

# Trace Metals in Aquatic Systems

Robert Mason

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Aquatic Systems**



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 **WILEY-BLACKWELL**  
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# Preface

This book is an outgrowth of a number of courses I have taught over the last seven years at the University of Connecticut. While written as an upper level text, it should also be useful to environmental scientists interested in trace elements in aquatic systems. Much of the information is derivative from a class in Environmental Chemistry that I introduced and later taught with Ron Siefert within the University of Maryland Center for Environmental Science. Readers will see the influences of my graduate and post-doc mentors, Bill Fitzgerald, Francois Morel and Harry Hemond, in the book's focus, and my exposure to books such as Broecker and Peng *Tracers in the Sea*, Stumm and Morgan *Aquatic Chemistry* and Morel and Hering *Principles and Applications of Aquatic Chemistry*, and their related texts. These excellent primary texts have been supplemented in recent years by many other books, including compilations such as the *Treatise on Geochemistry*, but I always find myself constantly referring to the earlier works. In studies of trace metals and metalloids one must always reflect on the underlying principles which are easy to forget, especially if an element is studied in isolation.

Much of my graduate work focused on making precise and accurate measurements of mercury speciation in the ocean and freshwaters, which solidified my appreciation for the care and rigor needed for environmental research. These pursuits took me to the equatorial Pacific in late 1989, and important research findings. Many other journeys, including oceanic cruises in the Atlantic and Pacific, and studies in small and large lakes and in the atmosphere, are what delivered me to where I am today, and the contents of this book. I acknowledge the many students who have helped me refine my teaching approach and improve the delivery of the often complex messages relating to the biogeochemical cycling of elements in aquatic systems, which is reflected in the book. There is obviously more emphasis on certain elements over others, but I have endeavored to focus on a particular topic because of its biogeochemical importance and potential impact on humans and the environment, rather than because of personal bias. I hope that I have succeeded as it is not possible to cover all topics in detail within the page limits of the publisher, or in a book suitable as a one semester course. In this vein, I have chosen focus topics in the latter chapters as examples demonstrating chemical principles and focusing on problems of global importance.

While the book has almost 1000 references this is clearly the tip of the publication "iceberg". I have referred to the primary literature except in cases when there was a high quality recent compilation chapter or review article. The reader is encouraged to examine the references within these reviews. I am sure that some readers may not understand why I did not cite their work, but I endeavored to remove bias in the choice of citations. The book was an undertaking of many years and so the citations reflect the order the chapters were written, which was not totally chronological. Where possible, I used examples from locations around the world.

I thank Stan Wakefield and Ian Francis for helping me get connected with the publisher about 6 years ago and for the help of many people at Blackwell during the process of publication. I thank the reviewers of the original book proposal for their comments that helped frame the content. I especially thank two anonymous reviewers for their comments on the first complete draft of the book. This was a tall order that they did with diligence and their comments were very useful. I also thank those who read sections of the book, or helped with the editing, especially Elsie Sunderland, Brian DiMento and Amina Schartup. Also, I acknowledge support from the University of Connecticut Small Grant Program for student support for the book compilation and also for funds to help cover the costs of obtaining permission to reuse figures. Obtaining permissions, and the associated costs, are an unfathomable detour along the road to publication even given the advances of the electronic age. I will endeavor in the future to make figures in my publications as clear as possible as even with electronic tools it is not always easy to reproduce figures already in the literature.

I never thought it would take this long, but it did. This lack of foresight is probably a good thing as I am sure my wife Joan would have been less enthusiastic had she known the truth. I thank her for her support through the process. The book writing occurred in stages and that may be evident to the reader, and was interrupted by the realities of academic life. For example, three of my PhD students have graduated since I started the book, and much new research has come to light, which was an ongoing challenge to try and keep the text as current as possible. I hope to have succeeded in this. Enjoy.

Robert P. Mason

# About the companion website

This book is accompanied by a companion website:

[www.wiley.com/go/mason/tracemetals](http://www.wiley.com/go/mason/tracemetals)

The website includes:

- Powerpoints of all figures from the book for downloading
- PDFS of tables from the book
- Answers to end of Chapter Problems

## CHAPTER 1

# Introduction

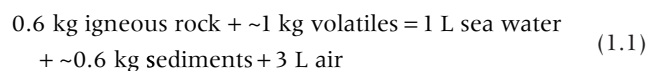
### 1.1 A historical background to metal aquatic chemistry

In terrestrial waters, much of the initial work by environmental engineers and scientists was aimed at understanding the processes of waste water treatment, and of the reactions and impact of human-released chemicals on the environment, and on the transport and fate of radioactive chemicals. This initial interest was driven by the need to understand industrial processes and the consequences of these activities, and the recognition of the potential toxicity and environmental impact of trace metals released during extraction from the Earth as well as during refining and use. Initial interest in the chemistry of the ocean was driven by the key question of why the sea is salty. Of course, it is now known that freshwaters, and even rainwater, contain a small amount of dissolved salts; and that the high salt content of the ocean, and some terrestrial lakes, is due to the buildup of salts as a result of continued input of material to a relatively enclosed system where the major loss of water is due to evaporation rather than outflow. This is succinctly stated by Broecker and Peng [1]: “The composition of sea salt reflects not only the relative abundance of the dissolved substances in river water but also the ease with which a given substance is entrapped in the sediments”.

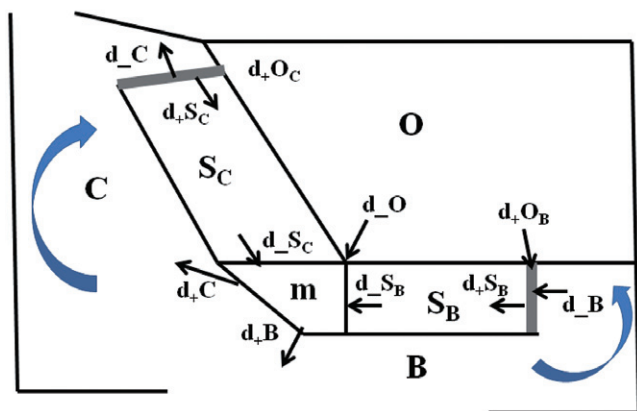
The constituents in rivers are derived from the dissolution of rocks and other terrestrial material by precipitation and more recently, through the addition of chemicals from anthropogenic activities, and the enhanced release of particulate through human activity. The dissolution of carbon dioxide (CO<sub>2</sub>) in rainwater results in an acidic solution and this solution subsequently dissolves the mostly basic constituents that form the Earth’s crust [2]. The natural acidity, and the recently enhanced acidity of precipitation due to human-derived atmospheric inputs, results in the dissolu-

tion (weathering) of the terrestrial crust and the flow of freshwater to the ocean transports these dissolved salts, as well as suspended particulate matter, entrained and resuspended during transport. However, the ratio of river to ocean concentration is not fixed for all dissolved ions [3, 4] as the concentration in the ocean is determined primarily by the ratio of the rate of input compared to the rate of removal, which will be equivalent at steady state. Thus, the ocean concentration of a constituent is related to its reactivity, solubility or other property that may control its rates of input or removal [1, 5].

Many of the early investigations looked at the aquatic ecosystem as an inorganic entity or reactor, primarily based on the assumption that aquatic chemistry was driven by abiotic chemical processes and reactions, and that the impact of organisms on their environment was relatively minor. In 1967, Sillen [6], a physical chemist, published a paper *The Ocean as a Chemical System*, in which he aimed at explaining the composition of the ocean in terms of various equilibrium processes, being an equilibrium mixture of so-called “volatile components” (e.g., H<sub>2</sub>O and HCl) and “igneous rock” (primarily KOH, Al(OH)<sub>3</sub> and SiO<sub>2</sub>), and other components, such as CO<sub>2</sub>, NaOH, CaO and MgO. His analysis was a follow-up of the initial proposed weathering reaction of Goldschmidt in 1933:



Sillen stated that “the composition may . . . be given by well-defined equilibria, and that deviations from equilibrium may be explainable by well-defined processes”, and proposed the box model shown in Fig. 1.1 [6]. However, he also stated that this did not “mean that I suggest that there would be true equilibrium in the real system”. In reality, the ocean composition is a steady state system where the



**Fig. 1.1** A representation of the global material cycle. The reservoirs are indicated as symbols C = continental rock; B: basaltic rock; O: ocean; S<sub>C</sub>: continental sediments; S<sub>B</sub>: basaltic sediments. The fluxes into (+) and out of (-) each reservoir are indicated by appropriate symbols that represent the flow paths. Redrawn from Sillen (1967) *Science* **156**: 1189–97. Reprinted with permission of AAAS [6].

concentrations are determined primarily by the relative rates of addition and removal, and that reversible equilibrium reactions are not the primary control over ocean composition [1]; something Sillen [6] alluded to. The major difference between these two conceptualizations is that the equilibrium situation would lead to a constancy of composition over geological time while the steady state model accommodates variation due to changes in the rate of input of chemicals to the ocean. The Sillen paper established the idea that the ocean was a system that could be described as being at geological equilibrium in terms of the major reactions of the primary chemicals at the Earth's surface, and that the average composition of the overall system could be described. The composition of seawater, for example, was due to a series of reversible equilibrium reactions between the ocean waters, sediments and the atmosphere [6]. Similarly, it was proposed that the composition of the biosphere was determined by a complex series of equilibrium reactions – acid-base and oxidation-reduction reactions – by which the reduced volatile acids released from the depths of the Earth by volcanoes and other sources, reacted with the basic rocks of the Earth and with the oxygen in the atmosphere.

A follow-up paper in 1980 by McDuff and Morel [7] entitled *The Geochemical Control of Seawater (Sillen Revisited)*, discussed in detail these approaches and contrasted them in terms of explaining the composition of the major ions in seawater. This paper focused on the controls over alkalinity in the ocean and the recycled source of carbon that is required to balance the removal of CaCO<sub>3</sub> via precipitation in the ocean, and its burial in sediments. These authors concluded that “while seawater alkalinity is directly controlled by the formation of calcium carbonate as its major sedimentary sink, it is also controlled indirectly by carbonate

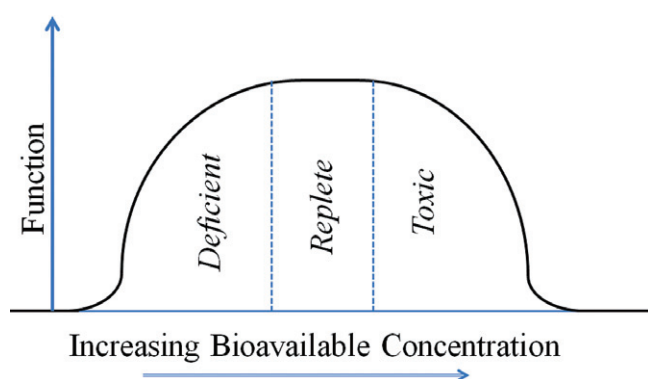
metamorphism which buffers the CO<sub>2</sub> content of the atmosphere” [7]. They concluded that the “ocean composition [is] dominated by geophysical rather than geochemical processes. The acid-base chemistry reflects, however, a fundamental control by heterogeneous chemical processes.”

McDuff and Morel [7] also focused attention on the importance of biological processes (photosynthesis and respiration) on the carbon balance, something that the earlier chemists did not consider [6]. These biological processes result in large fluxes via carbon fixation in the surface ocean and through organic matter degradation at depth, but overall most of this material is recycled within the ocean so that little organic carbon is removed from the system through sediment burial. Thus, the primary removal process for carbon is through burial of inorganic material, primarily as Ca and Mg carbonates. Recently, the short-term impact of increasing atmospheric CO<sub>2</sub> on ocean chemistry has been vigorously debated, and is a topic of recent research focus [8, 9] because of the resultant impact of pH change due to higher dissolved CO<sub>2</sub> in ocean waters on the formation of insoluble carbonate materials. Carbonate formation is either biotic (shell formation by phytoplankton and other organisms) or abiotic. Thus, there has been a transition from an initial conceptualization of the ocean and the biosphere in general, as a physical chemical system to one where the biogeochemical processes and cycles are all seen to be important in determining the overall composition. This is true for saline waters as well as large freshwaters, such as the Great Lakes of North America, and small freshwater ecosystems, and even more so for dynamic systems, such as rivers and the coastal zone [2, 4, 10].

It has also become apparent that most chemical (mostly redox) reactions in the environment that are a source of energy are used by microorganisms for their biochemical survival and that, for example, much of the environmental oxidation and reduction reactions of Fe and Mn are mediated by microbes, even in environments that were previously deemed unsuitable for life, because of high temperature and/or acidity [2, 10]. Overall, microorganisms specifically, and biology in general, impact aquatic trace metal(loid) concentrations and fate and their presence and reactivity play multiple roles in the biogeochemistry of aquatic systems. Understanding their environmental concentration, reactivity, bioavailability and mobility are therefore of high importance to environmental scientists and managers. Trace metals are essential to life as they form the basis of many important biochemicals, such as enzymes [10, 11], but they are also toxic and can cause both human and environmental damage. As an example, it is known that mercury (Hg) is an element that is toxic to organisms and bioaccumulates into aquatic food chains, while the other elements in Group 12 of the periodic table – zinc (Zn) and cadmium (Cd) – can play a biochemical role [11]. Until recently, Cd was thought to be a toxic metal only but the

demonstration of its substitution for Zn in the important enzyme, carbonic anhydrase, in marine phytoplankton has demonstrated one important tenet of the trace metal(loid)s – that while they may be essential elements for organisms, at high concentrations they can also be toxic [11, 12]. Copper (Cu) is another element that is both required for some enzymes but can also be toxic to aquatic organisms, especially cyanobacteria, at higher concentrations. This dichotomy is illustrated in Fig. 1.2, and is true not only for metals but for non-metals and organic compounds, many of which also show a requirement at low concentration and a toxicity at high exposure.

This dual role is also apparent for the group of elements, termed the metalloids, which occupy the bottom right region



**Fig. 1.2** Concentration-response curve for a trace element that is both required by organisms for survival but that can be toxic to the same organism at high concentration.

of the periodic table (Groups 13–17, from gallium (Ga) to astatine (As); see Fig. 1.3) [12]. They do not fit neatly into the definition of “trace metals,” as these elements are transitional between metals and non-metals in chemical character, but their behavior and importance to aquatic biogeochemistry argue for their inclusion in this book. Indeed, selenium (Se) is another example of an element that is essential to living organisms, being found in selenoproteins which have a vital biochemical role, but it can also be toxic if present at high concentrations [13]. As noted previously, the chemistry of both metals and microorganisms are strongly linked and many microbes can transform metals from a benign to a more toxic form, or vice versa; for example, bacteria convert inorganic Hg into a much more toxic and bioaccumulative methylmercury, while methylation of arsenic (As) leads to a less toxic product [14].

Therefore, in this book the term “trace metal(loid)” is used in a relatively expansive manner to encompass: (1) the transition metals, such as Fe and Mn, that are relatively abundant in the Earth’s crust but are found in solution at relatively low concentrations due to their insolubility, and because they play an important role in biogeochemical cycles [2, 10]; (2) the so-called “heavy metals,” such as Hg, Cd, lead (Pb) and Zn that are often the source of environmental concern, although some can have a biochemical role [4, 10]; (3) the metalloids, such as As and Se, which can be toxic and/or required elements in organisms; and (4) includes the lanthanides and actinides, which exist at low concentration and/or are radioactive [15]. Many of the lanthanides (so-called “rare earth elements”) are now being

■ hydrogen																■ noble gases															
1															2																
H	□ alkali earth metals														He																
3	4													5	6	7	8	9	10												
Li	Be													B	C	N	O	F	Ne												
11	12													13	14	15	16	17	18												
Na	Mg	■ transition metals												Al	Si	P	S	Cl	Ar												
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86														
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn														
87	88	89	104	105	106	107	108	109	110	■ poor metals																					
Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno	Une	Unn																						
■ alkali metals																■ rare earth metals															
																58	59	60	61	62	63	64	65	66	67	68	69	70	71		
																Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
																90	91	92	93	94	95	96	97	98	99	100	101	102	103		
																Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

**Fig. 1.3** The Periodic Table of the elements.

actively mined given their heightened use in modern technology [16]. Many of the actinides, including uranium (U), plutonium (Pu), are used or produced in the nuclear industry, while others, such as thorium (Th) and protactinium (Pa) are formed naturally from the decay of U in the environment and have been used as geochemical tracers. The elements that are the primary focus of the book are contained in Table 1.1, along with some key details about each element. The Periodic Table (Fig. 1.3) and the information in Table 1.1 provide an indication of the differences between these elements.

While Fe is not truly a trace element, being one of the most abundant elements on Earth, it is a metal that has been shown to be a limiting nutrient to oceanic phytoplankton [17]. This reason, and the fact that its chemistry plays a vital role in the overall fate and transport of many trace metals and metalloids argues for its inclusion in this book, along with Mn. The focus of the book will be on the metal(loid)s for which the most information is available, or which are the most environmentally relevant. While there will be a focus on metals of the first transition series, and all the metals of Groups 11 and 12, as they are either important

**Table 1.1** Characteristics of the elements that will be principally discussed in this book. The average ocean and river concentrations for unpolluted waters are taken from various sources [4, 5, 17, 18].

Element	Symbol, Atomic Number	Atomic Mass	Abundance ( $\mu\text{mol kg}^{-1}$ or as noted)	Main Oxidation States	Average Ocean Concentration (nM)	Average River Concentration* (nM)
Aluminum	Al 13	26.982	Most	III	20	1850
Titanium	Ti 22	47.88	0.6%	IV	<20	
Vanadium	V 23	50.942	0.02%	II–V	30	
Chromium	Cr 24	51.996	2700	III, VI	4	19
Manganese	Mn 25	54.938	0.085%	II, IV, VII	0.3	145
Iron	Fe 26	55.847	2nd most	II, III	0.5	720
Cobalt	Co 27	58.933	500	II, III	0.02	3.4
Nickel	Ni 28	58.69	1500	II	8	8.5
Copper	Cu 29	63.546	1100	II, I	4	24
Zinc	Zn 30	65.39	1200	II	5	460
Gallium	Ga 31	69.72	270	III	0.3	1.3
Germanium	Ge 32	72.59	20	IV	0.07	0.1
Arsenic	As 33	74.913	28	III, V	23	23
Selenium	Se 34	78.96	0.6	–II, IV, VI	1.7	
Molybdenum	Mo 42	95.94	11	VI	110	5.2
Silver	Ag 47	107.868	0.7	I	0.025	2.8
Cadmium	Cd 48	112.41	1.3	II	0.6	0.2
Tin	Sn 50	118.71	18	II, IV	0.004	0.01
Antimony	Sb 51	121.75	1.7	III, V	1.6	8.2
Tellurium	Te 52	127.60	0.008	–II, IV, VI	<0.001	
Cerium	Ce 58	140.12	430	III, IV	0.02	
Other Lanthanides	59–71	140.91– 174.97		II, III	La 0.03	La 0.4
Tungsten	W 74	183.85	0.6	IV–VI	0.06	
Rhenium	Re 75	186.207	0.016	–I, VI, VII	0.04	
Osmium	Os 76	190.2	0.011	II, III, IV	0.05	
Platinum	Pt 78	195.08	0.19	II, IV	0.003	
Gold	Au 79	196.967	0.015	I, III	<<0.001	0.01
Mercury	Hg 80	200.59	0.33	0, II	0.002	0.01
Lead	Pb 82	207.2	50	II	0.01	0.48
Bismuth	Bi 83	208.98	0.12	III, V	<0.025	
Polonium	Po 84	(209)	No data	II, IV, –II	<<0.001	
Thorium	Th 90	232.038	26	IV	<0.001	0.4
Protactinium	Pa 91	231.036				
Uranium	U 92	238.029	7.6	VI	14	1.0
Plutonium	Pu 94	244.064				

\*Average for unpolluted rivers. For some elements, variability in river concentrations is high.



commercially, or are toxic/required elements, it is also necessary to discuss the radioactive and rare earth elements. Few of the elements from the second and third transition series have important biochemical or biogeochemical reactions, besides molybdenum (Mo), and possibly tungsten (W), but some of these elements, such as rhenium (Re) and osmium (Os) have been used as tracers of environmental processes. Overall, the elements of the second and third transition series have been little studied. The lanthanides, as a group, have been used by aquatic chemists as chemical tracers, and have similar chemistry, because, while the inner 4f orbital is being filled through the series, the electrons lost are the outer orbital electrons and they mostly behave as +3 cations in solution. For the actinides, which are often radioactive, the focus will be on the chemistry of U, Th, Pa, Pu as well as the products of nuclear fission reactions, which are often radioactive [4].

There are many texts that cover one or more aspects of the topic of this book, which are referred to throughout, such as Stumm and Morgan [2], Morel and Hering [10], Cotton and Wilkinson [18], Drever [3], Buffle [19], Langmuir [4] and Wilkinson and Leads [20]. A compilation by Holland and Turekian [21] and authors therein, *Treatise on Geochemistry*, synthesizes in the various volumes many of the topics that are contained in this book. Some books are specific to ocean metal chemistry [1, 5].

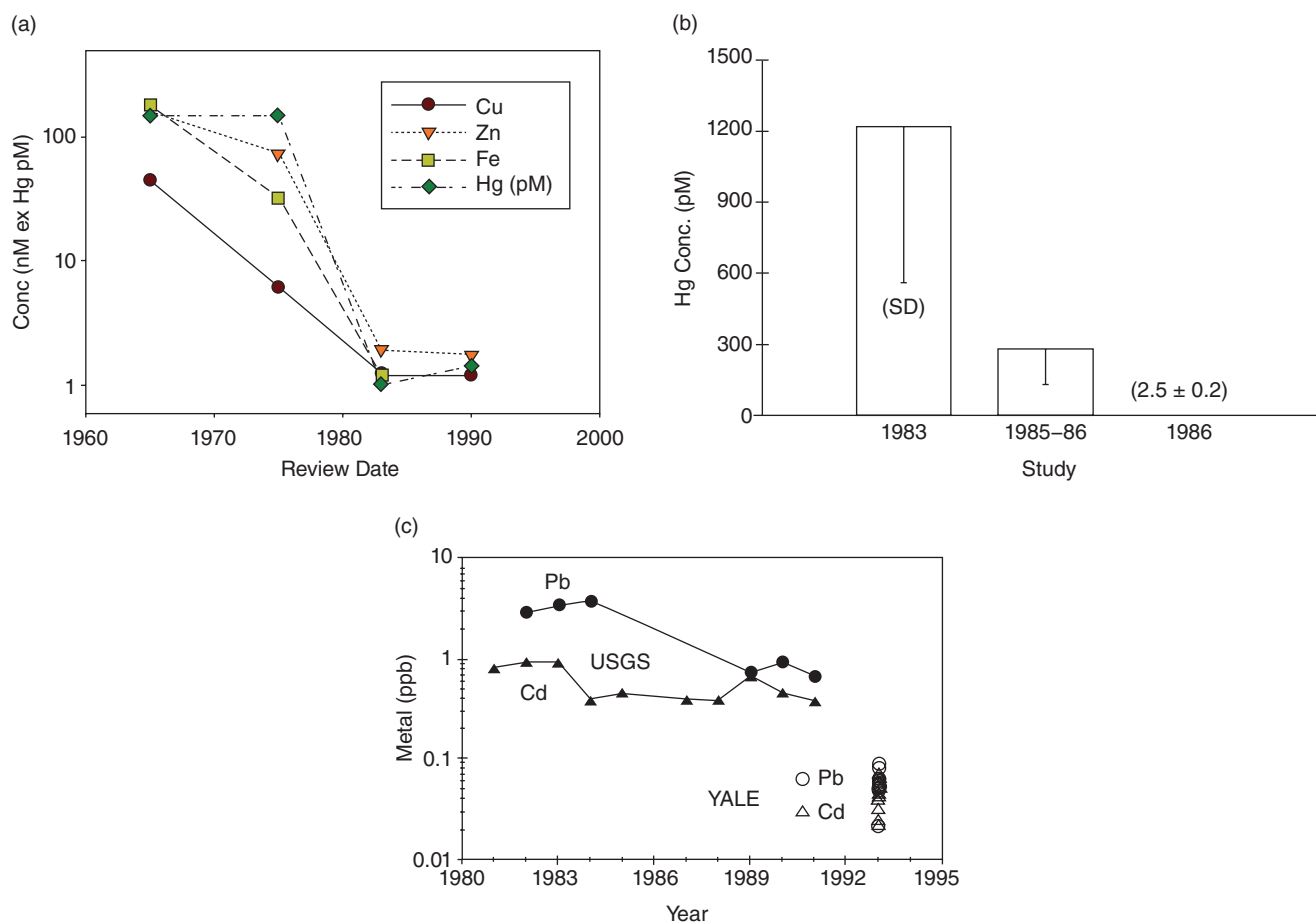
## 1.2 Historical problems with metal measurements in environmental media

While the concentrations of metals in solid phase media – rocks, sediments – and in biota are mostly sufficiently high that they can be analyzed using “typical” conditions found in a geochemical laboratory, this is not always the case, and it is certainly not true for the more trace constituents such as Cd, Hg, and Ag, and especially when making measurements in natural waters. Additionally, many other metals, such as Fe, Zn, and Cu, whose concentration in dust and in general laboratory materials (e.g., acids, plastics) is elevated, are difficult to accurately quantify without the proper scientific care. The potential for sample contamination during collection and analysis in many early environmental studies was not initially appreciated prior to the 1980s, and subsequently the techniques and approaches applied to the analysis of rocks were found not to be suitable for the analysis of natural water samples [22]. The difficulty in making measurements of the actual concentration of a metal in the water samples when collected, compared with the concentration in the sample bottle at the time of analysis, was not initially appreciated by many environmental scientists [23–25], and this still could cause erroneous results. Differences in concentration could result from any inadvertent addition of metal during sampling, handling, and analysis, and due to contaminants in the bottle plastics and in the reagents used.

Losses, due to adsorption to container walls are a problem for some metals in water samples, and the subsequent leaching of these metals back into solution can produce sampling artifacts. The impact of all these factors on the measurement of the dilute metal concentrations in natural solutions (Table 1.1) was not fully appreciated in the early environmental studies of natural waters.

The first convincing demonstration of the errors in many of the measurements of trace metals in environmental waters was made by Patterson and Settle [22]. Their landmark paper, *The Reduction of Orders of Magnitude Errors in Lead Analyses of Biological Materials and Natural Waters by Evaluating and Controlling the Extent and Sources of Industrial Lead Contamination Introduced during Sample Collection and Analyses*, [22] fundamentally changed the approach to the collection of samples of natural waters for trace element analysis, and led to the development of protocols, so-called “clean techniques”, for the analysis of low level trace metal samples. These investigators, and the scientists who adopted their approaches, clearly demonstrated the potential for contamination of samples due to traces of metals in the plastic materials, the acids and other reagents used in storage and analysis, and the importance of excluding dust in laboratory settings and the potential for introduction of metals from humans during handling. They showed the extent of preparation and care that was needed at all stages of the process: in sample container cleaning and preparation, during sample collection and manipulation, and during analysis. Such precautions that are now routinely used by environmental scientists (acid cleaning of glassware and plastics, use of gloves, cleaning of sampling devices and sampling lines, use of specific materials for the contaminant prone metals (e.g., use of Teflon for Hg sampling), and use of non-metallic materials where possible) were not done routinely in the early studies.

Patterson and Settle [22] showed that their measurements of Pb in ocean waters were orders of magnitude lower than those reported by other investigators and furthermore, that their results were “environmentally and geochemically consistent”. This realization of the magnitude and extent of the contamination of samples subsequently led to a revolution in the way that samples were collected and analyzed, and, as a result, in the reported concentrations of metals in environmental waters. This is illustrated in Fig. 1.4 for a number of metals. In Fig. 1.4(a), a compilation of data from various sources shows the dramatic decrease in the reported concentration for the metals Cu, Fe, Zn, and Hg in open ocean seawater over time [49–52]. In all cases, the change between the reported concentrations in 1983 and 1990 are relatively small compared to the dramatic decrease between 1965 and 1983, especially for Fe, Hg, and Zn. For Cu, the reported concentration decrease is about a factor of 50, while it is more than two orders of magnitude for the other metals. Similar decreases in the reported metal concentrations for river water are illustrated by a comparison over time [23] (see Fig. 1.4b). Again, the use of clean approaches to



**Fig. 1.4** (a) Graph showing the trend in the reported mean concentration of several metals in ocean waters. Early data are taken from reviews by Brewer [24]; Bruland [49]; Bruland et al. [40] and Goldberg [25]. The 1990 data are taken from Refs [50, 52] and are for the Pacific Ocean. Figure redrawn using this information and Mason [26]; (b) reported mercury concentrations for Vandercook Lake in Wisconsin over time. Figure reprinted

from Fitzgerald, W. and Watras, C.J. (1989) *Science of the Total Environment* **87/88**: 223–32 with permission of Elsevier [27]. (c) Figure showing the difference between the reported concentrations of lead and cadmium for the Quinnipiac River. Figure reprinted with permission from Benoit, G. (1994) *Environmental Science and Technology* **28**: 1987–91, Copyright (1994), American Chemical Society [23].

sampling and analysis lead to more than an order of magnitude decrease in the measured concentrations of Cd and Pb in river water compared to the values reported previously. Finally, data from samples collected in a lake in Wisconsin show a similar trend for Hg [27] (Fig. 1.4c). The decrease in reported concentration was again more than two orders of magnitude between 1983–6. As noted earlier, the changes in the reported concentration in all these instances was not primarily the result of a “cleanup” of the environment, although there is evidence for changing concentrations over recent decades, but rather a realization and appreciation that the investigators themselves, and the plastics and other materials used for sampling contain significant traces of metals, and that these were being leached into the samples during handling and storage.

For the ocean, sampling methodologies that used metal wire cables led to contamination, as did the use of untreated

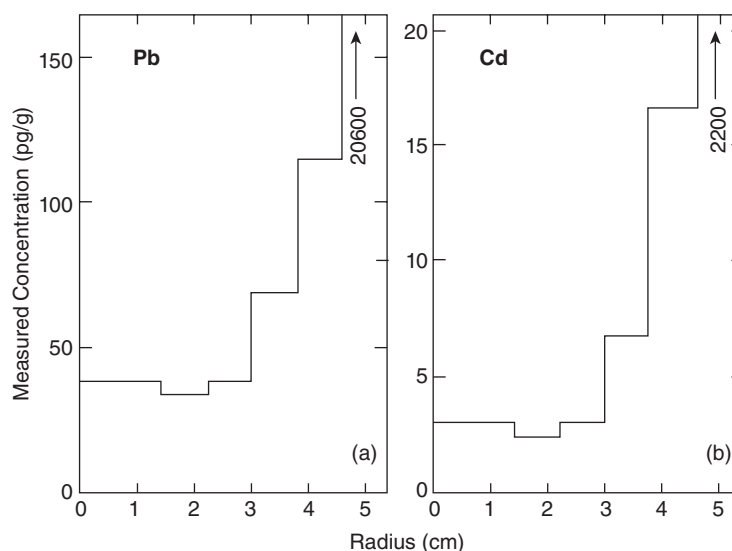
plastic sampling bottles used to collect samples at depth (e.g., Niskin bottles). Metal inputs from the vessels themselves can also be a source of contamination. These sources of contamination were most severe for those waters that have low concentration due to their remoteness (e.g., the middle of the Pacific Ocean). A comparison by a reader of the reported concentrations of metals in the ocean in the recent literature would further illustrate the point. Such an examination indicates that while the reported concentrations of Al (~40 nM), Cr (40 nM) and other metals that are present in seawater at relatively high concentrations are similar to those in Table 1.1, many of the concentrations reported in various books are 2–100 times higher, especially for the heavy metals (e.g., Hg, Pb) and even for some of the transition metals (Ni, Co, Zn). So, there is still a need for caution when reading the literature and certainly much care and application is needed when doing field studies.

The extent of potential sample contamination is obviously, but not exclusively, a function of the concentration, with potentially more contamination likely for metals that are present at low concentrations. Cadmium provides one example where this is not true as, even though it exists in natural waters at low concentrations, there has been less evidence of its contamination in earlier studies. Sampling and analytical difficulties are most severe for those metals that are present in low concentration and which are routinely used in materials, or are part of typical sampling equipment and vessels, or occur in high abundance in atmospheric aerosols, such as Fe, Cu, Zn, Hg, and Pb. One example is the use of metal-containing dyes in plastics, such as in the coloring of pipette tips. Use of these tips with acidic solutions can lead to metal leaching and contamination. One recent example of contamination for Zn that has been highlighted in ocean studies is the use of Zn as “sacrificial anodes” on metal sampling devices to prevent corrosion – dissolution of Zn was found to be sufficient to contaminate samples during a recent international intercalibration study as part of the GEOTRACERS program [28].

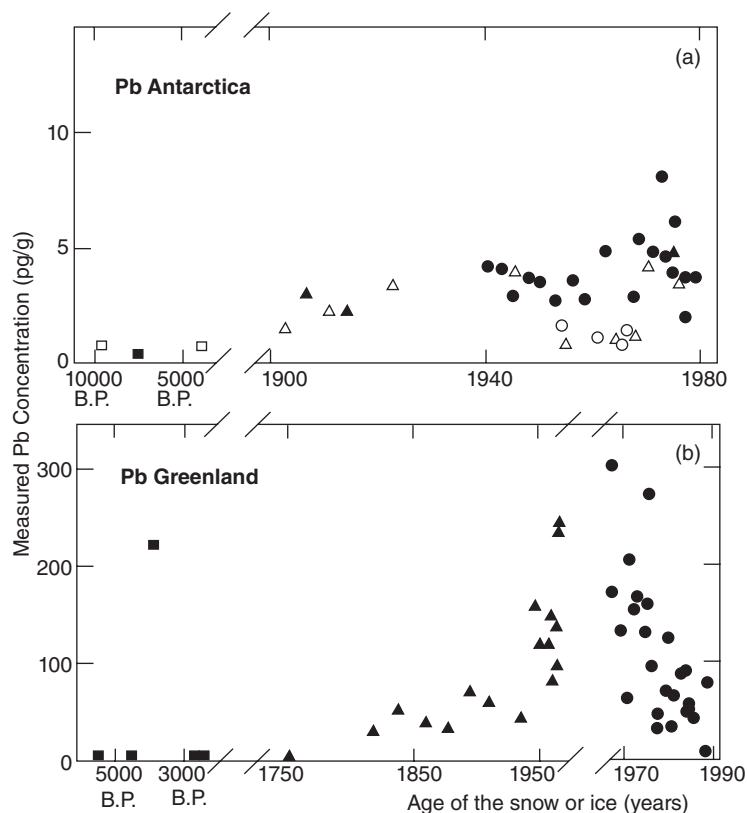
The introduction of these approaches has led to a wealth of information on metal distributions in the ocean and in freshwaters that has resulted in an enhanced understanding of their toxicity to aquatic organisms, and their requirement as essential nutrients, and to the factors that control their cycling. Accurate measurements also led to a clearer and better understanding of the role of human inputs in environmental contamination, and the need to curb industrial and other emissions of metals to the atmosphere and aquatic systems. The importance of this development and the result-

ant explosion of high quality research can be illustrated by the papers presented at a special symposium held in honor of Claire Patterson on his retirement, in December 1992. The papers presented at the meeting were published in a special issue of *Geochimica et Cosmochimica Acta* in 1994 and many papers cover topics related to Pb and other metals, and their geochemical cycle, such as using ice core records and ocean measurements and Pb isotope ratios to examine recent changes and those over geological timescales [29–37]. The paper by Boutron et al. [29] illustrates the difficulty in making measurements of trace concentrations of metals in a situation where the ice core needed to be drilled and recovered using contaminating techniques. These authors measured the concentration of the metals in successive layers of ice shaved from the outside to the inside of the ice core and showed that while the outer layers were highly contaminated, the inner core was not (Fig. 1.5). This analysis further provided a clear record of the impact of human use and release of Pb, primarily from its use as a gasoline additive, on the concentrations of Pb in remote precipitation (Fig. 1.6) [29].

Other papers presented at the symposium, such as the review paper of Bruland et al. [40], detail measurements of reactive trace metals (Al, Fe, Mn, Zn and Cd) in ocean waters. These authors discussed the notion, first proposed by Whitefield and Turner [38], that the profiles of such elements reflect their biogeochemistry. Some metals such as Zn and Cd have so-called “nutrient (recycled) profiles” in the ocean as their concentration is depleted in surface waters and higher at depth, while others, such as Al, reflect their primary atmospheric input and their high association with



**Fig. 1.5** The measured concentrations of lead and cadmium in successive layers of ice shaved from an ice core recovered from Vostok Station in East Antarctica. Figure reprinted from Boutron et al. (1994) *Geochimica et Cosmochimica Acta* **58**: 3217–25 with permission of Elsevier [29].



**Fig. 1.6** Lead profiles for ice cores collected in polar region. Figure reprinted from Boutron et al. (1994) *Geochimica et Cosmochimica Acta* 58: 3217–25 with permission of Elsevier [29].

the particulate phase (so-called “scavenged profiles”; high surface concentrations and low deep water values). Other metals, such as Hg, have a more complex ocean distribution due to their complex chemistry and cycling [39].

The notion that a metal, such as Zn, could have an ocean profile that is similar to that of the major nutrient elements [40] (i.e., nitrogen (N), phosphorous (P), and silica (Si) – required by diatoms), and that the concentration of Zn and Si appear closely correlated for open ocean waters [17] was reconciled with the knowledge that Zn has a biological role and forms part of many enzymes important to cellular biochemistry [11]. At the time, the correlation of Cd and P profiles was more of a “mystery” as Cd was considered a toxic heavy metal with no biological function and there was “no biological or chemical explanation for the (relationship)” [1]. It has since been shown that Cd can substitute for Zn in one important enzyme for ocean photosynthetic organisms (carbonic anhydrase) and therefore its role as a nutrient has been established [11].

It is worth noting that contamination is not only a problem in trace metal research where quantification of *in situ* concentrations is the principal focus. Fitzwater et al. [41] demonstrated, for example, that the introduction of metals into solutions from container vessels and reagents could lead to

substantial under-estimation of the primary productivity when using  $^{14}\text{C}$ -incubation approaches. They demonstrated the potential for leaching of Cu from glass bottles even after acid washing, and the converse, the adsorption of Cu onto glass containers in unacidified solutions. High metal levels were found in the standard  $^{14}\text{C}$  solutions and in other solutions used in productivity studies. As a result, more recent techniques have been devised that use trace metal free “clean techniques” [42] for productivity and other studies with phytoplankton and other microbes, if experiments are performed under natural conditions.

The environmental scientist is therefore strongly cautioned to check the reported concentrations in any publication against other sources as, while there is obviously variability between ecosystems and especially for systems with high or variable TSS (total suspended solids) loads, there is still the possibility that reported concentrations in the literature are not reflective of actual concentrations. However, on the contrary, while it is often considered that the lowest concentration must be correct, this is not always the case, as losses and incomplete recovery of the metal during sample analysis is a real possibility, and therefore this metric should not be used exclusively to gauge whether a reported value is correct or not.

**Table 1.2** Comparison of techniques for determining metal concentrations in water samples showing relative precision and other analytical metrics [46].

Technique	Linear Range	Precision	DL Cd (nM)	DL Cu (nM)	DL Zn (nM)	Interferences
GFAA	$\sim 10^2$	0.5–5 %	0.02	0.2	0.3	Relatively few
ICP-AE	$\sim 10^5$	<2%	0.9	6	3	Spectral; many lines overlap
ICP-MS	$10^5$ – $10^7$	1–3%	$10^{-3}$	$3 \times 10^{-3}$	$4.5 \times 10^{-3}$	Many; isotopes, oxides and other molecular mass

### 1.3 Recent advances in aquatic metal analysis

While the previous section outlined the historical problems associated with sample contamination, this issue has been mostly addressed and most recent studies have demonstrated the ability to accurately quantify the total concentration of an element in environmental waters. Some recent intercalibration exercises in open ocean seawater indicate that contamination is always a possibility, and care and application of “clean techniques” is necessary as the concentrations are low (nM or pM; Table 1.1). Comparison and confirmation of accuracy can be achieved through the continued use and further development of low level reference materials. Standard (or Certified) Reference Materials (SRMs or CRMs) are environmental materials that have been repeatedly measured, often by more than one technique, so that their concentration is well-defined by an accepted value and a standard deviation which reflects the overall precision of the measurement. Such materials allow an analyst to confirm that the method and approach used is providing an accurate answer. The US National Institute for Standards and Technology (NIST), the European Institute for Reference Materials and Measures (IRMM), and other organizations in other countries around the world, provide an impressive array of SRMs in many different media. However, it is often difficult to provide adequate SRMs for the low levels of many metals in seawater or freshwaters (nM or lower concentrations), and the number of SRMs for water are limited. There are recent concerted efforts to develop such SRMs, and the international GEOTRACERS Program [43] is one avenue through which such reference materials are being developed.

While accurate measurement of the total concentration is a goal, there is an acknowledgement that the total concentration of an element in solution is not often an accurate predictor of the bioavailability, toxicity, or reactivity of the element [2–4, 10], as most metals do not exist in solution purely as the free metal ion, and are often associated with dissolved organic matter or can be in colloidal phases in the filtered fraction, as discussed in Chapter 2. Therefore, protocols have been developed to examine the distribution

and *speciation* (chemical form) of the metal(loid) in solution, as well as isotope ratios and other more detailed analysis [2, 10, 40, 44, 45]. Analytical advances and improvements in sensitivity have also improved the amount of information that is collected. For example, graphite furnace atomic adsorption spectroscopy (GFAAS) was often the preferred method for trace metal analysis in the early 1980s but this method is slow as each element requires a different lamp, and the linear calibration range is small, often requiring reanalysis of samples [45]. The analysis is also time-consuming although there is the potential to use an autosampler. Additionally, extensive pretreatment is required to concentrate samples to levels sufficient for analysis, and to remove interferences from the matrix, although techniques, such as Zeeman correction, have evolved to reduce these issues. As shown in Table 1.2 [46], the detection limits (DL) of GFAAS for the metals shown are within an order of magnitude of their concentrations in seawater (Table 1.1), and so sample preconcentration and/or matrix elimination is often required. The development of ICP (inductively coupled plasma) as an atomization technique has allowed for the more rapid analysis of samples although when coupled with atomic emission quantification (ICP-AES) results in a higher detection limit which is unsuitable for many metals in environmental waters, or even in sediment extracts (Table 1.2). However, coupling to a mass spectrometer (ICP-MS) provides high throughput, and low DL with high precision. However, ICP-MS is prone to substantial interferences such as different elements with the same atomic mass, or interferences due to the formation of oxides and other molecules that form after atomization (e.g.,  $^{40}\text{Ar}^{16}\text{O}$  and  $^{56}\text{Fe}$ ;  $^{40}\text{Ar}^{35}\text{Cl}$  and  $^{75}\text{As}$ ) but there are a variety of approaches to circumvent these interferences [47]. The severity of the interferences depends on the resolution of the MS, which is relatively low (0.8amu) for a quadrupole ICP-MS, which are the most robust and stable instruments. Therefore, analysis using these instruments needs to contend with interferences. One approach that has been used to circumvent molecular interferences is the use of a reaction cell, which is designed to break up diatomic and polyatomic molecules prior to the MS, thereby removing the interferences [47]. High resolution instruments are also available

that are capable of resolving these interferences because of their much higher resolving power, such as that with  $^{40}\text{Ar}^{16}\text{O}$  and  $^{56}\text{Fe}$ , and these are used in many instances. However, these instruments are more delicate and require more maintenance than a quadrupole [47]. More recently, multicollector ICP-MS instruments have been more widely used in aquatic metal analysis as these instruments are able to quantify the isotope ratios of specific elements and can be used to examine isotope fractionation and the factors causing such fractionation. Such isotope fraction can be used to examine environmental processes in a similar fashion to the more widely used fractionation of the major organic elements (C, N, S). Isotope analysis provides a new avenue for research and exploration as many abiotic and biotic processes can cause isotope fractionation in the environment. This is discussed further in Section 7.5. Additionally, ICP-MS is now being used to analyze radioisotopes in natural waters (e.g., Th, Pa, U, Pu) as this can be done with more accuracy and precision than can be obtained with conventional counting techniques.

Therefore, the amount of information has expanded rapidly with the development of more accurate and precise measurement techniques and with the ability to sample at higher resolution. Many of the factors that caused contamination in early studies have been overcome and sampling approaches that were not feasible 20 years ago, such as sampling for metals in seawater with an automated sampling system (rosette sampler), are now being used [43, 48], resulting in a higher throughput of sample collection. In freshwater systems, automated water samplers, such as Isco devices ([www.isco.com](http://www.isco.com)), are now used to collect samples without contamination. In addition to intercalibration studies, which have allowed for more detailed understanding of sources of sampling and analytical error, methods have been developed to examine the distribution of metals between dissolved, colloidal and particulate fractions without contamination, using ultrafiltration and other approaches. Analytical class-100 clean rooms are now routinely used for most metal analysis and high precision instrumentation has also allowed for a better characterization of blanks and sources of error.

As concentrations in water samples are generally too low for direct analysis, sample preconcentration often occurs. This can additionally remove potential matrix effects and other interferences. Preconcentration techniques typically rely on [44]: (1) co-precipitation of insoluble (hydr)oxides (e.g., Fe, Mn, Mg); or (2) solvent or solid-phase extraction of the analyte from the matrix using organic ligands and organic solvents or onto chelating resins, with subsequent elution into a small volume. Analysis on board ship or in the field often relies on techniques other than ICP-MS as it is not transportable. Many of these analyses rely on flow injection approaches, which allow for preconcentration prior to detection using spectrometry of a metal-ligand

complex, or after reaction of the metal with a complex that changes the signal, as occurs, for example, with the reaction of  $\text{Fe}^{\text{II}}$  or  $\text{Mn}^{\text{II}}$  with luminol [44]. Alternatively, as discussed in Chapter 6, many metals can be determined using electrochemical techniques using mercury drop electrodes.

One example of a detailed approach to standardizing methods and analysis is the GEOTRACERS Program intercalibration study [28, 43]. This program has provided a detailed manual on how to collect ocean water samples for the determination of a suite of metals, metalloids, radionuclides and other tracer compounds (TEIs). The manual that has been developed covers the sampling, filtration and storage with details on which type of equipment, filters and other methods to be used, and the best container and sample preservation protocols. These methods are for both radioactive elements as well as stable trace metal(loid)s and other elements, and their stable isotopes; see Section 6.4.2 for further details.

Finally, the development of *in situ* detection methods for the analysis of metal(loid)s in environmental waters is in its infancy but there is the promise of a further explosion of information as such techniques become available. It will be apparent through the discussions in the later chapters of the book, especially Chapters 6 and 7, that there has been enormous progress in recent decades in the understanding of the fate, transport and transformation of metal(loid)s in aquatic systems and the dynamics of the interactions between metals in solution and the solid phase, and with microorganisms that inhabit these waters. Many of the recent discoveries would not be possible without the development of new techniques and approaches, including the methods to quantify different fractions of an element in aqueous systems.

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## Problems

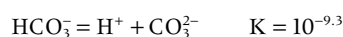
- 1.1. Discuss briefly the chemistry of the elements that form the “rare earths” and provide brief details of the use of four of these elements in industrial applications.

1.2. A chemist makes a standard solution for the analysis of metals by ICP-MS. She wants the final standards to cover the range from one tenth to 10 times the average concentration of the element in seawater. To do this she will make a composite stock solution that is 1  $\mu\text{M}$  in the following metals (Co, Cu, Zn, Cd, Ag) and 100 nM in Pb and Hg. How much metal does she need to weigh out for each element, using the anhydrous chloride salt (e.g.,  $\text{CuCl}_2$ ) given that the final solution will be made in 1 l of acidified water?

1.3. Examine the concentrations of the elements in Table 1.1 and summarize any evident trends between the concentrations in seawater versus those in river water. Discuss why this may be so, and comment on the elements that do not fit the trend and why you may suspect they do not.

1.4.

- a. If the pH of seawater is 8.1 and the pH is mostly controlled by the acid-base chemistry of the carbonate system, calculate the concentration of dissolved carbonate assuming the total carbonate concentration (all species) is 2 mM. The following acid-base constants are appropriate for this problem:



Equilibrium constants have been adjusted to account for ionic strength effects.

(Hint: given the pH, it is reasonable to assume that the bicarbonate concentration is approximately equivalent to the total carbonate concentration.)

- b. If the pH decreased to 7.9, how much would the carbonate concentration change?

1.5. It has been stated that the concentrations of Fe and Mn in seawater are controlled by the precipitation of their solid phases. Estimate the concentrations based on the precipitation of  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$  and compare these values to those in Table 1.1. If the concentrations are different, provide a reasonable explanation for the differences.



## CHAPTER 2

# An introduction to the cycling of metals in the biosphere

### 2.1 The hydrologic cycle

As the focus of this book is aquatic systems, it is worthwhile briefly considering the movement and distribution of water at the Earth's surface (Table 2.1) [1–4]. Water is exchanged between the principal reservoirs (freshwater bodies and the ocean) and the atmosphere by precipitation and evaporation (Fig. 2.1). Freshwater refers to waters with relatively low total dissolved solids (TDS) ( $<10^3 \text{ mg l}^{-1}$ ) while seawater has  $35 \times 10^3 \text{ mg l}^{-1}$  TDS on average. Brackish water has intermediate TDS [1]. The freshwater and ocean ecosystems are linked through the input of water to the ocean via surface continental runoff, groundwater input and wet deposition. The exchange volumes relative to the various reservoir sizes indicates the rapidity of recycling between each reservoir. Precipitation adds about  $3.5 \times 10^{17} \text{ l yr}^{-1}$  to the ocean, for example, while evaporation removes about  $3.8 \times 10^{17} \text{ l yr}^{-1}$ . The difference is due to terrestrial inputs ( $0.36 \times 10^{17} \text{ l yr}^{-1}$ ) [1]. Note that the atmospheric (pluvial) flux is about 10 times the fluvial input. The inputs are small compared to the overall reservoir size. It can be seen from Table 2.1 that the majority of the water at the Earth's surface is in the ocean (97%) and the amount in the atmosphere is trivial.

The precipitation input to the terrestrial reservoir is about  $1.1 \times 10^{17} \text{ l yr}^{-1}$  and evaporation removes  $0.73 \times 10^{17} \text{ l yr}^{-1}$ . The difference is the fluvial input to the ocean. The inputs into the terrestrial environment per year are of the same order as the reservoir size (Table 2.1) and therefore the *residence time* of water in the terrestrial surface layer is about a year. In this context, the residence time ( $\tau$ ) is the average time a molecule of water spends in a particular reservoir and is estimated as:

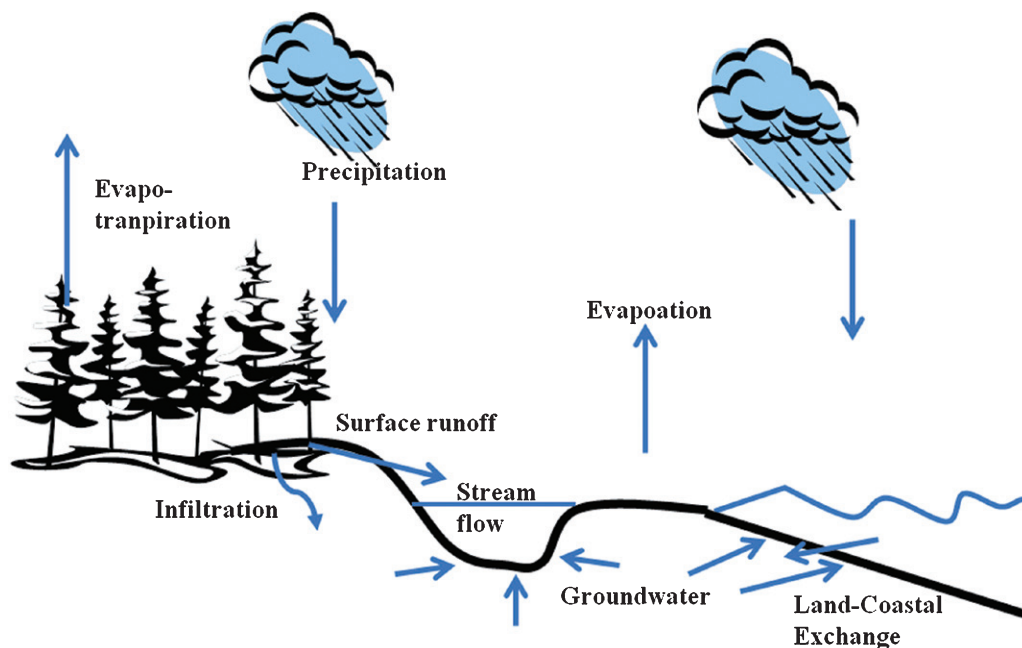
$$\tau = \text{reservoir size (mass units)} / \text{Input flux (mass yr}^{-1}\text{)} \quad (2.1)$$

In contrast to the ocean, inputs into the atmosphere are much greater than the atmospheric reservoir ( $0.13 \times 10^{17} \text{ l}$ ) and thus the residence time of water in the atmosphere is very short – about 10 days on average [1]. The cycling of water in the surface terrestrial environment is complex as water is lost from the surface to the atmosphere by both direct evaporation and by transpiration from plants. Losses to deeper layers result from infiltration of water into soils. Transport of water from its site of deposition to rivers is through both overland flow, which occurs mainly during high precipitation events, and through transport in the subsurface. The subsurface environment is divided into the *unsaturated (vadose) zone*, the region above the water table, and the *saturated (phreatic) zone*, which is below the water table. An *aquifer* is a saturated zone with enough water to allow for water extraction.

For the various ocean basins, based on the estimations of Budyko [5], the sources and cycling of water are different. For the Atlantic Ocean, because of the inputs from large rivers and its relatively small surface area, about 70% of the water input is from precipitation, while greater than 90% of water input to the Pacific and Indian Oceans is from precipitation. The Arctic Ocean, being small and also having large river inputs, has only about 50% of its water input from the atmosphere. For all the major oceans, loss to the atmosphere via evaporation is the dominant loss term (>90%) with water exchange between ocean basins being a minor component of the hydrological cycle; again, the Arctic Ocean is an exception as most of its water loss (~75%) is via exchange with the major oceans. Overall, ~36% of the freshwater input is to the Atlantic Ocean, with ~40% to the Arctic. Continental runoff to the Pacific and Indian Oceans are relatively minor components of the overall global water cycle.

**Table 2.1** The distribution and cycling of water at the Earth's surface. Data taken from various references [1–6].

Reservoir	Volume ( $\times 10^{18}$ l)	Inputs ( $\times 10^{18}$ l/yr <sup>-1</sup> )	Outputs ( $\times 10^{18}$ l/yr <sup>-1</sup> )	Exchange time (yrs)
Surface Ocean	338	Precip. 0.35	Evap. 0.38	800
Deep Ocean	1032	Runoff 0.036		
<i>Total Ocean</i>	<i>1370 (97%)</i>			<i>3240</i>
Lakes and Rivers	0.13	Precip. 0.110	Evap. 0.073	
Saline Lakes and Inland Seas	0.10		Runoff 0.036	
Ice	29 (2%)			
Groundwater	9.5			
<i>Total Freshwater</i>	<i>39</i>			<i>354</i>

**Fig. 2.1** The basic parts of the hydrologic cycle at the Earth's surface. Adapted and redrawn based on the understanding of the hydrologic cycle and various references [2–4, 10].

A simple, first-order estimate of the importance of the relative inputs for metal(loid)s can be made by assuming that these elements have the same concentration in precipitation as in riverine (estuarine) inputs. If so, then the dominant source of metal(loid)s to the ocean would be atmospheric deposition, based on the hydrologic fluxes. This simplistic view is illustrative of the potential importance of atmospheric deposition as a source of trace elements to the ocean and aquatic systems. However, while the water flux to the ocean is dominated by the atmosphere, the particulate flux is dominated by surface waters inputs. So, for those metals that reside primarily in the particulate phase, it may be suggested, based on these first-order considerations, that the riverine input will be the dominant source. This basic approach does not account for the large removal of particles in the estuarine mixing zone, and, with it, much of the

strongly particulate bound metals, as discussed in Section 2.2.6. Thus, while there is a strong flux of Fe, Mn, and Al to coastal zones due to particulate transport in rivers, more than 90% of the particulate is removed in estuaries and only a small fraction is exported to the shelf and ocean reaches [7].

For freshwater environments, and particularly lakes, the relative importance of the fluvial versus pluvial flux is related to the watershed to waterbody : surface area ratio, and the degree of retention of metal(loid)s within the watershed [8, 9]. In the absence of point source inputs, the flux of an element in a river is some fraction of the overall atmospheric deposition to the watershed, assuming that atmospheric deposition is the major metal(loid) source. The validity of this assumption is discussed in Section 2.2.5. Thus, for a waterbody:

$$\begin{aligned}
 \text{Total Metal (loid) Input (F}_T\text{)} & \\
 &= \text{Fluvial flux (F}_F\text{)} + \text{Pluvial Flux (F}_A\text{)} \\
 &= F_A \cdot A_{WS} \cdot T_{WS} + F_A \cdot A_{WB} \\
 &= F_A (A_{WS} \cdot T_{WS} + A_{WB})
 \end{aligned}
 \tag{2.2}$$

where  $F_A$  is the atmospheric deposition flux ( $\text{mol m}^{-2} \text{yr}^{-1}$ ),  $A_{WS}$  is the watershed area ( $\text{m}^2$ ),  $A_{WB}$  is the water body surface area ( $\text{m}^2$ ) and  $T_{WS}$  is the *transmission factor* for the watershed. The transmission factor is a *measure of the propensity of the watershed to retain metal(loid)s* and is generally defined as the fluvial flux relative to that of watershed deposition, and is sometimes termed the *retention factor*. It should be noted that measurements of retention (transmission) factors are based on current atmospheric deposition and river fluxes, and are often yearly averages, while it is known and acknowledged that metal(loid)s are not transmitted from their deposition location to the river within a year, and that their residence time in the watershed could be relatively long. For example, during an experiment in the Experimental Lakes Area in Canada where different Hg isotopes were added directly to a lake and its watershed, the isotope added directly to the lake surface water was measurable in the fish within months while the isotope added to the watershed (via a crop-duster plane) had hardly migrated and a very small fraction of the isotope added had made it to the lake within five years [6]. Thus, there is an implicit assumption in these calculations that inputs have not changed dramatically over the relevant time period for transport of the metal(loid) from its deposition site to the river [8, 9]. This is not likely to be the case in many instances for metal(loid)s that interact and are strongly bound up in the solid phase, as changes in landuse will impact flux. This is also true for ecosystems close to local sources, or those changed by human activity (biomass clearing or burning).

It can be deduced from Equation 2.2, for example, that for a strongly retained metal(loid) (e.g.,  $T_{WS} < 0.1$ ), the fluvial flux will be the same as the pluvial flux when  $A_{WS}/A_{WB} > 10$ , and thus the fluvial flux will only dominate if the watershed is large relative to the water body. For a metal(loid) that is poorly retained in the watershed, this is not so, and the fluvial input is important for both relatively small and large watersheds. Retention and/or transmission factors have been estimated for various metals and metalloids by a number of investigators. Metal(loid)s such as Pb and Hg, and the crustal metals (Fe, Mn) are often strongly retained in the watershed (>80% retention) while metals such as Cu and Cd (50–70% retained) and the metalloids As (<10% retained) and Se (60–70% retained) appear to be more mobile [8, 9].

Overall, the global cycle of each metal(loid) is different due to the differences in sources, the relative importance of anthropogenic point source inputs to the atmosphere, and the propensity for the element to remain in solution or be taken up by biotic or abiotic particles. It is therefore useful

to examine in some detail the sources and cycling of the more important metals and metalloids, and to understand the factors that influence their concentration in solution. This will be briefly discussed in this chapter and dealt with in more detail throughout the book.

## 2.2 An introduction to the global cycling of trace metal(loid)s

### 2.2.1 The sources and cycling of metal(loid)s in the biosphere

In considering the cycling of metal(loid)s at the Earth's surface, it is worthwhile discussing briefly the main processes involved in their global cycling. Beginning in the terrestrial realm, these cycles involve processes within the surface layers as well as the extraction of metal(loid)s from deep reservoirs in the Earth, and their transport to the atmosphere or surface waters. The extraction from deep reservoirs in the pre-industrial world was primarily due to volcanoes and oceanic hydrothermal inputs. However, more recently, mining activity (e.g., metal ore extraction and processing) and extraction of coal and hydrocarbon production have greatly exacerbated the inputs of metal(loid)s to the atmosphere and to aquatic ecosystems. Additionally, metal(loid)s are also reduced during the consumption of these products, especially through coal and hydrocarbon burning for energy and for transportation. The sources of metal(loid)s to freshwaters (rivers and lakes) are the erosion of surface terrestrial material, the input of metal(loid)s associated with groundwater and runoff, and deposition of metal(loid)s from the atmosphere. Again, these processes have a natural component but the input has been increased by human activity. Direct inputs from point source emissions are obviously an important local component in many ecosystems. Changes resulting from forest clearing and other landscape perturbations have also lead to metal(loid) mobilization.

For most metal(loid)s, transport at the Earth's surface predominantly occurs through the particulate phase: suspended solids in rivers and the coastal zone, and aerosols in the atmosphere. This is primarily due to the fact that many metal(loid)s are strongly associated with particles due to: (1) their dominance in terms of abundance in crustal material; (2) their strong partitioning to inorganic and organic solid phases; and (3) their accumulation in the particulate residue of high temperature combustion for industrial and energy extraction (small diameter atmospheric aerosols). Some elements are volatile enough, or form volatile compounds (e.g., Hg, Se, and As), so that their atmospheric transport may occur in the gas phase. Clearly, the major metal constituents of the crust, Fe, Mn, and Al, and many other metals, are transported and associated with particulate material primarily because they are incorporated into crustal material and

their oxidized forms are highly insoluble. Other elements, such as Cr, and some of the other transition metals, are also relatively abundant in crustal material but are more mobile because of their speciation in solution (Table 1.1). In only a few cases are metal(loid) elements less soluble in freshwaters compared to the ocean. Of the elements listed in Table 1.1, it is only Mo that has a much higher concentration in seawater than in rivers, and this is primarily due to the fact that it exists as a highly stable and soluble oxyanion in solution. Arsenic, which is also found as an oxyanion in solution, also has a relatively high ocean concentration compared to that of freshwater. Of all the first row transition metals, Ni appears to be the element that is least reactive, having an ocean concentration similar to that of rivers (Table 1.1).

The transport of metal(loid)s from the terrestrial environment to the ocean occurs through atmospheric transport and deposition of metal(loid)s, through transport in riverine discharge, as well as through hydrothermal sources. There is a substantial removal of metal(loid)s in the coastal zone in combination with particulate deposition that occurs during the mixing of river water and seawater in the estuary, and results in their trapping in the sediment. Deep ocean sedimentation and burial is the long-term sink for metal(loid)s and would have balanced the net surface erosion and volcanic inputs in a pre-industrial steady state world.

### 2.2.2 Metal(loid) partitioning and solubility in natural waters

The extent that trace metals and metalloids cycle through the various pathways in the biosphere depends on their chemistry, their abundance, and their usefulness to humans. Many metals (e.g., Fe, Cu, Zn, and Au) are purposefully extracted from the Earth's interior while other elements are often added as a result of human activity, such as the burning of fossil fuels (e.g., V, Se, and Hg). Some metals fit both descriptions (e.g., Hg, Zn, and Pb). In aqueous systems, the factors that determine the overall concentration of the metal(loid) in solution are the strength of metal(loid) complexation, the solubility of the hydroxide and carbonate phases, and the propensity of the metal(loid)s to adsorb onto inorganic and organic solids and form complexes with dissolved natural organic matter (NOM) [2, 10]. A measure of the propensity of an element to be associated with the particulate phase can be defined by the partition coefficient ( $K_D$ ), which is the ratio of the concentration of an element in the solid phase (on a mass basis) to that in solution:

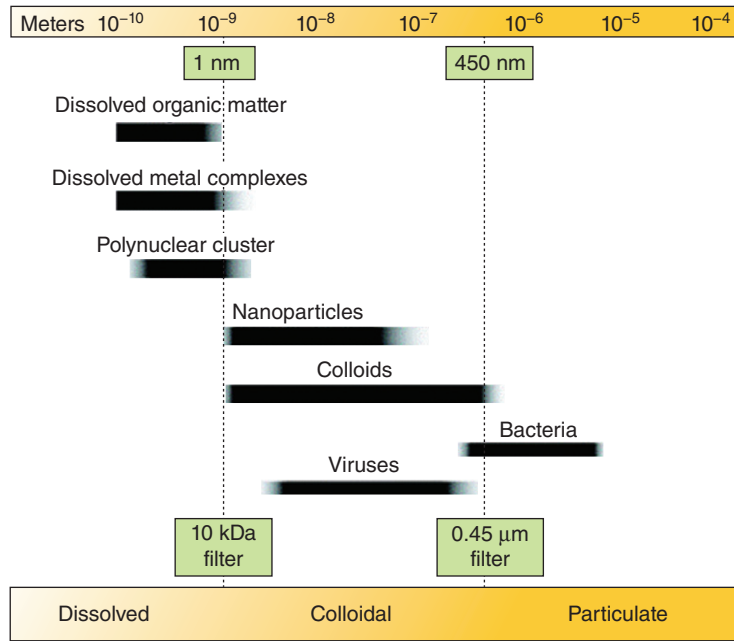
$$K_D = C_p / C_w \quad (2.3)$$

If the solid concentration ( $C_p$ ) is expressed in moles per kilogram of solid, and the dissolved concentration ( $C_w$ ) is in molar units, then the  $K_D$  is essentially unitless (assuming that 1 l of solution is 1 kg). This measure is widely used as an overall measure of partitioning. It does not distinguish

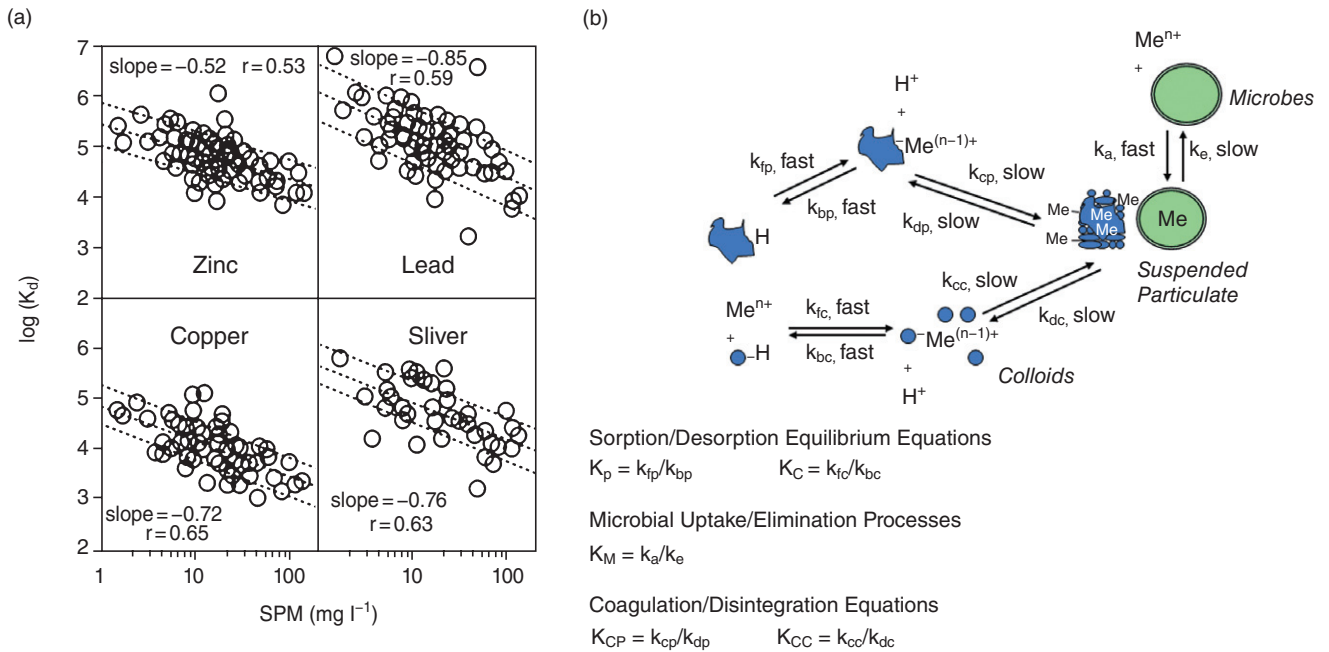
between sorption to or binding to the solid phase, or uptake into living organisms, but it can be a useful relative measure of the tendency of a particular element to remain in solution. The  $K_D$ s for metals range widely in the water column, from values that are  $>10^5$  (e.g., Ag, Hg and Pb) to other metals where values are  $<10^4$  (e.g., Cd) [2, 4, 8, 10]. However, values vary for a particular metal as well across ecosystems due to differences in the characteristics of the suspended material and the presence or absence of NOM in solution. In addition to passive sorption, the metal(loid)s that are required nutrients for algal growth can be actively assimilated and this can have a dramatic impact on their aquatic concentration. This is especially true in remote locations, such as the open ocean, or in remote temperate lakes.

Additionally, the distribution of metal(loid)s between the dissolved and particulate phases is not simple as there is a continuum of particle sizes, ranging from microorganisms and dust, which are all typically  $>0.4\mu\text{m}$  (the typical size cutoff size of filters used by environmental scientists to separate the filtered fraction from the particulate fraction), to colloidal material, which are typically  $<500\text{nm}$  ( $0.5\mu\text{m}$ ) in size. The continuum of sizes for various types of particles is shown in Fig. 2.2 [11]. Colloids, both inorganic and organic in nature, are produced biotically or abiotically and include small organisms such as viruses and some small bacteria, and are often operationally defined as the  $>0.02$  and  $<0.4\mu\text{m}$  fraction. Their presence in the filtered fraction can distort estimates of partitioning as they are considered within the dissolved fraction in Equation 2.3 [10–12].

The partition coefficient,  $K_D$ , should be independent of particulate load as it is a normalized value, but, as shown in Fig. 2.3, the measured values often show a strong relationship with total suspended solids (TSS). For all metals shown (Zn, Pb, Cu, and Ag), there is a strong decrease in the value of  $K_D$  with increasing TSS and all have a similar slope [12–14]. The accepted explanation for this trend is that the experimentally separated dissolved fraction (typically  $0.4\mu\text{m}$  filtered) contains both truly dissolved and “colloidal” material and that the relative amount of colloidal material is related to the TSS. Therefore, at high TSS, the error is enhanced and the value measured experimentally ( $K_D$ ) is lower than the true value ( $K_p$ ). The overall mechanism used to explain this phenomenon has been termed *colloidal pumping* [12]. Overall, it stipulates that the partitioning between the particulate and truly dissolved metal(loid) fractions involves the intermediate stage of colloidal material, and that there is a dynamic steady state between these three fractions. This further suggests that particles or colloids are not discreet entities but can be aggregates and can be formed by the combination and coagulation of smaller particles and colloids, especially in coastal waters and freshwaters. In the open ocean, it is generally accepted that in addition to colloids, there are two distinct groups of particles: the suspended smaller particles, which consist of phytoplankton



**Fig. 2.2** Range in sizes for various fractions existing in a natural water sample and the typical constituents of these fractions. Typical filtration is using either a 0.2 or 0.45 μm pore size. Reprinted with permission from Aiken et al. (2011) *Environmental Science & Technology* 45: 3196–201, Copyright (2011), American Chemical Society [11].



**Fig. 2.3** (a) Relationship between particulate load and measured distribution coefficients for zinc, copper, lead, and silver. Reprinted with permission from Honeyman and Santschi (1988) *Environmental Science & Technology* 22: 862–71, Copyright (1988), American Chemical Society [12]; (b) Diagram representing the interactions that can occur between microorganisms, particles, colloids and dissolved species and how this impacts metal cycling in aquatic systems. Note that SPM and TSS both refer to the same suspended solids.

and other microbes, and small detrital material, and larger sinking particles, which comprise zooplankton fecal pellets, skeletal material, and other biogenic debris. The larger fraction also includes agglomerations of smaller particles due to coagulation and adherence to the surfaces of “sticky” biological material, and this fraction forms the bulk of the sinking particulate matter [15, 16].

It is possible to define partition coefficients in terms of both the particulate ( $>0.4\mu\text{m}$  material) and colloidal fractions if measurements of the colloidal fraction are made using ultrafiltration or other techniques [14]:

$$K_D = C_P/C_W \quad (2.4)$$

$$K_P = C_P/C_D \quad (2.5)$$

$$K_C = C_C/C_D \quad (2.6)$$

where  $C_P$  and  $C_C$  are particulate and colloidal concentrations ( $\text{mol kg}^{-1}$ ) in suspended matter or colloidal material, and  $C_D$  is the truly dissolved concentration ( $[\text{M}] - \text{mol l}^{-1}$ ). Given the definition of  $K_D$ ,  $C_W$  is the concentration of dissolved and colloidal material (i.e., the total filtered fraction) on a molar basis, so:

$$C_W = C_D + C_C \cdot M_C \quad (2.7)$$

where  $M_C$  is the mass of colloidal material (in  $\text{kg l}^{-1}$ ). Substituting Equation 2.7 into Equation 2.4, rearranging, and using Equation 2.5, it is apparent that:

$$K_D = K_P/(1 + K_C M_C) \quad (2.8)$$

Therefore,  $K_D$  approaches the true value of  $K_P$  at low colloidal mass concentrations or if the  $K_C$  value is much smaller than that of  $K_P$ .

The adsorption of metal(loid)s to particulate and colloidal material is often considered to be through surface complexation with active acidic sites (see Section 3.4). The interaction is often considered to be reversible and essentially at instantaneous equilibrium given changes in concentration; however, this is not always the case. As an example, metal adsorption to particulates from the Changjiang River, the fourth largest river in the world and the largest in China, showed that the adsorption followed typical adsorption isotherms but that the maximum adsorption was achieved only after five or more hours, and more than a day for Cd [17]. A number of studies of both dissolved–particulate interactions and interactions in sediments between the solid phase and porewater also suggest that while adsorption may be rapid, desorption is often a much slower process [10, 18]; therefore, it is not always appropriate to model the system as a reversible equilibrium system. One reason for differences in the rate of adsorption versus desorption is that metals may become incorporated into the inner matrix of the particulate, which in the environment may not be a well-ordered, spherical, non-porous solid, as many models assume. The particulate phase is much more likely a porous

material due to the coagulation processes discussed previously, the heterogeneity of the particles, and the likely presence of pores in terrestrial material.

On encountering a solid phase, dissolved metal(loid)s first bind to the more abundant but relatively weaker sites. This rate is rapid compared to desorption, where the metal(loid)s are being released from the less abundant but stronger binding sites where they have migrated over time since adsorption. Studies have shown that while metal(loid)s reach a steady state in terms of  $K_D$  after addition of a metal(loid) to a particle-containing solution relatively rapidly, this initial  $K_D$  value is often lower than that measured using environmental samples. Reasons for this include the fact that some of the metal(loid) in natural solids is likely unavailable for exchange with the dissolved phase due to its incorporation into the internal structure of the particle. This has led to the notion that metal(loid)s exist in particulate in two phases – an *exchangeable* fraction and a *non-exchangeable* fraction. As an example, in the Changjiang Estuary in China,  $<25\%$  of the metals measured were in the exchangeable fraction, likely reflecting the dominance of eroded terrestrial material in the TSS [17]. In contrast, in Galveston Bay,  $>50\%$  was in the exchangeable pool [19]. Differences in fractionation reflect both differences in the solid phase composition, and in the quantity and strength of binding ligands in solution.

Therefore, the partitioning between the dissolved and particulate phase is not a simple reversible equilibrium situation. One approach to modeling the differences in exchange dynamics is to assume the  $K_D$  (or more appropriately the  $K_P$ ) is related to the ratio of the adsorption and desorption constants, which are assumed to be first order:

$$K_P = k_{ad}/k_{ds} \quad (2.9)$$

Where  $k_{ad}$  is the adsorption rate constant and  $k_{ds}$  is the desorption rate constant. If  $k_{ds}$  can be determined, then  $k_{ad} = K_P/k_{ds}$ . Then, the half-life to steady state is  $t_{1/2} = (k_{ad} + k_{ds})^{-1}$  and is mostly determined by the rate of desorption. Another approach is to use a binary or multi-component model with different rates of binding of metal(loid)s to the various phases [20].

A number of studies examining the adsorption and desorption of metals from sediments are detailed in a publication edited by Allen [18]. The rates of adsorption and desorption estimated in the various studies of a number of metals (transition metals, Zn, Cd, and Pb) allow a number of conclusions or tenets to be proposed. It appears in many instances that adsorption and desorption are multiphasic and that the process can often be represented by a two-phase system with a “fast” and a “slow” process [21]. This reflects the fact that there are many different binding sites on the surfaces of marine solids (carboxylic acidic groups, N-containing groups, thiols and both organic and inorganic binding sites). Additionally, given that desorption is slower than adsorption, some studies have likely not reached viable