g., Pb) exhibit stable isotopic abundances that fall within a narrow range of values in geological materials. Moreover, many anthropogenically derived substances exhibit isotopic values that differ from non-mineralize (lithogenic) rocks. Thus, these isotopes can serve as a highly sensitivity tracer that allow for the determination of sediment and contaminant provenance even where multiple sources exist, or where elemental concentrations are near background values [35,116]. In the following sections, the use of isotopes as a geochemical tracer of trace metal contaminants is explored.

4.1. Pb Isotopes

To date studies have focused extensively on the use of Pb isotopes as an environmental tracer in a wide range of media, including air and aerosols [117–122], snow and ice [123–127], soils [128–132], lacustrine and reservoir deposits [133–136], wetlands and peat [137–140], plants, mosses, and tree rings [141–143], human tissues and blood [121,144,145] and other biota [146–152]. Within riverine environments there is little question that the isotopes of Pb have been most extensively utilized as an isotopic tracer in forensic investigations (see Bird [29] for a detailed review of Pb as a contaminant tracer in rivers).

Pb has four stable isotopes that are used in environmental forensics, including the daughter products ^{206}Pb , ^{207}Pb , and ^{208}Pb which are derived from the radioactive decay of ^{238}U , ^{235}U , and ^{232}Th , respectively (Table 1). The fourth isotope, ^{204}Pb , has no known radiogenic parent. The natural Pb isotopic composition of a geological material depends upon the relative proportion of U, Th, and Pb in the system, various mixing processes associated with metamorphism, and the age of the rocks and minerals as some U and Th will decay through time to Pb [42,145]. The isotopic abundances of Pb found within rocks, sediments, soils, *etc.* are typically reported as ratios (e.g., $^{206}\text{Pb}/^{204}\text{Pb}$), but no consistent set of ratios have been used in the literature. While one study may report the values in terms of $^{206}\text{Pb}/^{207}\text{Pb}$, others, particularly geologically oriented investigations, may report the same measured abundances in terms of $^{207}\text{Pb}/^{206}\text{Pb}$, making it difficult to compare the results between investigations. Moreover, many geological studies have focused on the ratio of the radiogenic isotopes to ^{204}Pb (*i.e.*, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$) [29]. In contrast, most studies using Pb isotopes as a geochemical tracer have avoided the use of ^{204}Pb because of its low relative abundance (Table 1), and the difficulty of measuring it at low concentrations. In addition, Sangster *et al.* [152] found that 86% of the discriminative (fingerprinting) power of Pb isotopes is due to ^{206}Pb , ^{207}Pb , and ^{208}Pb .

Table 1. Selected properties of Pb isotopes used in environmental studies.

Isotope	Abundance	Half-life and Parent Isotope
²⁰⁴ Pb	1.48%	²⁰⁴ Pb (stable)
²⁰⁶ Pb	23.60%	²³⁸ U to ²⁰⁶ Pb; ½ life of 4.5×10^9 years
²⁰⁷ Pb	22.60%	²³⁵ U to ²⁰⁷ Pb; ½ life of 7.1×10^8 years
²⁰⁸ Pb	52.30%	²³² Th to ²⁰⁸ Pb; ½ life of 1.4×10^{10} years

The pronounced effectiveness of Pb isotopes as a geochemical fingerprint/tracer is related to several factors. First, the radiogenic isotopes of Pb can be measured with a high degree of precision and accuracy. Early on the analysis was primarily carried out by Thermal Ionization Mass Spectrometry (TIMS), a method that provided precise measurements ($\geq 0.005\%$ RSD) [153], but required considerable sample preparation [29,154]. More recent investigations have relied extensively on the use of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) which requires less time and effort. The development and availability of multi-collector (MC) ICP-MS and magnetic sector (MS) ICP-MS, both of which produce highly precise (*ca.* $\geq 0.002\%$ RSD) [29,154] and accurate isotope measurements, have particularly increased the use of ICP platforms for sample analysis. The highly-precise measurements of the Pb isotopic ratios make them a particularly sensitive tracer that allows specific Pb sources to be identified with a minimal number of samples and statistical manipulation [42].

Second, effective fingerprints/tracers exhibit conservative behavior over a wide-range of environmental conditions. In the case of sediment in river systems, this means that the tracer moves with the sediment without significant loss in elemental mass, or a change in the isotopic abundances [29,155]. Pb has a high affinity for particulate matter, and once deposited, is generally immobile [132,135]. Moreover, the heavy nature of Pb, combined with the low relative atomic weight differences among its isotopes, limit the degree to which mass-dependent isotope fractionation by physical, chemical, and biological processes occur [29,42,145,153,156]. This is an extremely beneficial trait in that the Pb isotopic abundances found within the ore deposits do not change during mining, smelting, or other industrial or biological processes. Thus, the Pb released into the environment from a contaminant source retains the isotopic signature of the source material as it is dispersed through the river system. Observed differences in Pb isotopic ratios between the source materials and the alluvial sediments at any given site can therefore be attributed to its mixing with sediments from other Pb sources [42].

Third, the most effective tracers exhibit a wide range of values in geological materials. Although the isotopic ratios of Pb in ore deposits on a global scale are highly variable [29], there is a strong tendency for ore-derived Pb to be more radiogenic. Therefore, Pb ratios within anthropogenically derived materials created from those ores tend to differ from the more geogenic Pb found within non-mineralized country rocks [157]. It is often possible, then, to effectively fingerprint both natural and anthropogenic sources of Pb contained within alluvial sediments.

4.2. Applying Pb Isotopes as a Tracer in Riverine Environments

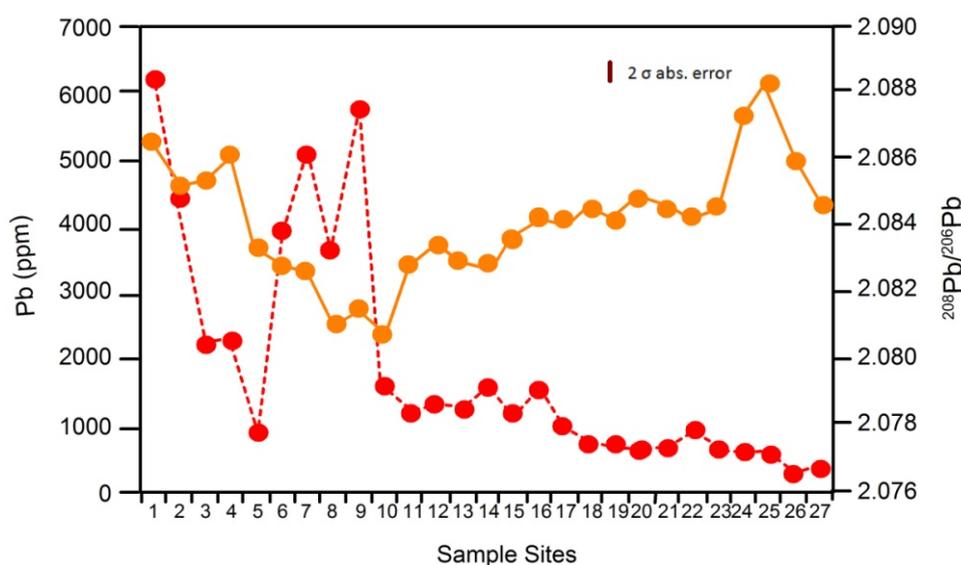
As shown earlier for other geochemical tracers, spatial variations in Pb isotopic ratios along a channel can be used to assess the sources of Pb at any given point, and the downstream changes in Pb provenances that occur. The analysis is based on the assumption that the analyzed sediment represents

a mixture of particles from all of the potential source areas in the catchment, and that the relative abundance of the Pb isotopes reflects the contributions from each source. Theoretically, however, there is some evidence to suggest that physical sorting processes may lead to differences in the observed isotopic ratios from one location to another; for example, Bird [29] notes that Pb isotopic signatures may differ between sediment sizes (e.g., fine-grained, chemically reactive silts and clays and coarser mineral fragments). This is supported by recent sequential extraction analyses. Sequential extraction is a method that treats a sample in different reagents in a stepwise manner to determine how, and with what, a trace metal is bound within the sediment. It has demonstrated that Pb isotopic ratios can vary between Pb that is associated with different physiochemical phases (e.g., the exchangeable, reducible, oxidizable, and residual phase) that are often grain size dependent [158–161]. Thus, it is possible that downstream changes in sediment size or the partitioning of sediments on the basis of size or density into specific depositional units may contribute to differences in isotopic values that occur. While this is a topic that is in need of additional research, differences related to these processes are likely to be minor along highly contaminated river systems. It follows, then, that changes in Pb isotopic signatures within alluvial sediments primarily reflect the input of Pb from different sources characterized by different Pb isotopic abundances.

An excellent example of the use of Pb isotopes to assess Pb provenance is provided by Shepherd *et al.* [162] for the River Wear located in northeast England. They analyzed a variety of geological materials within the catchment as well as the channel bed sediments along an 87 km reach of the river. The isotopic variations measured within the channel bed sediments are shown in Figure 8. As is commonly done, Pb concentration data are also shown on the figure to provide additional details on the levels of contamination that are associated with the various Pb sources. The data reveal that at Site 1 the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio is comparable to geological materials found in the outer mineralized zone of an orefield. Thus, the high Pb concentrations found in the bed sediments are likely to reflect the influx of Pb-contaminated sediment to the river from abandoned mines, waste piles and an old processing plant associated with historic mining operations that produced about 60,000 t of lead concentrate [163]. The rapid downstream declines in concentration from Sites 1 to 5 are thought to result from dilution and the deposition of dense, finely milled Pb ore within the channel bed. Downstream of Site 5, Pb concentrations increase significantly until reaching Site 9. Interestingly, however, $^{208}\text{Pb}/^{206}\text{Pb}$ ratios continue to decline. The decline in $^{208}\text{Pb}/^{206}\text{Pb}$ ratios reflects the influx of mine waste from two tributary valleys where the Pb ore was derived from the inner zone of the orefield. The rocks within the inner zone exhibit a much lower $^{208}\text{Pb}/^{206}\text{Pb}$ ratio than those found within the outer zone of the orefield. The $^{208}\text{Pb}/^{206}\text{Pb}$ ratio between Sites 10 and 11 increases abruptly, reflecting the input of Pb from Bollihope Beck, a tributary containing another cluster of mines. Pb concentrations, however, do not increase indicating that the tributary provides a relatively limited quantity of the Pb to the main stream of the River Wear (about 18% of the total). Downstream of Site 11, there are no further direct inputs of Pb from mining operations in the catchment. Without the isotopic data, decreasing Pb concentrations downstream of Site 11 could reasonably be interpreted as reflecting the dilution of sediment-born Pb by relatively “clean” sediments from the underlying bedrock. However, the increasing $^{208}\text{Pb}/^{206}\text{Pb}$ ratio suggests that other source(s) of Pb characterized by a higher $^{208}\text{Pb}/^{206}\text{Pb}$ ratio are entering the channel. Shepherd *et al.* [162] argued that this additional Pb was derived from the influx of diffuse anthropogenic sources from tributaries draining an abandoned coalfield. The abrupt

rise and following increase in $^{208}\text{Pb}/^{206}\text{Pb}$ between sites 24 and 27 were interpreted to result from either: (1) an increased influx of diffuse Pb in the vicinity of Durham; or (2) the influx of tetra-ethyl lead from leaded gasoline. The point to be made by the analysis conducted by Shepherd *et al.* [162] is that a much more detailed understanding of Pb sources and their relative contributions to the contamination of the river was made possible by combining Pb concentration data with Pb isotopic fingerprinting and tracing methods.

Figure 8. Downstream changes in total Pb concentration (red circles) and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (orange circles) along the River Wear, Northern England. Sample sites 1 through 27 are shown on ordinal axial and cover a distance of 86.5 km. Error bar refers to isotopic measurements (from Shepherd *et al.* [162]).

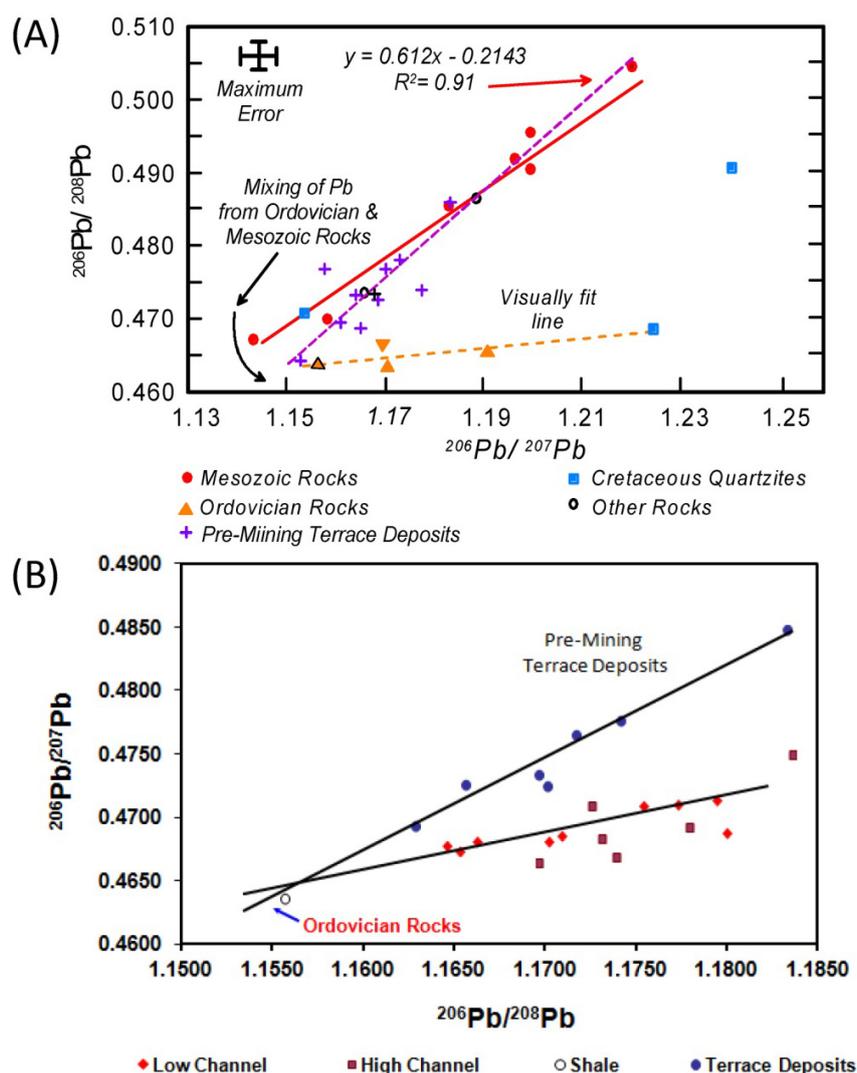


In addition to examining the spatial variations in isotopic ratios along a channel, Pb sources are often identified by analyzing three-component scatter diagrams depicting differences between two isotopic ratios [64,164–170]. When the values of the analyzed samples form a strong linear trend, Pb within the samples is often interpreted to be derived from two primary sources, where the sources exhibit minimum and/or maximum values of the examined ratios at the end of the line. The trend, then, represents a mixing line between the sources. In the case of alluvial sediments, one end-member (Pb source) is typically anthropogenic, whereas the other represents Pb from the underlying bedrock or the soils developed from it [29,171]. The signature of the latter “geogenic” Pb may be determined by analyzing a number of different materials including the underlying bedrock [172], channel bed materials from uncontaminated tributaries or areas upstream of the contaminant influx [145], uncontaminated alluvial terraces [64,172,173], or old alluvial sediment found at depth within a sediment core [32].

Miller *et al.* [64,172], for example, used bivariate scatter diagrams for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ to assess the sources and contaminant transport processes along the Rio Pilcomayo downstream of the Cerro Rico de Potosi precious metal-polymetallic tin deposits of Bolivia. Mining of the deposits has continuously occurred since 1545 and the river is severely contaminated by a wide-range of trace metals [172,174]. Miller *et al.* [172] found that (1) the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios differed

between bedrock units within the catchment, and (2) alluvial sediments collected from pre-mining terrace deposits formed a mixing line defined by the isotopic ratios of Ordovician and Mesozoic rocks. In contrast, samples collected in 2000 from the highly contaminated channel bed exhibited a significantly different trend (Figure 9) in which the isotopic end members were formed by the Ordovician rocks and mine/mill processing waste from the operations at Cerro Rico. In 2000, then, the channel bed material was dominated by natural Pb from the underlying Ordovician rocks and Pb from the ore deposits that were released anthropogenically into the river system. Pb input from the Mesozoic rocks was apparently minor and the isotopic signature was masked by the large inputs from the other two sources.

Figure 9. (A) Pb isotopic ratios measured in pre-mining (and uncontaminated) terrace deposits (purple line) vs. those measured within Ordovician, Mesozoic and Cretaceous rocks. Pre-mining terrace deposits appear to be composed of sediment from Mesozoic rocks with relatively high Pb ratios and Ordovician rocks (from Miller *et al.* [172]). (B) Pb Isotopic data collected in 2000 from modern channel bed (red circles and brown squares). High ratio end member is consistent with isotopic values obtained from ore deposits mined and milled from Cerro Rico, indicating Pb is derived from the mines and the underlying rocks (particularly Ordovician Rocks (From Miller *et al.* [64]).



One of the significant advantages of using Pb isotopic fingerprinting methods is that accurate estimates of the relative contributions of Pb from the two sources can be made where a mixing line is defined by two distinct end-members. The estimates are typically based on a simple binary model [29,168,175] where,

$$\%A = \frac{\left(\frac{{}^{20x}\text{Pb}}{{}^{20x}\text{Pb}} \right)_S - \left(\frac{{}^{20x}\text{Pb}}{{}^{20x}\text{Pb}} \right)_A}{\left(\frac{{}^{20x}\text{Pb}}{{}^{20x}\text{Pb}} \right)_B - \left(\frac{{}^{20x}\text{Pb}}{{}^{20x}\text{Pb}} \right)_A} \quad (7)$$

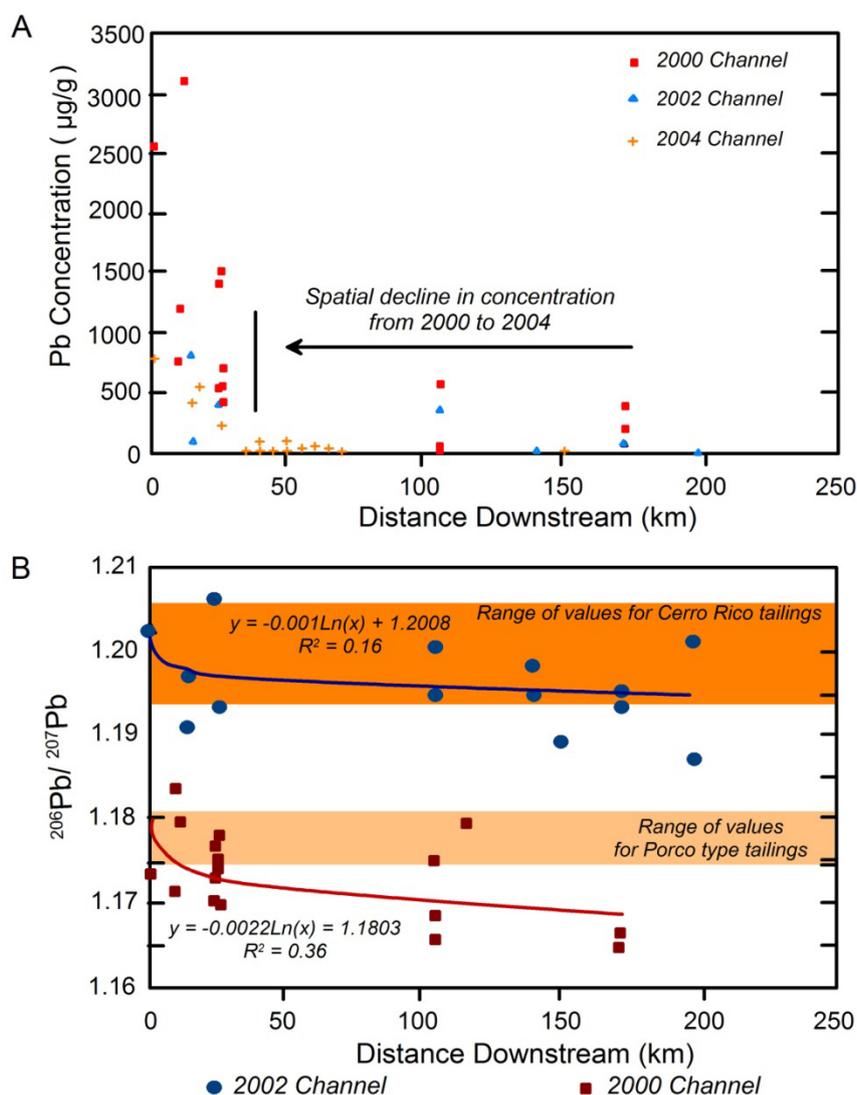
where %A is the contribution of source A in a sample and ${}^{20x}\text{Pb}/{}^{20x}\text{Pb}$ and ${}^{20x}\text{Pb}/{}^{20x}\text{Pb}$ are the average ratios in the sample (S), end-member for source 1 (A) and end-member for source 2 (B). In the case of the Rio Pilcomayo, Miller *et al.* [172] were able to use the approach to estimate that the contribution of Pb from the upstream mining operations in the samples collected in 2000 ranged from >99% to about 56% of the total Pb present (note that these values were recalculated from Miller *et al.* [65] on the basis of a more accurate understanding of the isotopic signatures of the ore deposits).

The data collected along the Rio Pilcomayo indicate that a significant proportion of the Pb was derived from the underlying bedrock, a conclusion that has been reached by other investigators as well [172,176]. In addition, Miller *et al.* [172] found that the Pb isotopic ratios measured in the channel bed sediment changed from 2000 to 2002 to 2004. The differences appear to be related, in part, to the fact the mined ores were characterized by two distinct isotopic signatures, which they referred to informally as the Porco and Cerro Rico type ores. Ore bodies characterized by more than one isotopic signature have been described for a number of locations, and are not an uncommon phenomenon for many metallic deposits. In 2000, the channel bed samples immediately downstream of the mills exhibit ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ and ${}^{206}\text{Pb}/{}^{208}\text{Pb}$ ratios similar to Porco type ores, whereas in 2002 samples collected from along this reach exhibited a signature comparable to Cerro Rico type ores (Figure 10). This led them to argue that the change in isotopic ratios from 2000 to 2002 was likely to represent the processing of differing ore types.

Another interesting observation from along the Rio Pilcomayo is that ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ values within samples collected from the lower channel tended to decrease downstream toward the values observed within the Ordovician rocks. In contrast, ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ ratios measured in samples collected in 2002 showed no downstream trend; rather, the ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ ratios were either indistinguishable from the ratios within the Cerro Rico type ore deposits, or fell between the two types of ore deposits (Figure 10). The change in spatial patterns of the isotopic ratios was coincident with a decrease in: (1) Pb concentrations at any given location along the channel; and (2) the downstream extent of highly elevated Pb concentrations (Figure 10a). Miller *et al.* [172] suggest that the observed changes in Pb concentration and Pb isotopic values reflected annual differences in system hydrology and upland sediment inputs to the river. During wet years, such as 2000, the highly dynamic nature of the Rio Pilcomayo allowed larger quantities of Pb-contaminated sediment from the mines and mills to be transported downstream over longer distances, resulting in relatively high Pb concentrations. However, the proportion of the Pb derived from the mines decreased downstream, as indicated by the isotopic ratios, because significant quantities of uncontaminated fine-grained sediments were eroded from upland areas and delivery to the channel via tributaries as a result of significant runoff. During dry years, such as 2002, the transport of Pb-contaminated sediment from the mines and mills is reduced

decreasing the overall concentrations within the alluvial bed sediments. However, because there is much less sediment eroded from the surrounding uplands and delivered to the channel during the dry years, most of the Pb found in the channel is derived from the upstream mining operations. The study by Miller *et al.* [172] demonstrates that the source of Pb to the channel can vary over relatively short timeframes (*i.e.*, a year) as a function of the hydrology and sediment transport processes that characterize dynamic catchments. To date, very few studies have examined these types of short-term variations in isotopic signatures within alluvial sediments, and the topic clearly requires additional attention.

Figure 10. (A) Changes in Pb concentrations within channel bed sediments along the Rio Pilcomayo from 2000 to 2004. (B) Comparison of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios measured in channel bed sediments sampled in 2000 and 2002. In 2000, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios decreased downstream indicating that the relative contribution of Pb from mining operations at Cerro Rico declined as “clean” sediment from tributaries was introduced to the channel during relative high runoff events. In 2002, runoff events were limited during relatively low rainfall. As a result, the Pb ratios were generally indistinguishable from the Cerro Rico type ore deposits, which suggests that nearly all of the Pb was from mining operations (from Miller *et al.* [172]).



Within larger river systems contaminated by multiple Pb sources, or which are underlain by a wide range of bedrock types, the Pb isotopic signature of the alluvial sediments will reflect a complex mixture of material from the Pb sources [177]. As a result, well-defined mixing lines may not exist on binary scatter plots, and determining the relative contribution of Pb from the identified sources becomes much more difficult. However, where the Pb sources can be defined on the basis of isotopic ratios, statistically based mixing models may be used to determine the relative contributions of Pb to the river [168,169,172]. Bird *et al.* [169], for example, were able to use a two-tiered approach to assess Pb provenance within the River Maritsa catchment of Bulgaria and Turkey. Within smaller tributary basins, a binary approach was used to assess the contributions of Pb from mining operations to the alluvial sediments. However, the Pb isotopic composition of the lower catchment areas where sediment was derived from a wide range of geological materials inhibited the use of this binary method. Thus, they applied a multi-element geochemical mixing model (similar to that described earlier) to assess sediment/Pb provenance. A similar approach was used by Bird and his colleagues [168] along the lower Danube Catchment in Eastern Europe.

Miller *et al.* [172] used a slightly different approach by applying a mixing model directly to Pb isotopic ratios. In this case, they found that the majority of samples collected from agricultural fields located along the Rio Pilcomayo (described above) exhibited $^{206}\text{Pb}/^{208}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios within the limits formed by the four identified Pb source, (including, the Porco and Cerro Rico type ores, and Mesozoic Rocks and the Ordovician Rocks) (Figure 11). They were then able to use a mixing model similar to the one described earlier to determine the relative contribution of Pb within agricultural soils located along the Rio Pilcomayo. Miller *et al.* [172] found that within agricultural terrace soils, both Pb concentrations and the percentage of Pb from the mining and milling operations at Cerro Rico semi-systematically decreased downstream. In upstream reaches (within 30 km of the mills) Pb from mining accounted for more than 80% of the Pb found in the examined agricultural fields. Downstream at Sotomayor, located approximately 170 km from the mills, the relative contribution of Pb from the mines was highly variable between fields, but ranged from approximately 15% to 35%.

Pb isotopic data also have been combined with bulk concentration data to differentiate changes in contaminant provenance within floodplain deposits through time [45,170]. Villarroel *et al.* [45], for example, used a combination of bulk Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to assess the source of Pb and other correlated trace metals contaminants to floodplains used for agriculture along the Rio Chilco-Rio Tatasi River system of southern Bolivia. Figure 12 shows, as described earlier, that Pb and Zn were delivered to the axial drainage system from Sb mines located along the Rio Chilco and Pb/Zn mines located within the Rio Tatasi basin. Since Pb was derived from both of the major mining districts in the catchment, variations in Pb concentrations alone could not be used to assess which set of mines provided the majority of the trace metal contaminants to the river, or when. However, the incorporation of $^{206}\text{Pb}/^{207}\text{Pb}$ data into the analysis allowed the provenance of the Pb within the floodplain deposits to be determined for different depths/ages of deposition (Figure 12).

Figure 11. Soil samples from floodplain agricultural fields collected along the Rio Pilcomayo, Bolivia, exhibit Pb isotopic values that fall within the range established by four Pb sources, including Ordovician rocks, Mesozoic Rocks, and two types of ore deposits from Cerro Rico. As a result, mixing models could be used to assess the relative contribution of Pb from the underlying bedrock and mining operations (from Miller *et al.* [172]).

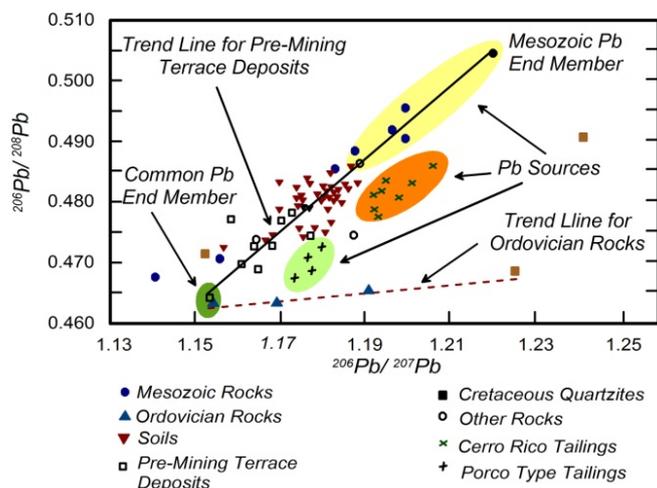
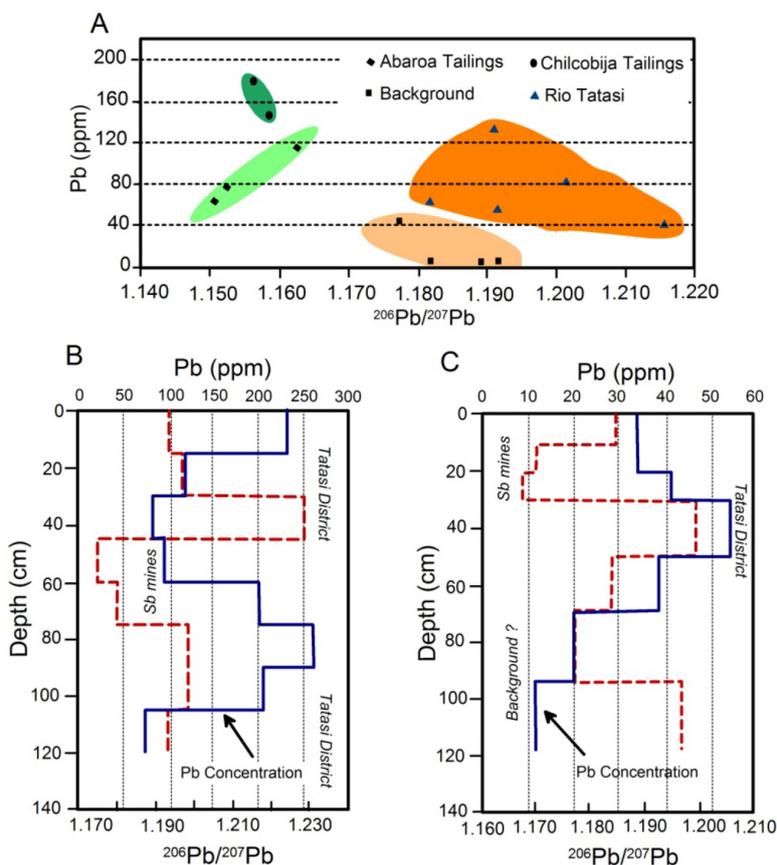


Figure 12. Pb from the local geological units, as well as from Abaróa, Chilcobija, and Rio Tatasi mines can be fingerprinted on the basis of total Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (A). The defined geochemical fingerprints can be used to assess changes in Pb contributions to the river system through time as recorded in floodplain deposits sampled at two different sites (B, C) (from Villarroel *et al.* [45]).



A different approach has occasionally been used to assess the relative contribution of Pb where three end-member sources can be identified on the basis of Pb concentration and a Pb isotopic ratio (e.g., [104,176]). In this case, sample concentrations and their associated isotopic ratios are graphically plotted. Linear mixing lines are subsequently calculated and drawn between the three sources creating a ternary diagram. The three mixing lines between the sources are calculated using two equations. The equations are:

$$R_{mix} = \frac{(R_1 C_1 X_1) + (R_2 C_2 X_2)}{C_{mix}} \quad (8)$$

and,

$$C_{mix} = (C_1 X_1) + (C_2 X_2) \quad (9)$$

where R_1 , R_2 , and R_{mix} are the isotopic ratios for end-member 1 and end-member 2 as well as a mixture composed exclusively of these two Pb sources, respectively, C is the concentration of Pb in the mixture and end-members, and X is the relative (fractional) contribution of Pb from the end-members. The fractional contribution from the two end-members must sum to unity (1). The relative contributions of Pb from the three sources then can be extracted from the ternary plot.

In addition to determining Pb and correlated trace metal provenance in riverine sediments, Pb isotopes have begun to be used for a wide range of other purposes, including the assessment of Pb loadings in both the dissolved and particulate form in river waters [133,166], Pb cycling, such as is involved with sediment/rock/water interactions [177,178], and the source of Pb in aquatic and terrestrial biota [147]. The use of Pb isotopes for these purposes is likely to expand significantly in the future.

4.3. Other Stable Isotopes as Geochemical Tracers

In addition to Pb, a number of other isotopes such as those of Nd, Sm, and Sr have been widely used by the geological community to determine the provenance of sediments in marine and riverine environments [109,179–182]. However, prior to the 1990s, the precision of determining the isotopic content of geological materials for many trace metal and metalloid contaminants was limited as a result of relatively small mass differences between the isotopes. This lack of precision in isotopic analysis inhibited their use as geochemical tracers as the variation in the measured isotopic composition *within* a given material was similar to that observed *between* geological materials. Recent advances in analytical capabilities have allowed for the precise determination of the relative isotopic abundances of elements with an atomic mass greater than 40 amu. These newly acquired methods have opened up the potential to utilize a wide range of non-traditional stable isotopes as geochemical fingerprints and tracers in forensic environmental studies. Given the novelty of the methods, only a handful of studies have examined the potential to effectively apply these isotopes as geochemical tracers of anthropogenic contaminants, and even fewer studies have focused on their potential use in riverine sedimentary environments. Here, we focus on six trace metal and metalloid contaminants (Cd, Cu, Cr, Hg, Sb, and Zn) that show some potential for use in river systems (Table 2).

Table 2. Summary of Selected Elemental Isotope Characteristics and Use as a Geochemical Fingerprint and Tracer.

Element	Stable Isotopes *	Frequently Used Isotopic Ratios ¹	Primary Fractionation Processes	Comments	Selected References Relevant to Riverine Environments
Cd	¹⁰⁶ Cd, ¹⁰⁸ Cd, ¹¹⁰ Cd, ¹¹¹ Cd, ¹¹² Cd, ¹¹³ Cd, ¹¹⁴ Cd, ¹¹⁶ Cd	¹¹⁴ Cd/ ¹¹⁰ Cd	Evaporation and condensation, including that associated with ore processing; biological processes	Possible use to assess nutrient uptake and translocation in microorganisms and plants; may be used to trace source, but not adequately tested	Gao <i>et al.</i> [183]; Cloquet <i>et al.</i> [184]; Weiss <i>et al.</i> [185]; Shiel <i>et al.</i> [186,187]
Cu	⁶³ Cu, ⁶⁵ Cu	⁶⁵ Cu/ ⁶³ Cu	Redox reaction; biogenic accumulation; solution speciation	May be used to assess redox processes during biogeochemical cycling and to trace source of Cu, but not adequately tested	Weiss <i>et al.</i> [185]; Bird [29]; Kimball <i>et al.</i> [188]; Zhu <i>et al.</i> [189]; Petit <i>et al.</i> [190]
Cr	⁵⁰ Cr, ⁵² Cr, ⁵³ Cr, ⁵⁴ Cr	⁵³ Cr/ ⁵² Cr	Redox reactions; equilibrium adsorption	May be used to assess redox processes during biogeochemical cycling of elements	Weiss <i>et al.</i> [185]
Hg	¹⁹⁶ Hg, ¹⁹⁸ Hg, ¹⁹⁹ Hg, ²⁰⁰ Hg, ²⁰¹ Hg, ²⁰² Hg, ²⁰⁴ Hg	²⁰² Hg/ ¹⁹⁸ Hg	MDF—Redox reactions, biomethylation, evaporation, condensation; absorption; MIF—photoreduction, biological transformations	May be used to assess redox processes during biogeochemical cycling of elements	Mil-Homes <i>et al.</i> [105]; Bergquist and Blum [191]; Yin <i>et al.</i> [192]; Sonke <i>et al.</i> [193]
Pb	²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb ²⁰⁶ Pb/ ²⁰⁸ Pb ²⁰⁷ Pb/ ²⁰⁸ Pb	Negligible; Isotopic composition dependent on initial geological source	Extensively utilized to assess Pb sources	Bird [29] Villarroel <i>et al.</i> [45]; Miller <i>et al.</i> [64,172]; Cheng [131]
Sb	¹²¹ Sb, ¹²³ Sb	¹²¹ Sb/ ¹²³ Sb	Redox reactions; biological activity; volatilization	Possible use to trace Sb sources; may be used to assess redox processes during biogeochemical cycling of elements	Rouxel <i>et al.</i> [194]; Wilson [195]
Zn	⁶⁴ Zn, ⁶⁶ Zn, ⁶⁷ Zn, ⁶⁸ Zn, ⁷⁰ Zn	⁶⁶ Zn/ ⁶⁴ Zn	Evaporation and condensation, including that associated with ore processing; biogenic uptake; diffusion, adsorption/complexation on organics and Fe oxides	Use appears promising for tracing Zn sources from industrial processes, particularly from ore processing; may be used to assess of Zn cycling in environment	Bird [29]; Sivry <i>et al.</i> [196]; Shiel <i>et al.</i> [187]; Bentahila <i>et al.</i> [197]; Petit <i>et al.</i> [190]

Note: ¹ Frequently used within environmental studies.

4.3.1. Zn and Cd Isotopes

Two important characteristics of Pb is that the Pb isotopic composition of an anthropogenic substance depends upon the ore deposits from which the Pb was derived, and the Pb isotopic signature of metallic ores differ from most other (geogenic) rocks and minerals. In addition, because mass-dependent fractionation of Pb by industrial or biological processes is negligible the measured Pb isotopic ratios within alluvial sediments result exclusively from the mixing of particles with different isotopic abundances. In contrast, variations in the isotopic abundances of Cd and Zn tend to be limited within natural geological materials (e.g., rocks, minerals, and ore deposits). However, measurable, but small variations in the isotopic composition of a material derived from the original rocks, minerals, ores, *etc.*, may occur as a result of isotopic fractionation processes (Table 2) [184,186,198,199]. The created isotopic variations may then be utilized as a geochemical tracer to determine contaminant sources [199,200].

Interest in using the non-traditional isotopes of Cd and Zn as tracers is partly related to the desire to directly track the transport and fate of these potentially toxic trace metals in environmental media, and the recognition they may provide information that cannot be derived from the use of Pb isotopic fingerprinting methods alone. For example, since the Pb isotopic composition of a material depends on the initial source of the Pb, it may not be possible to separate Pb coming from different industrial processes if the utilized Pb is from the same ore deposit [131]. Geagea [201] found, for instance, that Pb from municipal waste incineration plants was indistinguishable from the Pb associated within a steel plant, inhibiting the use of Pb isotopes as a tracer of Pb provenance. In contrast, the isotopic composition of an anthropogenic substance with regards Cd and Zn depends on mass-dependent fractionation processes (e.g., evaporation and condensation). Thus, the isotope composition of industrial materials with regards to Cd and Zn are likely to differ, even if the materials are produced at the same location, as long as they are created by different processes.

The use of Cd, Zn, and other non-traditional stable isotopes as tracers, however, is not without its challenges, in part, because fractionation is produced by a number of biotic and abiotic processes that allow the isotopic composition of the source materials to change after its release into the environment [202]. Thus, the measured isotopic abundances within a given media (e.g., alluvial sediment) will not only reflect the mixing of sediments from different sources, but isotopic fractionation as it is dispersed and cycled through the environment. As a result, a sound understanding of elemental cycling within the system is required for their utilization, and their potential use on a large (watershed) scale may be limited.

Unlike the isotopic abundances of Pb which are expressed as a ratio, the isotopic abundance of the non-traditional stable isotopes including Cd and Zn are expressed per 1000 (δ) or per 10,000 (ϵ) relative to a standard, due to extremely small variations that occur in nature. Mathematically,

$$\delta^{i/j} X = \left\{ \frac{\text{isotopic ratio of sample} - \text{isotopic ratio of standard}}{\text{isotopic ratio of standard}} \right\} \times 1000 \quad (10)$$

and

$$\epsilon^{i/j} X = \left\{ \frac{\text{isotopic ratio of sample} - \text{isotopic ratio of standard}}{\text{isotopic ratio of standard}} \right\} \times 10000 \quad (11)$$

where $\delta^{i/j}X$ and $\varepsilon^{i/j}X$ are the δ and ε values of the element, respectively, for the isotopic ratio represented by i/j . In most instances, the lighter isotope is used as the denominator, such as $\delta^{114/110}\text{Cd}$ (often shown as $\delta^{114}\text{Cd}$), in which case, $\delta > 0$ is heavier than the standard, and $\delta < 0$ lighter.

To date, the use of Zn has received the most attention of the two elements, and shows the most promise as a tracer in riverine environments [29,196,203–206]. The mass-dependent fractionation of Zn is dominated by evaporation and condensation processes, although biogenic uptake, diffusion, and adsorption onto organic, Fe oxides, and other materials may also lead to fractionation (Table 2) [186,205]. Zn isotopes may therefore be used to tracer Zn derived from metal mining and refining operations, the steel industry, coal power plants, vehicle traffic, and urban waste incineration [204].

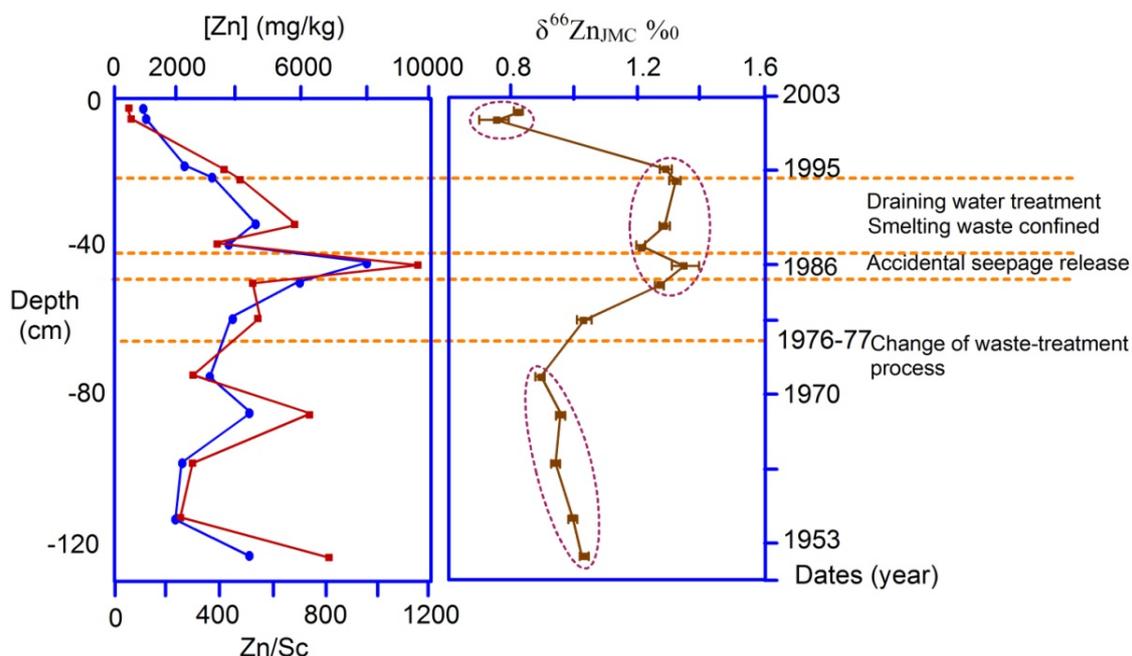
Due to the high relative abundances of ^{66}Zn and ^{64}Zn , and the ability to precisely measure their contents in geological materials, most studies have utilized $^{66}\text{Zn}/^{64}\text{Zn}$ ratios, reported as $\delta^{66}\text{Zn}$. Unfortunately, studies to date have utilized a number of different materials as a standard, making the direct comparison of reported $\delta^{66}\text{Zn}$ values difficult [203].

With regards to the fingerprinting and tracing of Zn within river systems, one of the most detailed studies to date is provided by Silvry *et al.* [196] in an examination of Zn contamination within the Lot River basin, France by the industrial exploitation of Zn ore (the same river system described in the section above on the construction of pollution histories, Figure 5). Sivry *et al.* [196] found that the Zn isotopes within the ore (exhibiting $\delta^{66}\text{Zn} \sim -0.16\text{‰}$) was highly fractionated during metallurgical processing forming tailings materials with $\delta^{66}\text{Zn}$ values up to $+1.49\text{‰}$. In addition, they were able to demonstrate that $\delta^{66}\text{Zn}$ values within sediments of the Riou Mort, a contaminated tributary, were significantly different than sediments found upstream of contaminant influx and the assumed regional background materials ($\delta^{66}\text{Zn}$ values of $+0.91 \pm 0.04\text{‰}$ as compared to $+0.31 \pm 0.06\text{‰}$). The changes in $\delta^{66}\text{Zn}$ values were consistent with the influx of tailings materials via the Riou Mort.

Sivry *et al.* [196] also found that systematic changes in $\delta^{66}\text{Zn}$ values were present within a dated sediment core extracted from a downstream hydroelectric reservoir (Figure 13). Sediments deposited between approximately 1952 and 1972 exhibited a mean $\delta^{66}\text{Zn}$ value of $+0.95 \pm 0.08\text{‰}$, and are thought to be representative of the metallurgical processes used for Zn extraction at the time. Sediments deposited during the late 1970s exhibit increasing $\delta^{66}\text{Zn}$ values until reaching a maximum value in 1986, after which they remain relatively constant until the mid-1990s (Figure 13). The heavier $\delta^{66}\text{Zn}$ values were shown to correspond to a change in ore processing techniques and increases in Zn extraction efficiencies. Thus, it is likely that sediments within the reservoir contain a record of inputs to the river by different industrial processing methods.

As noted above, a limitation of using Zn isotopes to assess pollution histories is that the Zn stored within the sediments may undergo fractionation after deposition. Weiss *et al.* [202], for example, showed that diffusion of dissolved Zn in ombrotrophic peat bogs altered its isotopic composition, resulting in higher $\delta^{66}\text{Zn}$ values at the bottom of collected cores, exactly where diffusion related Zn fractionation was expected to be most pronounced. In spite of the potential for post-depositional fractionation, the work by Silvry *et al.* [196] suggests that it may not be a significant problem in all depositional environments.

Figure 13. Vertical (depth/time) variations in total Zn concentrations (red squares), Zn/Sc ratios (blue circles), and $\delta^{66}\text{Zn}$ values (brown diamonds) measured in samples from a core extracted from the Cajarc reservoir along the Lot River, France (figure from Sivry *et al.* [196]; Zn and Zn/Sc variations from Audrey *et al.* [101]). The correlation between Zn concentration and isotopic trends suggest that Zn isotopes can be used to determine Zn source.



Although our focus in this review is on the use of geochemical tracers to identify trace metal sources in sediments, it is worth noting that Zn isotopes hold considerable promise in tracing anthropogenic contaminants in river waters [204–206]. Chen *et al.* [204], for example, found that spatial and temporal variations in Zn concentrations and enrichment factors varied semi-systematically with $\delta^{66}\text{Zn}$ values, showing that it was possible to use Zn isotopes as an indicator of anthropogenic contamination.

In comparison to Zn, much less work has been conducted on the use of Cd isotopes as a tracer of Cd provenance within alluvial sediments. In fact, with the exception of Gao *et al.* [183], the application of Cd isotopes as a tracer in riverine sedimentary systems seems to be lacking at the present time. However, recent studies have shown that Cd isotopes may prove effective at assessing Cd sources and cycling dynamics in river waters [207]. Like Zn, evaporation and condensation are the primary processes involved in the mass-dependent fractionation of Cd isotopes (Table 2). Thus, significant Cd fractionation is likely to accompany industrial evaporation and condensation processes, an assumption supported by the work of Cloquet *et al.* [184,208]. Other analysts suggest that fractionation also is associated with biological processes [185,209].

While generally small, the degree of fractionation, particularly by metallurgical processes (smelting, refining, *etc.*), appears to be significant enough to use Cd isotopes to identify specific anthropogenic Cd sources. For example, Cloquet *et al.* [184] argued that systematic variations in $\delta^{114/110}\text{Cd}$ ($\delta^{114}\text{Cd}$) values in top soil near a smelter in northeast France could be used to trace Cd provenance. Similarly, Shiel *et al.* [187] suggested that differences in $\delta^{114}\text{Cd}$ values measured in

marine bivalves was related to variations in the relative contribution of Cd from natural and anthropogenic sources.

4.3.2. Cu and Cr Isotopes

In contrast to Cd and Zn which are stable at the Earth's surface in a single valence state, Cu and Cr are stable in two oxidative states [210]. As a result, redox reactions which are not involved in the fractionation of Cd and Zn play a key role in the isotopic fractionation of both Cu and Cr. In the case of Cu, a number of studies have shown that the abiotic oxidative dissolution of Cu sulfide minerals, in which Cu(I) is the common form, will result in an aqueous Cu(II) product being heavier than in the original mineral [188,211]. In the presence of certain microbes, however, the fractionation between aqueous Cu and mineral Cu appears to decrease, apparently as a result of the preferential accumulation of the heavier ^{65}Cu with the bacterial cell wall [210]. In the case of Cr, the reduction of highly toxic and water-soluble Cr(VI) by both abiotic and biotic processes appears to result in relatively insoluble Cr(III) that is approximately 3‰ to 5‰ lighter than the remaining Cr(VI) [185,210,212,213].

The oxidation of Cu sulfide minerals is a common process along many mine contaminated river systems resulting in acid mine drainage. As a result, variations in the Cu isotopic values observed between sulfide minerals, river waters, and secondary mineral precipitates may be useful for assessing various biogeochemical processes that influence the dispersal and cycling of Cu within mine contaminated riverine environments [29,214,215]. The use of Cu isotopes to tracer to source of Cu in rivers is less clear. Their use in the sedimentary components of the river may be limited because: (1) Cu isotopic variations within a deposit are often greater than those observed between deposits [216]; and (2) redox reactions may alter Cu isotopic ratios both during dispersal and after deposition. Nonetheless, Bird [29] argued that while the use of Cu isotopes was not without its challenges, they have potential to effectively determine Cu provenance.

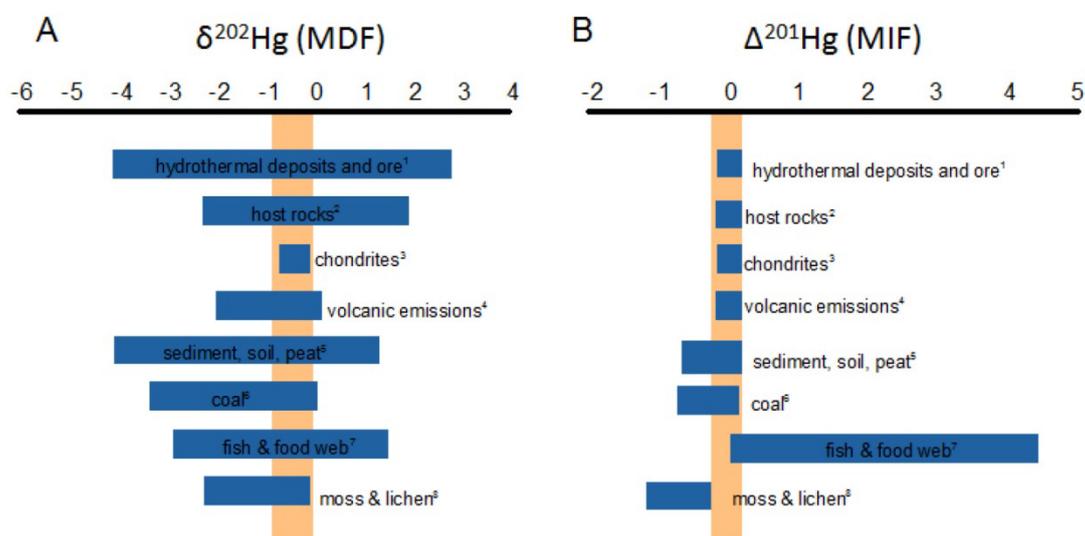
As for Cu the use of Cr isotopes to determine contaminant provenance in rivers has yet to be adequately demonstrated. However, isotopic contrasts between insoluble Cr(III) and Cr(VI) in the coexisting waters should allow for Cr isotopes to distinguish between natural and anthropogenic Cr in aquatic systems [210]. In fact, Cr isotopes have been used to identify anthropogenic sources and to assess Cr migration processes (e.g., dilution and reduction) in groundwater [217–219].

4.3.3. Mercury Isotopes

Hg is considered a priority pollutant on a global scale and once released into the environment, its biogeochemical cycling is highly complex, owing in part to the fact that it possesses a stable gaseous form (Hg^0), and may undergo a wide range of redox, phase, and biologically mediated transformations. In fact, methylmercury, the form predominantly accumulated in biota, is primarily produced by sulfate reducing microbes. Until recently, understanding the primary sources and biogeochemical cycling of Hg in a particular system relied on an analysis of total Hg concentrations within the media of interest, its chemical speciation in those media, and/or the application of mass balance and geochemical models [193]. It is now clear, however, that numerous inorganic and organic reactions result in Hg isotopic fractionation (Table 2), producing large variations in the Hg isotopic composition of natural and anthropogenic materials (Figure 14) [191]. These variations in Hg isotopic values may be

used to assess Hg source(s), pollution histories, and transformations during biogeochemical cycling [105,191–193,220]. Thus, significant effort has recently been devoted to determining the mechanisms of Hg fractionation, and how Hg isotopes may be used to assess Hg transport and fate in atmospheric, aquatic, and terrestrial systems.

Figure 14. Summary of published Hg isotopic data (from Bergquist and Blum, [191]). The horizontal bars represent range in mass-dependent fractionation (A) and mass-independent fractionation (B). The vertical bars represent the estimated crust- and mantel-derived Hg. Data sources: 1, Hintelmann and Lue [221], Smith *et al.* [222], Smith *et al.* [223]; 2, Smith *et al.* [223]; 3, Lauretta *et al.* [224]; 4, Sonke *et al.* [225], Zambardi *et al.* [226]; 5, Jackson *et al.* [227], Foucher and Hintelmann [228], Biswas *et al.* [229], Ghosh *et al.* [230], Jackson *et al.* [231], Fourcher *et al.* [232], Gehrke *et al.* [233]; 6, Biswas *et al.* [229], Gosh *et al.*[230], Carignan *et al.* [234], Bergquist *et al.* [191].



There are seven stable isotopes of Hg. Variations in Hg isotopic values within a given media results from both mass-dependent and mass-independent processes (Table 2). Mass-independent fractionation of stable isotopes is highly unusual and, in the case of Hg has only been observed to affect the odd isotopes (¹⁹⁹Hg, ²⁰¹Hg). Thus, the ratio of ¹⁹⁹Hg to ²⁰¹Hg may be particularly useful for characterizing chemical pathways, such as photochemical reduction, associated with mass-independent fractionation processes [191].

Mass-dependent isotopic compositions are reported using δ notation and the NIST Hg standard 3133 expressed mathematically as:

$$\delta^{202}X = \left\{ \frac{\left(\frac{{}^{202}\text{Hg}}{{}^{198}\text{Hg}} \right)_{\text{Sample}}}{\left(\frac{{}^{202}\text{Hg}}{{}^{198}\text{Hg}} \right)_{\text{SRM3133}}} \right\} - 1 \times (1000) \tag{12}$$

Mass-independent fractionation of the odd isotopes is reported as the difference between the measured δ¹⁹⁹Hg and δ²⁰¹Hg values to the predicted mass-dependent values as follows [235]:

$$\Delta^{201}\text{Hg} = \Delta^{199}\text{Hg} - (\delta^{202}\text{Hg} \times 0.2520) \quad (13)$$

and

$$\Delta^{201}\text{Hg} = \Delta^{201}\text{Hg} - (\delta^{202}\text{Hg} \times 0.2520) \quad (14)$$

As was the case for Cd and Zn, studies have suggested that metallurgical processes will result in waste products with distinct Hg isotopic signatures. As a result, the initial studies of Hg isotopes suggest that their analysis within samples from sedimentary deposits, including those within riverine environments, may be used to assess both Hg sources and loading histories [105,193,232,236–238]. Sonke *et al.* [193], for example, found that within the Lot River basin, France metal refining resulted in slag residues that exhibited heavier Hg isotopic values, and both mass-dependent and mass-independent Hg isotopic signatures of contaminated sediments were significantly different (heavier) than that of the local background materials. Once again a primary concern in the use of Hg isotopes within riverine environments is whether the contaminated source sediments will retain the original signature during transport and/or following deposition as a wide range of fractionation processes are available to alter its isotopic composition (Table 2) [237]. However, the work by Sonke *et al.* [193] suggests that Hg isotopes may behave conservatively in some sedimentary environments. Hg isotopes appear, then, to have considerable potential as a tracer of contaminant sources, transport processes, loading histories, and biogeochemical processes in river systems.

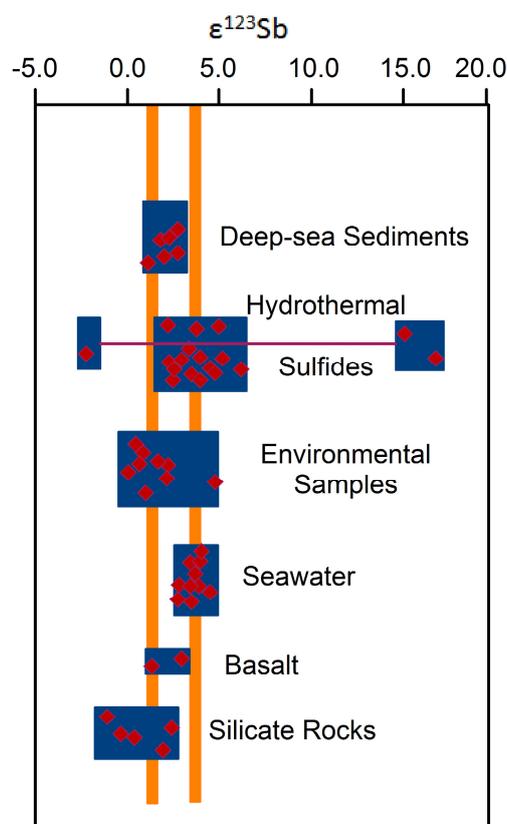
4.3.4. Sb Isotopes

Sb has two stable isotopes, ^{121}Sb and ^{123}Sb . Sb isotopic fractionation primarily occurs by redox changes of Sb(V) and Sb(III), the primary species found in aquatic environments, as well as by biological activity and volatilization [194]. The use of Sb isotopes as a geologic tracer has been limited to date, in part because Sb concentrations are typically low in many natural and anthropogenic materials, and the measurement of Sb isotopes is somewhat challenging. However, Rouxel *et al.* [194] demonstrated that precise measurements can be obtained for sea water and a variety of other geological materials using a MC-ICP-MS when Sb concentrations are at or above background values (Figure 15). Moreover, they found that the Sb isotopic composition of a variety of the studied materials varied significantly (Figure 15), leading them to suggest that Sb isotopes may serve as extremely useful tracers for the analysis of natural processes.

The only known application of Sb isotopes to riverine environments was conducted by Wilson [195] within the Rio Loa basin of northern Chile. The Rio Loa is extensively contaminated by Cu, As, Sb, and a variety of other trace metals from Cu mining and refining operations as well as by El Tatio, a natural geyser basin. Contaminated sediments from mining and refining operations and the geyser field were found to have similar Pb isotopic values, inhibiting the use of Pb as a tracer. Thus, Wilson [195] attempted to use Sb isotopes, which were hypothesized to serve as an effective tracer of sediment from geyser basin because: (1) the discharge of near boiling, silica-rich waters at El Tatio contain some of the highest reported surface water concentrations of Sb in the world; (2) the discharged Sb is incorporated at high concentrations (up to as much as 2 wt %) as Sb_2O_3 in silica based geyserite precipitates, and therefore should behave conservatively in sediment; and (3) concentrations

of Sb are relatively low in the local bedrock and the Cu mine related materials (ore, tailings, *etc.*). Wilson [195] found that the Sb isotopic composition of sediments from the geyser field varied significantly, and therefore like Pb, could not be used to distinguish between Sb from the mines and Sb from the geysers. However, the Sb isotopic composition of the mines and geyser field differed significantly from Sb associated with other geological materials in the basin (e.g., rocks, sediments, soils), suggesting that Sb may serve as an effective tracer in mining wastes in some riverine environments.

Figure 15. Summary of $\epsilon^{123}\text{Sb}$ values measured in various natural materials. Variations indicate that Sb isotopes may be used as a contaminant tracer in geological media (from Rouxel *et al.* [194]).



5. Summary and Concluding Remarks

Environmental forensic investigations have increasingly relied on geochemical tracers to determine contaminant provenance, transport, and fate in contaminated rivers. Historically, contaminant fingerprints/tracers for point-source pollutants (e.g., trace metals from mining and refining operations) were based on bulk elemental concentrations, or related ratios, of the contaminants of interest. Provenance was determined on the basis of the geographical patterns of tracer concentration along the channel in comparison to background values. More recent investigations have combined tracer concentration data with sediment mixing models to not only determine contaminant source, but the relatively contribution of contaminants from a specific source or tributary basin. Although the modeling results are highly useful, they yield non-unique results, which when combined with the assumptions required for their use, lead to uncertainties in estimated source contributions. New

innovative statistical methods are needed to more accurately assess relative contaminant contributions when multiple natural and anthropogenic sources of trace metal contaminants exist.

Stable Pb isotopes have been shown to be particularly sensitive tracers that are highly effective at determining both the source and source contributions of Pb in rivers. Pb isotopes are most effectively used where there is a dominant source of Pb in the basin in addition to the Pb from the underlying bedrock (as is often the case in rivers contaminated by mining and/or refining operations). Where multiple Pb sources exist, fingerprinting the source materials may prove more difficult, and source contributions (when more than three sources exist) will need to rely on sediment mixing/unmixing models.

Advances in analytical chemistry, particularly the advent of the MC-ICP-MS, have created the possibility that a wide range of non-traditional stable isotopes can be used as environmental tracers, including Cd, Cu, Cr, Hg, Sb, and Zn. In contrast to Pb, differences in the isotopic composition of geological and anthropogenic materials are due to physical and chemical isotopic fractionation processes. As a result, it may not only be possible to determine a contaminant source on the basis of these isotopes, but to link trace metal concentrations to specific industrial processes used during a given time period at a single source location. In addition, some isotopic systems (e.g., Cr and Cu which are redox sensitivity) may be used to gain insights into biogeochemical cycling with river systems. The use of these non-traditional isotopes, however, is complicated by the potential for isotopic fractionation during contaminated dispersal or following deposition. Detailed information regarding the cycling of the utilized isotopes is therefore required for their effective use. Based on a relatively limited number of studies, the isotopes of Zn and Hg appear to hold the most promise in riverine environments for determining trace metal provenance in sediments or, in the case of Hg, assessing the biogeochemical cycling of trace metals in the aquatic environment. There is a dramatic need for additional studies that explore the use of these non-traditional stable isotope systems as tracers in riverine environments.

Innovative environmental forensic investigations in the 21st century will be characterized by a highly multidisciplinary approach that: (1) combines geochemical tracer studies with detailed stratigraphic, geomorphic, and hydrologic data; and (2) utilizes multiple isotopic tracers to more fully understand the temporal and spatial changes in trace metal source and source contributions along the river as well as the biogeochemical cycling of the metals within the aquatic system. In doing so, the developed conclusions will be based on multiple lines of evidence that are likely to withstand the scrutiny of judicial review.

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Conflict of Interest

The author declares no conflict of interest.

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