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Application of Geochemical Tracers to Fluvial Sediment

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To Dale (Dusty) F. Ritter
(1932–2012)
Teacher, Mentor, Colleague, and Friend

Jerry R. Miller
Suzanne M. Orbock Miller

To Timothy J. Hodges
For His Constant Support and Encouragement

Gail Mackin

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Chapter 1
Introduction

1.1 Tracers, Fingerprints, and Riverine Sediments

Tuero Chico is a small village located along the Rio Pilcomayo of southern Bolivia. Soils associated with its farmed floodplains possess Pb concentrations that exceed recommended guidelines for agricultural use. The elevated levels of Pb raise a number of important questions: Is the Pb derived from upstream mining of the Potosi precious metal-polymetallic tin deposits, or waste products disposed of in the river from the City of Potosi? Perhaps it is natural, being derived from local mineralized rocks that underlie the catchment? Or, could the Pb come from a combination of all three sources? If it is from multiple sources, how much comes from each source? And, how far downstream does the Pb from a specific source impact sediment and water quality? These and other complex physical and biogeochemical questions are increasingly being addressed using environmental tracers. In this book we examine the past, current, and future use of environmental tracers to assess the provenance, movement, and ultimate fate of sediment within river systems, particularly sediments contaminated by chemical substances that have the potential to degrade aquatic ecosystems and/or human health. The term *tracer* has been defined in different ways depending on the media (e.g., air, ice, snow, ground- or surface waters) to which it is applied. For our purposes, a *tracer* is defined as a unique sediment-associated parameter or set of parameters that is distinct from other sediments in the catchment, and can therefore be used to track the movement and cycling of specific sediments from their point of origin to their ultimate point of deposition. The term 'tracer' is often defined and used synonymously with *fingerprint*. However, when applied to river (fluvial) systems, a fingerprint is most commonly associated with a specific type of analyses (fingerprinting studies) in which multiple parameters are used to distinguish between sediments from diffuse (non-point) sources to quantify the provenance of the sediment found in a river or riverine deposit.

The use of fingerprinting and tracing methods to assess the dynamics of sediment generation, transport and storage has a long history in both fluvial sedimentology and geomorphology, dating back to at least the early 20th century (e.g., Boswell 1933).

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It was not until the middle of the 1900s, however, that the potential for tracer studies to provide meaningful data on sediment dynamics began to be appreciated (Walling et al. 2013). Early studies were primarily aimed at understanding particle entrainment thresholds and transport distances of large bed material clasts within short reaches of the channel and were based on what Black et al. (2007) calls 'particle tracking'. Essentially, particle tracking refers to (1) the practice of tagging individual clasts in some fashion so their movement can be documented, especially during storm events, or (2) the addition of exotic constituents to a mixture of sediment so that the movement of sediment of similar characteristics can be monitored. These studies initially relied on rather unsophisticated methods (e.g., painting of a particle surface), but have evolved so that particle tracking now includes such sophisticated technologies as inserting magnets or radio-transmitters into individual clasts of varying size, or incorporating Rare Earth Elements, magnetic constituents (e.g., magnetite), and other materials in the sediment to monitor their incipient motion and transport distances in near real-time (Parsons et al. 1993; Zhang et al. 2003; Kimoto et al. 2006; Mentler et al. 2009; Guzmán et al. 2010; Hu et al. 2011; Spencer et al. 2011). These techniques can also be used to assess such things as transport step lengths and rest periods for variously sized particles, and have been applied to other problems such as soil erosion rates and redistribution patterns on hillslopes.

The 1980s and 1990s saw an expansion of tracer research to address a number of additional aspects of the sediment system, including the origin and transport mechanisms of particles found in both consolidated (sedimentary) and unconsolidated deposits. Walling et al. (2013) point out that these studies differed from earlier particle tracking methods in three important ways. First, particle tracking as originally conducted required the addition of a tracer material which was costly to use over large areas; thus, the addition of a tracer was (and continues to be) restricted to short reaches of river channel or small soil plots. To circumvent this problem, investigators began to utilize natural characteristics of the sediment (e.g., its mineralogy, grain size, color, chemical composition, and magnetic properties) as a tracer, or utilize some pre-existing constituent within the sediment. With respect to the latter, tracers often consisted of anthropogenic constituents (e.g., ^{137}Cs from surficial nuclear bomb tests or trace metals from mining operations). Second, the use of natural and pre-existing tracers allowed the area of study to be greatly expanded from short river reaches or small soil plots to the landscape scale. From this larger scale perspective, the sediment system can be envisioned as an integrated sediment generation and dispersal network in which sediments are produced in upland areas and ultimately deposited downstream in a basin that acts as a long-term repository (Fig. 1.1). These zones of sediment production and deposition are connected by a drainage network that intermittently moves sediment, primarily during flood events, from source to sink (Schumm 1977; Weltje 2012). Tracers, at this scale, can be used to address aspects of the entire, and highly complex, sediment dispersal system over a variety of temporal scales. Third, fingerprinting and tracing methods began to focus upon the fine-grained sediment fraction, rather than the coarse-grained bed load (Walling et al. 2013). Interest in fine-sediments resulted from the fact that the excessive generation and transport of particulates $<\sim 2$ mm in size pose a direct threat

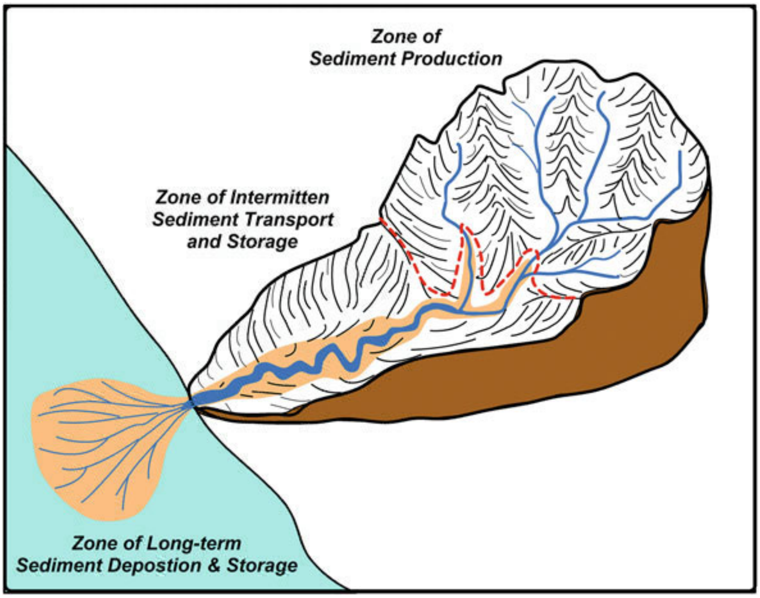

Fig. 1.1 Schematic diagram of riverine sediment-dispersal system (after Schumm 1977)

to ecosystem health. For example, the National Water Quality Inventory, a program in the U.S. developed to assess the current condition of the nations water resources, indicates that sediment is the second leading cause of river impairment (Fig. 1.2) (USEPA 2013). Moreover, anthropogenically derived sediment can result in rapid episodes of reservoir sedimentation, reduce reservoir storage capacity, impact water distribution systems, increase turbidity and reduce light penetration, degrade aquatic habitat, and lead to a loss in aesthetic quality of the riverine environment. The annual costs of human-induced sediment influx to rivers and streams have been estimated to range from 20 to 50 billion dollars in North America alone (Pimentel et al. 1995; Osterkamp 2004; Mukundan et al. 2012).

From a chemical perspective, fine-grained sediments, particularly those composed of clay minerals, Fe and Mn oxides and hydroxides, and organic matter are highly reactive (Horowitz 1991). Thus, sediment suspended within the water column and that forms the channel bed and banks, typically exhibit concentrations of hydrophobic contaminants that are orders of magnitude higher than those associated with the aqueous (dissolved) load. Gibbs (1977), for example, examined the concentration of selected metals (including Cu, Co, Cr, Fe, Mn, and Ni) associated with suspended sediment within the Yukon and Amazon River basins, two river systems characterized by different hydrologic regimes and geological terrains. He found that within both basins sediment-associated trace metal levels ranged from 6,000 to more than 10,000 times greater than their dissolved concentrations. As a result, trace metal transport was dominated by the particulate load (Fig. 1.3). Subsequent studies (e.g., Horowitz and Elrick 1988; Meybeck and Hemler 1989; Horowitz 1991) supported Gibbs'

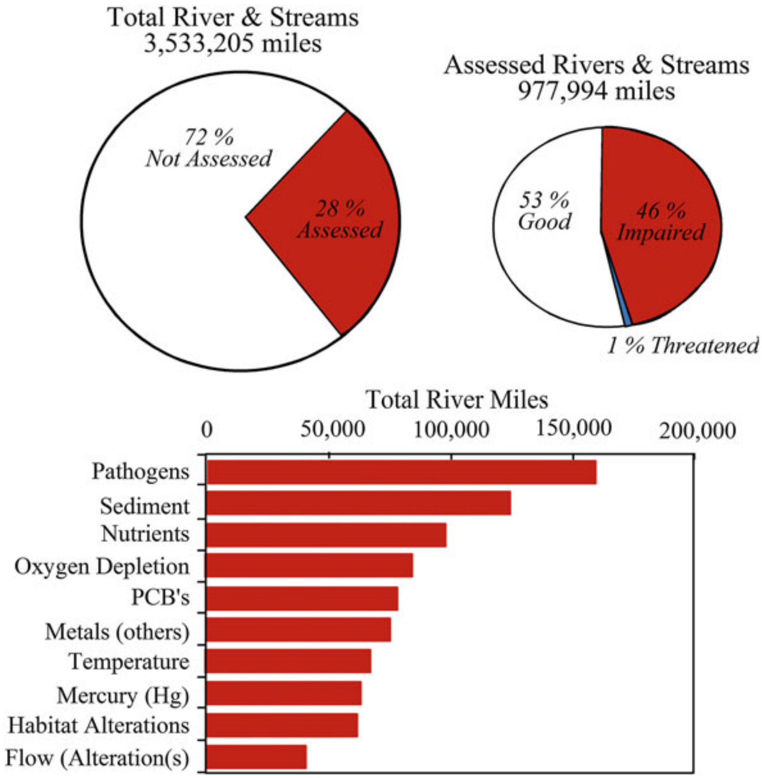

Fig. 1.2 Leading causes of river impairment in the U.S. as determined by the National Water Quality Inventory. Data reported for 2010–2012 (depending on state). Note that sediment is the second leading cause of impairment (data from USEPA 2013)

observed differences between dissolved and particulate concentrations. This led to the argument that within rivers exhibiting typically observed pH and Eh conditions more than 90 % of the trace metal load is transported as part of the sediment load (Table 1.1).

The potential for sediment and sediment-associated contaminants to negatively impact aquatic ecosystems has led to the general evolution in the application of environmental tracers from a state in which they were primarily used in academic studies to their use as a management and regulatory tool. While this evolution in tracer utilization has been slower with regards to rivers than it has been for, say, groundwater, it is likely to progress in the future. It is also likely to be closely linked to the developing field of *Environmental Forensics*. Haddad (2004) described Environmental Forensics as "that part of the Venn Diagram where environmental technical questions overlap legal issues". A more detailed definition, put forth by Wenning and Simmons (2000), is the "systematic examination of environmental information to determine sources of chemical contamination, the timing of releases to the environment, the spatial distribution of contamination, and the potential responsible party(ies)". It seems

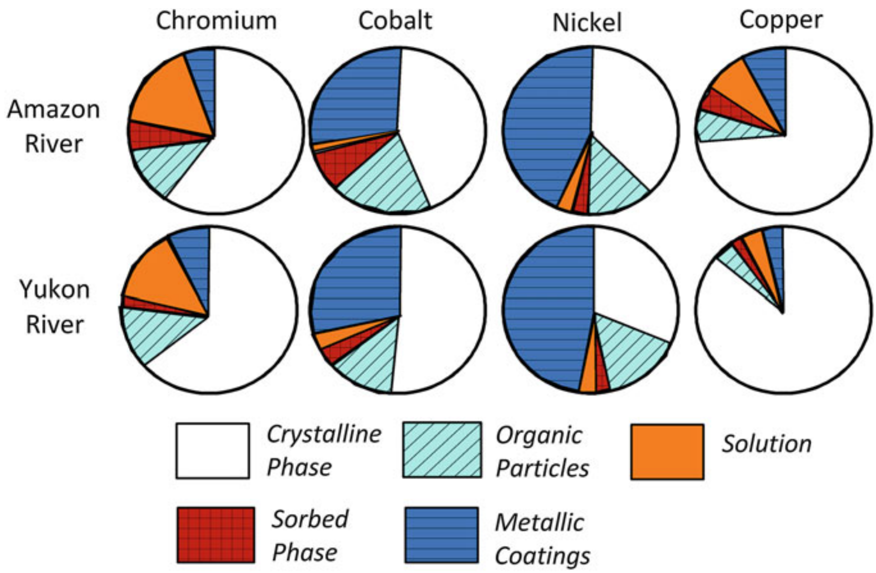

Fig. 1.3 Percentages of selected metals transported in the dissolved and particulate phases within the Amazon and Yukon Rivers. The percentages transported with particulate species are generally greater than 90 % (data from Gibbs 1977; figure from Miller and Orbock Miller 2007)

Table 1.1 Ratio of dissolved to total elemental transport in rivers

Percentage (%)	Elements	Dominant transport load
1–0.1	Ga, Tm, Lu, Gd, Ti, Er, Nd, Ho, La, Sm, Tb, Yb, Fe, Eu, Ce, Pr, Al	Particulate phase
10–1	P, Ni, Si, Rb, U, Co, Mn, Cr, Th, Pb, V, Cs	Particulate phase
50–10	Li, N[a], Sb, As, Mg, B, Mo, F[a], Cu, Zn, Ba, K	Mixed aqueous and particulate phase
90–50	Br, I[a], S[a], Cl[a], Ca, Na, Sr	Aqueous phase

Lower percentages indicate a greater proportion within the particulate phase
[a]Estimates based on elemental contents in shales
Adapted from Martin and Meybeck (1979)

fair to say that the field has grown over the past 20-years into a scientific subdiscipline in and of itself as indicated by the publication of multiple books on the topic (e.g., Morrison and Murphy 2006; Murphy and Morrison 2007; Morrison and Sullivan 2007; Hester and Harrison 2008; Mudge 2009; Bergslien 2012), the creation of two scientific journals devoted entirely or partially to the field (*Environmental Forensics* and *Environmental Science: Processes and Impacts*), and the creation of university degree programs in Environmental Forensics.

Even a cursory examination of the above mentioned books shows that tracer technology has become an integral part of Environmental Forensics. For example, tracers have not only been used to determine sediment/contaminant provenance in riverine systems, but they have now been applied to address a host of other issues ranging from the redistribution of sediment on hillslopes, to the exchange rates and residence times of sediment within the channel, to the rates of sediment movement to the catchment mouth, to the biogeochemical cycling of contaminants within the aquatic environment. Tracers have also been used to provide retrospective information on geomorphic and geochemical processes and process rates over the past several decades to centuries, data that cannot be obtained by traditional monitoring programs. For example, geochemical tracers may be incorporated into channel, floodplain, or terrace deposits where their analysis may be used to unraveled such things as the timing and history of contaminant influx to rivers and/or the dispersal pathways through which contaminants are distributed along the river (Miller 2013; Miller and Orbock Miller 2007). In light of the above, tracers can be used to decipher potential environmental impacts of sediment and sediment-associated contaminants on river systems, and determine potentially responsible parties associated with these impacts.

The primary objectives of the following chapters are to (1) provide an in depth discussion of the theory, methodology, and application of environmental tracer and fingerprinting methods that have and are currently being used to address the source, transport, and deposition of sediment and sediment-associated contaminants within river systems, and (2) provide an analysis of the strengths and limitations of the examined techniques in terms of their temporal and spatial resolution, data requirements, and inherent uncertainties in the generated results. We will focus on the use of natural and anthropogenic geochemical tracers that currently exist within surficial geological materials, rather than 'particle-tracking' techniques. It is important to recognize that our intent is not to replace other forms of analyses of the sediment system, but to show how tracer/fingerprinting studies can be used to gain insights into system functions that would not otherwise be possible. In fact, significant attention is given to ways in which fingerprinting and tracer technologies may be integrated with other hydrological, geochemical, geomorphic, and stratigraphic techniques to address the complexity inherent in the dispersal of sediment and sediment-contaminated materials through riverine environments. Given that the use of tracers to address legislative or legal issues will undoubtedly increase in the coming years, we will, where possible, address a number of topics that are critical to environmental forensics, including whether the methods represent (1) valid and testable approaches that have gained widespread acceptance through the peer review process, (2) generate results with quantifiable errors or levels of uncertainty, and (3) can be easily understood by individuals who may not have a scientific background (e.g., as a judge or jury).

1.2 Book Format and Overview

We begin our discussion of environmental tracers in Chap. 2 with an overview of what is typically referred to as geochemical fingerprinting. The fingerprinting approach is typically focused on sediment, rather than contaminants (although contaminants