METHODS FOR INVESTIGATING TRACE ELEMENT BINDING IN SEDIMENTS

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Abstract

Sediments play an important role in maintaining water quality. This review describes methods of investigating element binding in sediments, and assesses the value of each for characterising sediment contamination. Although easy to obtain, data from 'bulk' tests such as fractionation schemes or fitting adsorption isotherms cannot describe binding or phase composition definitively. Modern spectroscopic techniques can investigate the sediment surface on a molecular scale, but are not yet used routinely for sediment analysis. Proper assessment of the implications of sediment contamination normally requires more than one method to be used. Comparing contaminant remobilisation rates to the timescales of environmental factors causing remobilisation is also important.

I.   Introduction

Anthropogenic contamination in the environment is a growing concern. Worldwide, the increasing number of water bodies with elevated concentrations of heavy metals and other toxic elements threaten human health and cause degradation of the surrounding environment. Sediments often play an important role in maintaining water quality by removing contaminants from the water column. However, subsequent contaminant remobilisation from the sediment can keep dissolved concentrations elevated long after the initial source has been removed. The manner in which sediment contamination is treated ultimately depends on the sediment's chemical reactivity. Choosing the most appropriate treatment requires an understanding of how the contaminant binds to the sediment and the conditions under which the contaminant will be released back into the water column.

Sediments are heterogeneous mixtures that include both mineral phases (e.g., Fe oxides, Mn oxides) and detrital organic matter.[46] Contaminants may bind to these phases by adsorption, precipitation, and coprecipitation[4,23] and element mobility is controlled by both the binding phase and binding mechanism. Researchers originally presumed that, once retained in the sediment, a contaminant was trapped forever. However, it is now appreciated that contaminants can cycle across the sediment-water interface many times. In general, a contaminant is not fixed permanently and many physical and chemical variables can influence contaminant mobility. This review describes current methods used to investigate element binding in sediments and assesses the information that each method is able to provide. Sediment contamination may be examined from two perspectives, either focussing on how contaminants partition between different sediment phases or the conditions that cause contamination to remobilise back into solution. Proper assessment of the implications of sediment contamination requires investigation of both aspects, as well as consideration of the environmental factors causing remobilisation.

II.   Factors Affecting Remobilisation from Sediments

Contaminant remobilisation occurs when altered conditions create a gradient to drive the remobilisation. Common driving gradients are changes in redox potential and pH, often caused by the degradation of organic matter and biological activity.[47,48] Mimicking such gradients exactly in a laboratory is difficult. The development of driving gradients is controlled by the size and depth of the water body, as well as the surrounding climate. The complexity of trace metal distributions in lake waters and sediments is often attributed to the dynamic nature of lakes, where inputs, mixing and removal processes vary on a variety of time scales. Contaminant remobilisation has been well studied in deep lakes and estuaries.[10,25,42,184] A predictable sequence of events occurs: temperature stratification develops during summer, isolating the bottom waters from the mixed surface layer and limiting oxygen transport to the sediment. These anoxic conditions can last for weeks, promoting the dissolution of Fe and Mn oxides and the precipitation of sulphide minerals.[29,65] Deep lakes often reach equilibrium. However, in shallow lakes the sequence of driving forces is less predictable. While stratification can develop, often on a diurnal pattern,[9,63] regular wind events ensure that the lake rarely remains stratified for more than a day. The development of anoxic conditions at the sediment-water interface is therefore less frequent and occurs for a shorter period of time. Obviously the rate of contaminant remobilisation becomes more important in these circumstances.

Sediment resuspension is another process in which remobilisation rates may control release. Waves, currents and dredging can all resuspend the bottom sediments of a lake. Sediment resuspension releases interstitial porewater[111,126] and may lead to contaminant release from the sediment as well.[20,37,93] Benthic organisms also facilitate the movements of contaminants into and out of sediment by burrowing, respiration or feeding.[18,85,108,128]

The chemical composition of lakewater can change temporally and spatially and this also

affects the extent of remobilisation from sediments. Dissolved organic matter (DOM) is generally assumed to increase the solubility of elemental contaminants, either because the element is complexed by the DOM, preventing adsorption, or because DOM competes for sorption sites.[124,186] However DOM can comprise many varied compounds and determination of the mechanisms involved in reactions between metals and DOM is difficult.[77,96,145] The microbial degradation of DOM to carbon dioxide will affect the redox potential as the process requires an electron acceptor to complete the reaction.[158] In well mixed waters, oxygen is the most likely electron acceptor because oxygen reduction releases the largest amount of energy. However, in waters depleted in dissolved oxygen (e.g., in sediments or flooded soils) other electron acceptors are active, usually in a predictable sequence (Table 1). These reactions determine the redox potential of the sediments and affect both ion speciation and redox sensitive minerals. Iron redox cycling and the reductive dissolution of Fe and Mn minerals, in particular, is significant in controlling contaminant concentrations in deep lakes.[29,144] These reactions are often depicted as a one dimensional series but usually occur in a two or three dimensional matrix because sediment heterogeneity produces localised areas where only one or two electron acceptors are present.[45,136,189]

Redox reactions also alter pH. Water pH can change both naturally and as a result of human activity. Several studies have shown that the pH of waters with significant biological production fluctuates in response to changes in algal biomass on both diel and seasonal timescales.[30,39,100] Photosynthesis and respiration cause changes in the dissolved carbon dioxide concentrations of a water body, leading to pH fluctuations.[161] pH changes arising from anthropogenic causes, for example the effect of acid mine drainage, are more dramatic.[41] Large pH changes initiate the dissolution of sediment minerals, releasing incorporated contaminants; Fe oxides will dissolve at both low and high pH. Even small pH changes can affect the extent of adsorption of a solute on a surface. pH controls the

protonation of dissolved species and functional groups present on the sediment surface. This is the principal source of variable charge in sediments and so affects the extent of contaminant adsorption.[143,153]

III.   Characterising Contaminant Partitioning in Sediments

Using total concentrations to measure elemental availability is normally inappropriate because this approach includes the assumption that all phases have equal control of the element and that all phases act identically in different environments. Instead, the sediment phase (or phases) that are involved in elemental binding should be identified. Sediments are complex mixtures of both mineral phases and detrital organic matter and current characterisation techniques often produce ambiguous results. Most often chemical extraction and statistical studies have been used to characterise sediments. These 'bulk' analyses tend to lead to oversimplified interpretations that do not take sediment complexity into account. Sediment complexity also means that experiments using model minerals or phases are unable to mimic the behaviour of real sediments. In recent years, however, numerous spectroscopic techniques have allowed analysis at a molecular level, finally providing direct evidence of surface composition and bonding.

Chemical Extraction

The most popular method of investigating contaminant partitioning in sediments is by the use of chemical extraction, which is usually employed in one of two ways. A single extraction solution might be applied to a sediment sample in order to mimic a specific set of environmental conditions.[101] In particular, many solutions have been devised to determine element 'bioavailability', although often the choice of extractant is largely empirical.[129,151,173] Extractants to measure bioavailability can be devised on a more mechanistic basis, however, such as those containing the gastric and intestinal enzymes of organisms likely to come into contact with the sediment.[171,172]

The second application of chemical extractions is to investigate sediment mineralogy and contaminant partitioning and the most popular way of doing this by the use of sequential extraction, or fractionation, schemes.[23,44,53,73,116] Element partitioning between sediment phases is evaluated by treating the sediment with a series of sequential extracting solutions, each targeting a different phase. Analysing each final extractant quantifies the element concentration associated with each targeted phase. In general the same extraction mechanisms are used in all schemes and include ion exchange, acid and base dissolution, reduction, oxidation, and complexation. Each mechanism affects different sediment phases, although some extractants utilise more than one extracting mechanism. What is actually extracted ultimately depends on which extraction solution is used and the sediment being investigated. Many schemes for metals are based on that devised by Tessier *et al*.,[168] although trace element partitioning of anions like As can be more successful with a schemes specifically developed for P.[22,132,185] Table 2 lists a number of extraction solutions that have been used in fractionation schemes. A huge variety of different 'recipes' have been devised to extract the same phase, and this variety is an indication of the impossibility of finding one extractant that is entirely specific for one fraction.

The popularity of fractionation schemes stems from the fact that these schemes are simple, accessible, and seemingly straightforward to interpret. However, this is rarely the case. Chemical extraction is unlikely to be completely selective for only one phase. Results are influenced by both reagent choice and extraction time,[23] as well as the conditions under which the sediment is manipulated.[121] As a result, different extraction schemes may give different interpretations of partitioning in the same sediment.[14,57,64,89] Extracted contaminants can also readsorb onto other phases during the procedure and demonstrating post-extraction readsorption experimentally is difficult. Different approaches have yielded widely varying results.[12,56,62,127,167] Deionised water or ion exchangeable washes between extractions[132] or

determining correction factors using trace element spikes[56] have attempted to address the issue. However there is no consensus on whether these measures improve data interpretation.

Despite the pitfalls, researchers continue to use fractionation schemes and sometimes without due care. Some researchers argue that optimisation and validation is required every time a fractionation scheme is applied to a new sediment.[58,109] Testing to see whether repeated extraction is required to extract the entire fraction is also suggested.[11,117] However, the intrinsic nature of the method means that interpretation of results is always influenced by the fractionation scheme used. If the data are intended solely to indicate differences in sediment behaviour or as a tool to compare different sites this may be unimportant.[11,95,149] However, in most cases, interpretations from fractionation schemes should be corroborated by other methods. Combining fractionation data with spectroscopic and diffraction techniques has been used to monitor the extraction of crystalline phases[34,84] or speciation[142] but does depend on crystalline material being present in the sediment for the former. Such experiments are generally not suited to large numbers of analysis either. Fractionation analysis is enhanced by measuring major elements like Fe, Al, and Ca, which influence dissolution/precipitation and adsorption/desorption equilibria[180] or comparison to statistical trends in total metal concentrations.[95]

In order to eliminate some variability and to allow standardisation between laboratories, the Community Bureau of Reference (BCR, now EC Standards, Measurements and Testing Programme) devised a three-step fractionation scheme that was tested in interlaboratory trials and applied to a sediment reference material (BCR CRM 601).[73,119,174] However, even this method has shown variable recoveries for some samples,[26,133] as well as variability between analysts.[27] Modifications to the scheme were made to overcome analyst bias and an aqua regia digestion of both the residual and the whole sample was added as a measure of internal consistency.[122] This has resulted in improved precision and assessment of new reference

materials continues.[87,164]

Statistical Analysis

The analysis of statistical relationships between total element concentrations is another 'bulk' method that has been used to identify phase associations.[98,130,135] The approach is most successful when a single substrate acts as the main binder of a trace element as correlations are less evident when two or more phases influence binding. The technique has been used to both identify general trends in contaminant binding over a large number of different sites[98,181] and investigate processes in a single waterbody.[67,95] Statistical relationships have also been used to demonstrate that different mineralogy can exist at related sites.[135] Whilst the existence of a correlation does not prove that a phase association actually exists, the correlation may augment fractionation information and aid in identification of phases important in binding an element.[95] As well as using raw data, statistical trends can be investigated after normalization by the concentration of an element such as Al, to account for the dilution effect of minerals that the element does not associate with.[95] Normalization does require that the coefficient of variation (V = standard deviation divided by the mean) of the normalising element is similar or better than that of the trace element as otherwise correlation results will be compromised.[176] Principal component analysis (PCA) is another way of determining the influence of different sediment phases by identifying a set of components that encapsulates the maximum amount of variation in a dataset.[130,135]

Sediment heterogeneity may make assessment of sediment contamination difficult and normalization can be used to account for environmental variation as well.[81] The enrichment factor (EF) is a method commonly used to determine if element concentrations in sediment are above background.[15,79,134,135,188] Here, element concentrations are first normalised against the concentration of a representative matrix element, such as Al, Li, Fe and then ratioed to normalised values from a reference sediment.[130] An EF greater than one may then suggest

the sediment is contaminated with that element. Investigators must ensure, however, that the normalizing element is not subject to anthropogenic enhancement as well. The resulting EF will also be greatly influenced by the reference point and choosing an appropriate reference sediment is essential.[130,188]

Molecular scale techniques

Molecular scale techniques have been used to study elemental binding on surfaces since the early 1990s.[19,104,110,154] In particular X-ray Adsorption Spectroscopy (XAS) techniques such as X-ray Adsorption Fine Structure (EXAFS) and X-ray Adsorption Near-Edge Structure (XANES) can give direct evidence for surface species of oxidation state, number and type of near neighbours, coordination state and bond distance.[43,102,113,120,163] For a long time, however, these techniques lacked the sensitivity required to analyse contaminant binding in most environmental samples and application was limited to the most contaminated sediments[137,142] or to characterising adsorption on model phases.[43,102,120,163] While elemental adsorption has been confirmed on model sediment phases, there is no assurance that these studies actually mimic what is happening in the natural environment. Sorption experiments are usually performed over short timescales and there may be little similarity between the results from such tests and what actually occurs over months or even years in natural sediments. Long term studies of adsorption have demonstrated that sorption can occur in several steps, with rapid surface exchange or adsorption followed by a very slow continuous uptake.[2] This slower uptake has been interpreted as entrainment of the ion into the solid phase through aging. Thus application of results from short term studies must be applied with caution. Recently detection limits of XAS techniques have improved and more studies of real sediments are now appearing.[51,52,114,165] However access to facilities providing such techniques is not always available.

IV.   Binding Processes in Sediments

Sediments bind and release contaminants by one of two basic mechanisms: adsorption/desorption or precipitation/dissolution. However, to properly model partitioning between dissolved and particulate phases in a natural system requires very detailed information that is not always available.[99] As well as quantifying binding intensities, capacities, and the relative abundance of each important sediment component, the effect of particle coatings and of multi-component aggregation on the binding capacity of each substrate must also be assessed. The kinetics of redistribution among sediment components and the effect of major competitors should also be considered. Quantitative models have been employed to describe adsorption on well defined component surfaces, but such models have seldom been extended to the multicomponent systems typical of nature. Again, the advent of molecular scale techniques does help provide this information, but many experimenters still rely on empirical or macroscopic models and experiments.

Adsorption/Desorption

Adsorption is a process where a solute in the liquid phase becomes bonded to the surface of a solid, usually on a specific site. Metal adsorption to sediments is analogous to the formation of soluble complexes, with the surface site acting as the 'ligand' in the reaction.[32] The strength of the bond between the solute and surface site will vary.[6] Solutes can be weakly bound by non-specific forces (e.g., van der Waals forces) or by electrostatic attraction between a charged solute and the surface site. Solutes are strongly bound by specific adsorption, which occurs when chemical forces of attraction create covalent bonds between the solute and the surface site. Specific adsorption is slower than electrostatic adsorption and is sometimes partly irreversible. The process of adsorption is highly dependent on pH, E_h, temperature, and the composition of both the solid surface and the solution.

Contaminant sorption onto a solid at equilibrium, Γ (mol g^{-1}), can be expressed by the

equation:

$$\Gamma = \frac{n^{sed}}{m^{sed}}$$

[1]

where n^{sed} is the number of moles of a substance i bound per gram of sediment (m_{sed}).

If the equilibrium governing the partitioning of i between the dissolved and solid phases is disturbed, then the change in partitioning can be expressed using a mass balance:

$$n_o^{sed} + n_o^{wat} = n_i^{sed} + n_i^{wat}$$

[2]

where n_o^{sed} is the number of moles of i sorbed and n_o^{wat} the number of moles of i dissolved before the disturbance, and n_i^{sed} and n_i^{wat} the partitioning of i between the solid and dissolved phase after equilibrium has been reattained. If we express n^{sed} in terms of Γ, n^{wat} in terms of dissolved concentration, c, and the mass of sediment (m_{sed}) and volume of solution (v) in terms of slurry density S = m_{sed}/v then:

$$\Gamma_o S + c_o = \Gamma_i S + c_i$$

[3]

This concept has been widely used in experiments where adsorption is measured by adding a solid substrate to a solution of known composition. The amount of i sorbed onto the solid is calculated by measuring concentration changes in the solution.[155] Most commonly, values of Γ_i from a series of experiments are plotted against the final equilibrium aqueous concentration attained, c_i, producing an adsorption isotherm at a known temperature and pressure. These isotherms have been fitted to an array of empirical models, including Henry's Law, and the Langmuir and Freundlich equations.[86,161] Henry's law was initially an observational model used for partitioning of volatile substances between liquid and gaseous phases[36,86,182] and represents a situation where the affinity of the solute to the surface (K_H) remains constant:

$$\Gamma_i = K_H c_i \tag{4}$$

This model is valid at very low concentrations,[86] but increasing coverage of the surface by solute at higher concentrations usually supresses the sediment's adsorption capacity and the adsorption isotherm is no longer linear.

The Langmuir isotherm was derived using the assumption that adsorption sites on the surface of a solid become occupied by a solute with 1:1 stoichiometry. The isotherm assumes that sorption stops at monolayer coverage and that all sites have the same binding energy, regardless of how much surface has been covered.[159] The Langmuir equation has proved useful for summarising adsorption isotherm data and has been used extensively to provide modelling input[68] and is generally written as:

$$\Gamma_i = \frac{abc_i}{1 + ac_i} \tag{5}$$

where a is a measure of the site binding strength and b is a measure of the capacity of the surface.[178] At dilute solutions (i.e., $ac_i < 1$) the Langmuir equation [5] reduces to the same form as Henry's law [4].

The Freundlich isotherm is based on similar assumptions to the Langmuir isotherm except that the binding energy changes with increasing adsorption, i.e., the bonding strength of available sites is not constant. The equation is actually equivalent to the integral of a continuum of Langmuir equations with a log-normal distribution of Langmuir constants:[155,159]

$$\Gamma_i = Ac_i^{1/n} \tag{6}$$

where A is a measure of bonding strength, and n is a measure of surface heterogeneity and always > 1. The Freundlich equation models solids with heterogeneous surface properties very well over a wide concentration range,[159] but is inappropriate for $c \rightarrow 0$ because it does

not reduce to Henry's law [4].

Many investigators have used the fit of data to particular isotherms to make mechanistic interpretations about metal sorption on surfaces.[3,21,38,83,97,169,170] However, Γ can describe any type of sediment binding and these isotherms fit several different binding mechanisms, including precipitation.[31,90,107] Conformity to a particular isotherm does not prove that a particular mechanism is operational and sorption models that use macroscopic data are basically curve fitting exercises, useful for summarising and comparing experimental data but not accurately describing the phenomena occurring in the solid-liquid system.[59,178] Care must be taken when interpreting adsorption/desorption results to elucidate binding mechanisms or when fitting more flexible equations such as the Constant Capacitance model,[54] the Triple Layer model,[182] or the Basic Stern model.[159] These models incorporate so many parameters that almost any given set of data can be made to fit.[8,55,82,106,166] In some cases the ion adsorption has been correctly described, but using hypothetical surface species that do not necessarily exist.[72] Dispute also remains over whether variables determined for single ion systems can be used in multi adsorbate systems.[49] The results of surface complexation models will be improved by using the correct surface structure and number and types of surface sites involved and surface spectroscopy must be used to determine conclusively how a solute is adsorbed.[140]

Precipitation/dissolution

Precipitation occurs when one or more dissolved species accumulate and form a solid. This process has a Gibbs free energy of reaction, ΔG^o_f, expressed as thermodynamic solubility product, K_{sp}:[161]

$$\Delta G^o_f = -RT \ln K_{sp} \qquad\qquad [7]$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is temperature (°K). The solubility

product for the reaction where the precipitate A is in equilibrium with dissolved species B and C is:

$$aA(s) \leftrightarrow bB(aq) + cC(aq)$$
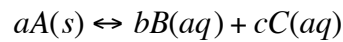
$$K_{sp} = \frac{\{B\}^b \{C\}^c}{\{A\}^a} \qquad [8]$$

where the {} denote species activity. The activity of a pure phase is unity, and in solutions of low ionic strength, the activity of a dissolved species can be approximated by concentration. For illustration, thermodynamic data for some common sediment minerals are given in Table 3.

Similar to K_{sp} is the ion activity product (IAP), which describes the relationship between the activity (or concentration) of the reactants and products of a reaction at a given time. Comparing the IAP with K_{sp} is often used to test whether precipitation has occurred. However, this approach is not always valid. Separate trace elements can become included in the crystal structure of precipitating solids, a process known as chemical substitution or coprecipitation. Replacement of a foreign constituent in a crystalline lattice causes decreases in the activity of the solid phase to less than one, therefore decreasing the solubility of the phase.[161] In many cases the observed occurrence of elements binding to sediments in solutions that appear to be formally unsaturated can be explained by the formation of a solid solution.[138,139,141] The formation of solid micro-niches within sediment can also occur, regardless of the bulk solution composition.[28]

The converse situation, where IAP that is larger than K_{sp}, does not guarantee precipitation either if the precipitated particles are small (e.g., < 1 μm) or if the supersaturation is too low to overcome the activation energy required to nucleate a new phase.[161] The rate is also a consideration as precipitation that is thermodynamically favoured can take geological

timespans to occur.[155]

Differentiating between adsorption/desorption and precipitation/dissolution

Distinguishing between adsorption and precipitation can be difficult. Adsorption on a surface is inherently two-dimensional, while precipitation produces a three-dimensional solid with thermodynamic properties.[155] Adsorption is limited by the amount of available surface and generally occurs faster than precipitation. However, both cause a loss of material from solution and the chemical bonds formed in each case can be very similar.[156]

Comparison of typical adsorption/desorption and precipitation/dissolution reactions shows that the equilibrium constant (K_s for adsorption/desorption and K_{sp} for precipitation/dissolution) for each has a similar form (Table 4). However, while [S-L], the concentration of ions adsorbed on a surface, depends on the mass of solid present, [SL] is an intrinsic property that is constant if the solid has a constant composition, as illustrated in Figure 1. Therefore one possible approach to conclusively differentiate dissolution from desorption is an analysis of the effect of S on trace metal remobilisation at fixed pH, E_h and temperature. For precipitation/dissolution control, the final solution concentration in a given medium is *independent* of S. However, if adsorption/desorption controls remobilisation the final solution concentration should *vary* with S. This method of differentiation is easily applied to natural sediments, but has only had limited application.[94] The differentiation is made by testing the mass balance equation [3] against the assumption that remobilisation is controlled by adsorption or dissolution.

For dissolution, the final concentration c_i will always be constant, except for very low S when the amount of solid that is available for dissolution is too small to reach equilibrium concentration. In this case, all of the solid will dissolve. Hence c_i will increase as S increases to S_{sat}, at which the constant saturation concentration (c_{sat}) is reached. If c_o is negligible and the amount of soluble mineral per gram of material is k_9, then:

$$c_i = k_9 S \qquad\qquad S < S_{sat} \qquad\qquad\qquad\qquad\qquad\qquad [9a]$$

$$c_i = c_{sat} \qquad\qquad S \geq S_{sat} \qquad\qquad\qquad\qquad\qquad\qquad [9b]$$

To model desorption a suitable isotherm must be chosen to describe the desorption. At trace concentrations, Henry's law [4] applies for equilibrium partitioning, and K_H (L g^{-1}) may be a summed term if the element is involved in more than one distinct equilibrium. If c_o is negligible, then rearrangement of equations [3] and [4] for the in terms of final equilibrium concentration and slurry density gives:

$$c_i = \frac{\Gamma_o S}{K_H S + 1} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad [10]$$

More complex equations can be derived for more concentrated solutions using the Langmuir and Freundlich equations. Figure 2 demonstrates the relationship between c_i and S for different cases of dissolution, described by equation [9], and desorption, described by equation [10]. In some cases, the form of the lines for dissolution and desorption can be very similar and experimental data may be fitted by both. A more incisive test of the suitability of the assumption of desorption versus dissolution is to calculate sets of Γ_i, c_i from the experimental data using equation [3]. Figure 3 shows the resulting plots of Γ_i versus c_i for the cases presented in Figure 2 and the difference between dissolution and desorption can be seen clearly. Henry's law produces straight line plots with a slope of K_H (and any curved Γ-c dependence would indicate any deviation from Henry's Law). For dissolution, Γ_i must remain near zero until c_{sat} is reached. This method has been used to examine As remobilisation from the sediment of a shallow lake.[93-95] Combined with other rate and adsorption studies, the protocol demonstrated that As remobilisation was controlled by the solubility of a thin, non-stoichiometric FeP_xFeAs_y oxyhydroxide surface and values of Γ_i, c_i deviated grossly from the

line representing Henry's law or any other adsorption isotherm.[94] This conclusion was further confirmed because As addition systematically decreased remobilisation from the sediment, as expected from the common ion effect on salt solubility. This result diverges from the generally held assumption that As mobility in the environment is controlled by adsorption/desorption, rather than precipitation/dissolution. Arsenic sorption experiments consistently fit 'adsorption' isotherms[21,38,97,169,170] and concentrations are usually undersaturated with respect to most pure As minerals, leading to the assumption that As precipitation cannot control As solubility.[97,103] In the case described, the data fitted all these common assumptions and therefore the dissolution mechanism would not have been discovered if Γ_i, c_i had not been plotted.

V.   Characterising Remobilisation Rates

Contaminant remobilisation is governed by both thermodynamic and kinetic processes. Chemical reactions can take place on timescales ranging from milliseconds to years.[153,154] Equilibrium studies alone are often inappropriate to simulate conditions in dynamic water bodies and kinetic investigations are necessary to properly understand contaminant release and mobility. The rate of contaminant remobilisation should always be compared with the timescales of remobilisation events.

Like the equilibrium sorption studies previously discussed, most kinetic methods are devised on the macroscopic scale and cannot intrinsically provide the mechanism of contaminant remobilisation. In simple systems, kinetic data can be used to determine the mechanisms by which a reaction proceeds.[161] However, in heterogeneous systems, reactions may take place in many steps and the resulting rate equation is often too complex to solve experimentally. For most laboratory experiments, mixing rates in the bulk solution are fast and therefore do not influence measurements of reaction rate.[7] The overall reaction rate will incorporate multiple chemical surface reaction steps and mass transfer, meaning the experiment will

produce apparent rate laws unless the overall reaction rate is controlled by a single step.[1] Experimental kinetic data from heterogeneous systems are usually fitted to simple (often empirical) equations, such as those listed in Table 5. These equations have been applied to both adsorption/desorption and precipitation/dissolution and cannot distinguish between the two mechanisms. Apart from the Empirical First order equation, all these equations retain a time dependence, meaning that, strictly, these equations are unable to fit dissolution data one the solution reaches saturation.

Regardless of whether the mechanism is dissolution or desorption, remobilisation must always involve the diffusion of a species from the solid surface to the solution bulk through the Nernst hydrodynamic boundary layer.[157,179] The thickness of this layer is determined by hydrodynamic factors such as solution stirring. If stirring is vigorous, the boundary layer thins and this step may then no longer influence the measured reaction rate. The rate of transport (j, mol s^{-1}) obeys Fick's first law:

$$j = \frac{DA\Delta C}{\delta} \tag{11}$$

where D is the ion diffusion constant, A the surface area of the solid, δ the Nernst layer thickness and ΔC (mol cm^{-3}) the concentration difference between the surface and the bulk. For most ions, $D/\delta \sim 10^{-2}$ cm s^{-1} in vigorously stirred solutions at 25 °C.[91,179] Comparison of measured rates with the rate estimated by Fick's first law is a good indication of whether transport across the boundary layer is controlling the overall rate. The role of transport is more complicated in porous solids, as mass transport within pores must also be considered. Many of the empirical equations in Table 5 arise from rate control by this step, depending on the complexity, or pore geometry, of the system. A unified treatment of this step has been provided using plots of rate^{-1} versus time.[1,153] The most simple demonstration of the relevance of 'pore' diffusion to rate analysis in a system is the 'interruption' test.[69]

Simple adsorption/desorption reactions are usually fast, unless stereochemical or complex bonding rearrangements are involved.[60,61,153] Such rearrangement has been described (for desorption or dissolution) as the detachment of an activated species [≡S],[70,160-162] assuming that only one functional group on the surface is involved. Far from equilibrium (i.e., when back reactions are negligible), the initial reaction rate is:

$$\frac{dc}{dt} = k_{12}[\equiv S] \qquad\qquad\qquad [12]$$

where k_{12} is constant, generally dependent on the surface morphology, crystallographic orientation, nature or density of defects, and the presence of impurities in the solid.[158] Many mineral reactions have been shown to obey equation [12].[71] A more general rate equation for dissolution of a crystal is:[17,159,161]

$$\frac{dc}{dt} = k_{13}(c_s - c)^n \qquad\qquad\qquad [13]$$

where c_s is the crystal solubility, c the solution concentration, and k_{13} and n constants, with n = 1 for most crystals (except close to saturation). c_s depends on both the solid and solution composition, including pH and any dissolved complexing agents.[70,161] The constant k_{13} depends on surface area and will vary if the crystal surface area changes during the reaction.[17] k_{13} must also vary when a thin scale layer dissolves completely or when the dissolving phase activity changes continuously (e.g., proportional to the mole fraction of dissolving phase present in a solid solution on the surface). Rate analysis for these last conditions has been uncertain,[70] however it has recently been demonstrated[94] that a possible equation is:

$$k_{13} = k_{14}(1 - F) \qquad\qquad\qquad [14]$$

where $F = c/c_E$ is the fraction of solid dissolved at time t, and c_E is the limiting concentration c_{sat}. Combined with other data, this rate constant may allow more appropriate modelling of

thin scale dissolution.

VI.   Conclusions

This review has described techniques commonly used to characterise sediments and trace element binding to sediments. However, readers should keep in mind the implicit assumption that the sediment sample being studied is representative of the field site of interest and has not been chemically altered during sampling, storage or treatment. In any environmental study involving sediment characterisation, it is extremely important that an appropriate sampling scheme is used and that the handling procedures adopted minimise sediment alteration.[16,131]

Although easy to obtain, data from established 'bulk' tests cannot independently provide definitive information regarding contaminant binding or sediment phase composition. Ideally data from modern techniques like XAS, which describe the sediment surface on a molecular scale, should be used in conjunction with macroscopic tests. However, spectroscopic techniques are much less accessible, more expensive, and still may not be sensitive enough for some natural sediments. Despite the inherent drawbacks, chemical fractionation schemes will remain a popular tool for solid phase characterization until surface techniques can be routinely applied. Results from these schemes are useful when comparing different sediments or the behaviour of different elements, even if a definitive interpretation may be elusive. The analysis of statistical relationships between total elemental concentrations can also help identify trends in elemental associations and may help identify which phases are most important in binding an element. Most importantly, an independent analysis serves as a reminder of the complexity of natural sediments and that fractionation data usually gives an oversimplified account of sediment partitioning. Determining the mechanism by which remobilisation occurs can be difficult because traditional methods, such as fitting data to adsorption isotherms or the calculation of IAP, do not conclusively distinguish between

adsorption/desorption and precipitation/dissolution. However, studies in which sediment slurry density (S) is varied may provide a 'bulk' method that is capable of differentiating between dissolution and desorption. Finally, kinetic studies of remobilisation must not be overlooked and rates of remobilisation should be compared to the rate of processes controlling remobilisation like sediment resuspension and the development of anoxic conditions.

VII.   Acknowledgements

VIII.   References

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IX. Figure Captions

Figure 1. Schematic diagram illustrating the difference between dissolution and desorption.

Figure 2. Relationships between final equilibrium concentration (c_i) and slurry density (S) for cases of both dissolution and desorption. The black line illustrates dissolution using equations [9a] and [9b] with $k_9 = 4$ µg g^{-1} and $c_{sat} = 133.3$ µg L^{-1}. The grey lines illustrate desorption using Henry's Law and equation [10]. In case A $\Gamma_o = 4$ µg g^{-1} and $K_H = 0.03$ L g^{-1}, in case B $\Gamma_o = 40$ µg g^{-1} and $K_H = 0.3$ L g^{-1}, and in case C $\Gamma_o = 400$ µg g^{-1} and $K_H = 3$ L g^{-1}. Dissolution and desorption could be experimentally indistinguishable for some cases when a limited amount of soluble solid is present

Figure 3. Relationships between final equilibrium sorption density (Γ_i) and solution concentration (c_i) for cases of both dissolution and desorption. The black line illustrates dissolution using equations [9a] and [9b], while the grey lines illustrate three cases of desorption, all using equation [10]. The parameters used for each case are the same as those in Figure 2. Plots of Γ_i against c_i can always experimentally distinguish between dissolution and desorption.
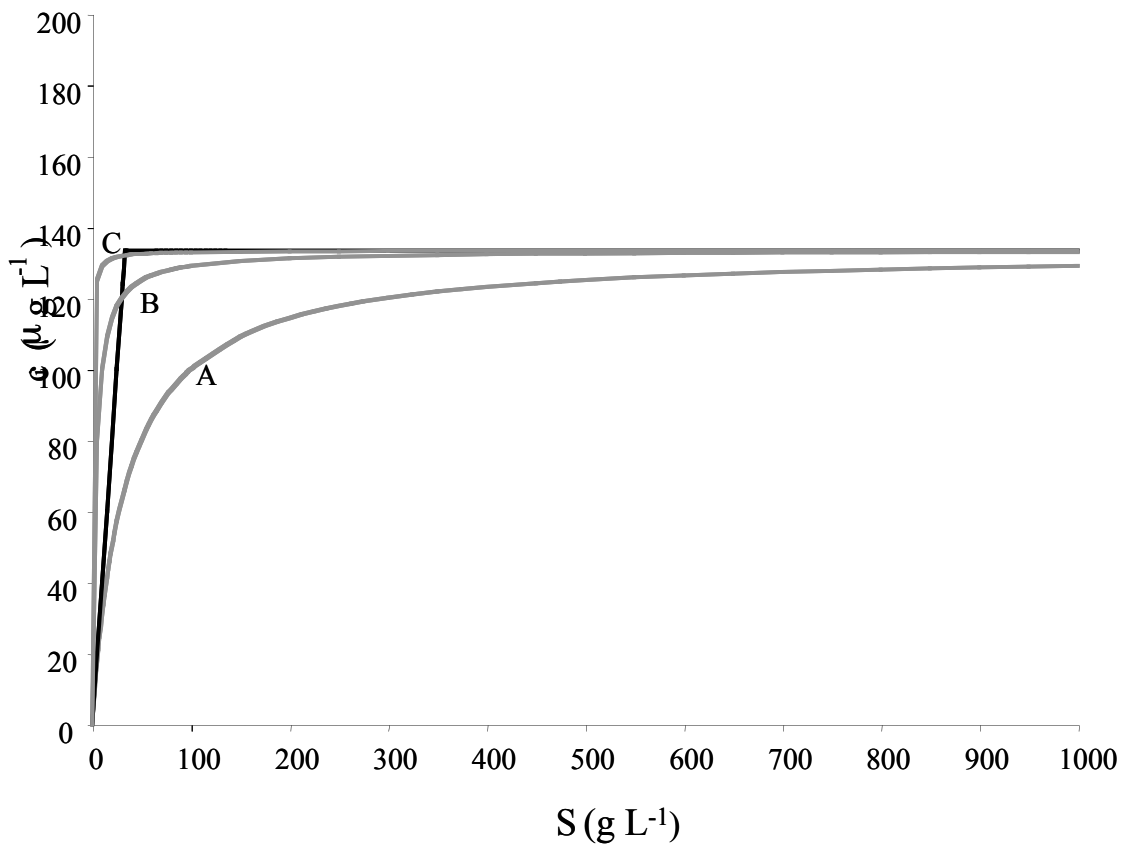
Dissolution
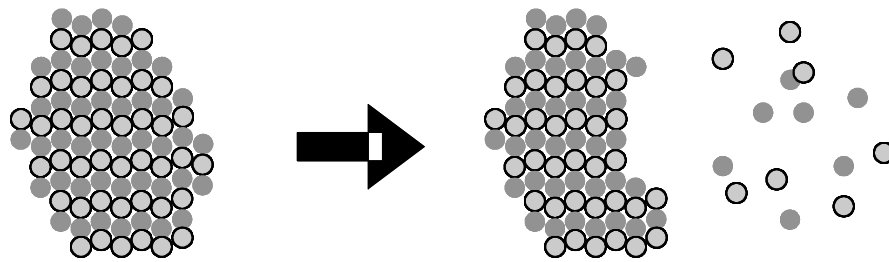
Remobilisation by dissolution is controlled by the activity of the solid
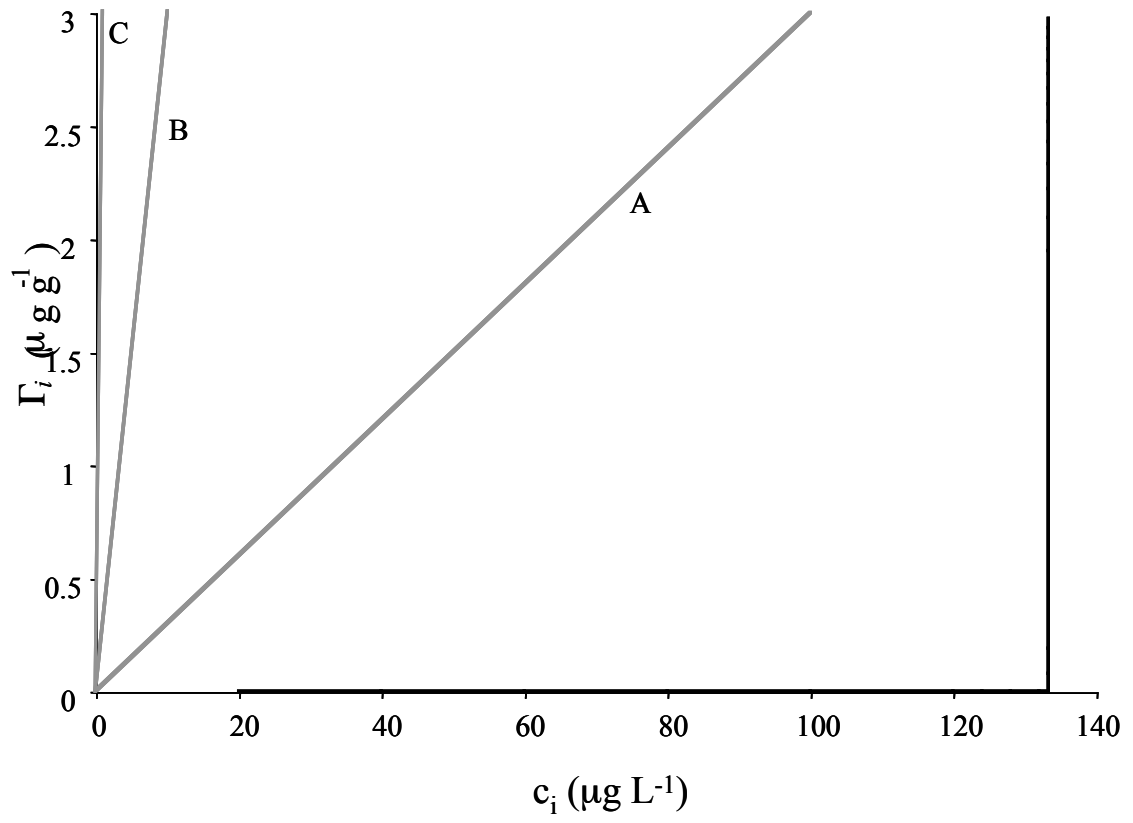
Desorption
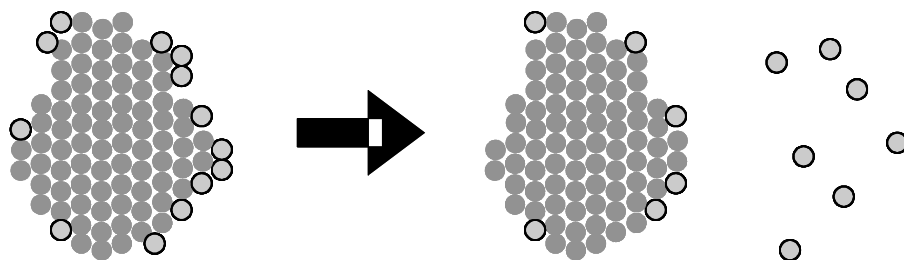
Remobilisation by desorption is proportional to the mass of the solid present

X. Tables

Table 1. Redox half reactions for common electron acceptors, adapted from Emerson *et al.*[40]

Reaction	E_h (mV)[136]
$O_2(g) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	0-750
$NO_3^- + 6H^+ + 5e^- \leftrightarrow 0.5N_2(g) + 3H_2O$	0-700
$MnO_2(s) + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O$	0-450
$0.5N_2 + 4H^+ + 3e^- \leftrightarrow NH_4^+$	
$FeOOH(s) + 3H^+ + 2e^- \leftrightarrow Fe^{2+} + 2H_2O$	0-100
$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O$	-200-0
Methanogenesis	-300-0

Table 2. Extraction schemes used for extracting trace elements.

Extraction Mechanism	Targeted phase	Examples of use	Comments
Ion exchange	Elements bound by electrostatic attraction.	$MgCl_2$ (1M),[12,95,132,168] $MgNO_3$ (1M),[5,148] KNO_3 (1M),[187] NH_4Cl (1M),[22,78,112,115] NaCl (1M).[76,185]	Replacement by competing ions occurs easily because there is no specific chemical bond between the bound element and the adsorption site.
		NaOAc.[125,175,177]	Sodium acetate can attack carbonate minerals, erroneously elevating results.[168]
Specific adsorption	Elements adsorbed on sediments by a chemical bond.	A concentrated solution of an ion that binds by the same mechanism as the race element of interest.	For example, phosphate effectively removes As specifically adsorbed to the surface of Fe oxides.[75,80]
Weak acid dissolution	Carbonates, most normally calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$.[35]	NaOAc buffer, with pH 4 – 7.[5,12,95,125,132,168,175,187]	Trace metal elements may coprecipitate with calcite both inorganically and biogenetically and both are dissolved by acidic sodium acetate. The pH used varies because of the effect on the sediment. A buffer pH below 5 can lead to an increase in Fe oxide dissolution,[58,152] but higher pH values decrease the efficiency of the extraction for carbonate minerals.[66]
Strong acid dissolution	Apatite, which forms with the aging of calcite with sorbed phosphate.[92]	HCl (1M),[95,132] H_2SO_4 (0.5M),[22,78] HCl (0.5M).[76,112,115]	Crystalline apatite minerals are more resistant to acidity than calcite and require stronger acids for dissolution. Freshly precipitated apatite may dissolve in the acetate extraction, however. Strong acids will also dissolve acid volatile sulphide minerals (AVS) and Fe oxides if not extracted previously.[74,150]
	Residual minerals, such as silicates.	Hot concentrated HCl, HNO_3 and HF.[125,148,168,175,187]	Acid digestion is used for determining total sediment concentrations or to determine residual element content after weaker, more specific extractions have been applied.[148,168,175] Hydrofluoric acid is the only extractant that will dissolve refractive silicates.[118] Elements associated with this residual are contained within the mineral crystal lattice and unlikely to have any short term impact on the environment.[187]
Base dissolution	Iron and Al oxides and organic matter.	NaOH (1M) for Fe oxides;[185] NaOH (0.1M) for Fe oxides,[22,78] or Fe bound P and organic bound P,[115] or Al bound P and organic bound P,[76] or Fe and Al bound P[112]	A fairly non-specific extractant that can dissolve a wide range of phases, depending on the concentration used. Weak solutions dissolve Fe oxides.[115,185] Stronger concentrations will also extract organic matter, especially humic acids, which are soluble at high pH.[33,146]
Oxidation	Organic matter	H_2O_2;[5,12,125,168,177,187] NaOCl (0.7M).[95,147,148]	Peroxide may produce oxalate as a by-product.[88] Oxalate extracts Fe and Mn oxides by complexation and therefore peroxide extraction is best applied after these have been removed. Sodium hypochlorite does not form oxalate and thus does not attack Fe and Mn oxides. Hence this extraction can be performed before Fe or Mn oxide extraction,

Method	Target phase	Reagent	Notes
			ensuring that the organic matter, which can be present as a coating on hydroxides and clays, does not interfere.
	Refractory organic matter and sulphur minerals.	High temperature ashing, followed by strong acid extraction of the residue[76,132]	Can be used to extract refractory organic matter not extracted by H_2O_2 or NaOCl, but is less specific;[132,145] ashing also been used to investigate sulphide minerals like pyrites.
Reduction	Manganese and Fe oxides.	$NH_2OH.HCl$ (0.04M), acidified with HOAc for Fe and Mn oxides,[168,187] or for Fe oxides only;[5,12] $NH_2OH.HCl$ (1 M), acidified with HOAc for amorphous Fe oxides (at pH 6) and crystalline Fe oxides (at pH 3);[175] $NH_2OH.HCl$ (0.1M), acidified with $HNO3$ (0.1M) for Mn oxides and amorphous Fe oxides,[125] or Mn oxides only;[12,147,148] $NH_2OH.HCl$ (0.1M), acidified with $HNO3$ (0.01M) for Mn oxides[5] or amorphous Fe oxides;[177] $NH_2OH.HCl$ (0.25 M), acidified with HCl (0.25 M) for amorphous Fe oxides.[24,95]	The association of trace elements with Mn and Fe oxides can vary from loosely adsorbed exchangeable forms, to moderately fixed forms (e.g., associated with amorphous Fe oxide), to relatively strongly bound forms (e.g., occluded in goethite). These different forms can be separately targeted by applying different extractants. Hydroxylamine hydrochloride is described as being specific to Mn oxides, leaving crystalline Fe oxides unaffected and dissolving minimal amounts of amorphous Fe oxide.[23] However, an acidified solution will dissolve amorphous Fe oxides as well.[24]
	Crystalline Fe oxides.	NaS_2O_4.[22,76,132,177]	Sodium dithionate is usually used in combination with reducing agents and complexing agents; bicarbonate is added to buffer pH and citrate is added to complex released Fe(II), preventing reprecipitation. Some trace metals (e.g., Cu, Zn) may precipitate as metal sulphides during the extraction and the dithionate salt can be contaminated with metal impurities such as Zn.[147]
Complexing agents	Aluminium phases and Fe oxides	$(NH_4)_2C_2O_2$ (0.2M), $H_2C_2O_4$ (0.2M) for crystalline Fe oxides;[95,125] $(NH_4)_2C_2O_2$ (0.2M), $H_2C_2O_4$ (0.2M), ascorbic acid (0.1 M) for crystalline Fe oxides;[147,148] NH_4F for Al associated P.[22,78]	Oxalate is used extensively to extract Al, including Al and Si associated with allophane. Acidic $(NH_4)_2C_2O_4$ (Tamm's reagent) dissolves amorphous Fe oxides when performed in the dark; light catalyses the reaction and crystalline Fe oxides then dissolve as well.[24] Combinations of oxalate and ascorbic acid solutions also dissolve all Fe oxides, but also dissolves Al unlike sodium dithionate. Oxalate extracts Fe from organic complexes[105] and should therefore be applied after extraction of the organic phase. Extraction of Al associated P using ammonium fluoride is done before Fe associated P.
	Humic substances	$Na_4P_2O_7$[13]	Sodium pyrophosphate removes humic substances by chelating cations that stabilise humic acids (e.g., Ca, Fe, Al). Very effective extraction that does not attack sulphides, unlike oxidation. However, may also extract amorphous Fe oxides.[105]

Table 3. Thermodynamic data at 25 °C. $-\Delta G_f^o$ is the standard free energy of formation, while K is the equation constant.

Reaction	log K	$-\Delta G_f^o$ (solid)	Reference
$Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2(s) + 2H^+$	-13.9	487	183
$Fe^{3+} + 2H_2O \leftrightarrow FeOOH(s) + 3H^+$	-41.7	490	183
$FeCO_3(s) \leftrightarrow Fe^{2+} + CO_3^{2-}$	-8.2	667	161
$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	-8.5	1129	161
$Fe_3(AsO_4)_2(s) \leftrightarrow 3Fe^{2+} + 2AsO_4^{3-}$	-34.1	1766	183
$Fe_2SiO_4(s) + 4H^+ \leftrightarrow 2Fe^{2+} + Si(OH)_4$	3.7	1379	161
$Ca_{10}(PO_4)_6(OH)_2(s) \leftrightarrow 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$	-114	6338	161
$Fe_3(PO_4)_2(s) \leftrightarrow 3Fe^{2+} + 2PO_4^{3-}$	-26	2457	161
$FeS(s) + H^+ \leftrightarrow Fe^{2+} + HS^-$	-5 (-3)	100	161
$FeS_2(s) + H^+ \leftrightarrow Fe^{2+} + HS^- + S$	-14.2	160	161

Table 4. Typical adsorption/desorption and precipitation/dissolution reactions.

	Typical Reaction	Equilibrium constant
Adsorption/Desorption	$S-L_{(s)} \leftrightarrow S_{(s)} + L_{(aq)}$	$K_s = \dfrac{[S][L]}{[S-L]}$
Precipitation/Dissolution	$SL_{(s)} \leftrightarrow S_{(aq)} + L_{(aq)}$	$K_{sp} = \dfrac{[S][L]}{[SL]}$

$S-L_{(s)} \leftrightarrow S_{(s)} + L_{(aq)}$

$K_s = \dfrac{[S][L]}{}$

Table 5. Simple kinetic equations.[7,50,123] C is concentration at time t, C_o is initial concentration, C_e is equilibrium concentration, and A, b, v, and k are constants.

Number	Equation	Rate form	Integrated form
1	Elovich		$C = A + \dfrac{1}{b}\ln(t + t_o)$
2	Two constant rate equation		$\ln C = \ln C_o + k \ln t$
3	Power Function/Freundlich		$C = kt^v$
4	Zero order	$\dfrac{dC}{dt} = k$	$C = kt$
5	Linear/First order	$\dfrac{dC}{dt} = kC$	$\ln C = \ln C_o + kt$
6	Empirical First order	$\dfrac{dC}{dt} = k(C_e - C)$	$\ln\left(\dfrac{C_e - C}{C_e - C_o}\right) = -kt$
7	Parabolic Diffusion Equation	$\dfrac{dC}{dt} = \dfrac{k}{2\sqrt{t}}$	$C = C_o + k\sqrt{t}$