Review

Environmental Risk of Metal Mining Contaminated River Bank Sediment at Redox-Transitional Zones

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Abstract: Diffuse metal pollution from mining impacted sediment is widely recognised as a potential source of contamination to river systems and may significantly hinder the achievement of European Union Water Framework Directive objectives. Redox-transitional zones that form along metal contaminated river banks as a result of flood and drought cycles could cause biogeochemical changes that alter the behaviour of polyvalent metals iron and manganese and anions such as sulphur. Trace metals are often partitioned with iron, manganese and sulphur minerals in mining-contaminated sediment, therefore the dissolution and precipitation of these minerals may influence the mobility of potentially toxic trace metals. Research indicates that freshly precipitated metal oxides and sulphides may be more "reactive" (more adsorbent and prone to dissolution when conditions change) than older crystalline forms. Fluctuations at the oxic-anoxic interface brought about through changes in the frequency and duration of flood and drought episodes may therefore influence the reactivity of secondary minerals that form in the sediment and the flux of dissolved trace metal release. UK climate change models predict longer dry periods for some regions, interspersed with higher magnitude flood events. If we are to fully comprehend the future environmental risk these climate change events pose to mining impacted river systems it is recommended that research efforts focus on identifying the primary controls on trace metal release at the oxic-anoxic interface for flood and drought cycles of different duration and frequency. This paper critically reviews the literature regarding biogeochemical processes that occur at different temporal scales during oxic,

reducing and dry periods and focuses on how iron and sulphur based minerals may alter in form and reactivity and influence the mobility of trace metal contaminants. It is clear that changes in redox potential can alter the composition of secondary iron and sulphur minerals and influence the sorption of toxic trace metals and susceptibility to dissolution when further redox potential changes occur. However further work is needed to determine: (i) The extent to which different duration and frequency of wet and dry cycles influences the dissolution and precipitation of iron and sulphur minerals in mining contaminated river bank sediment; (ii) The temporal effects on mineral reactivity (sorption capacity and susceptibility to dissolution); (iii) The key biogeochemical processes that control the mobility of contaminant trace metals under these dynamic redox potential conditions.

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1. Introduction

Mining impacted catchments are known to play a critical role in the distribution of metal contaminants through river systems with the bulk of metal flux to the sea around England and Wales reported to arise from highly mineralized catchments with a legacy of metal mining [1]. Where traditional approaches to management and remediation of mine water pollution tended to focus on point sources from adits and shafts [2–4], there is now a greater emphasis on dealing with diffuse (non-point) sources of mining pollution at a catchment scale, the regulatory driver being the EU Water Framework Directive 2000/60/EC [5–7]. Diffuse sources of pollution are known to contribute significantly to total contaminant metal flux to rivers. Over fifty per cent of the 226 water bodies known to be impacted by non-coal mine water pollution in England and Wales show evidence of diffuse pollution [8] and that may pose a significant barrier to meeting the EU Water Framework Directive's ultimate target of achieving "good" ecological and chemical status for all surface and groundwater by 2015 [9].

Diffuse sources of pollution at metal mining impacted sites can arise from runoff from tailings piles and waste heaps [10–12], through inputs of contaminated sub-surface water via the hyporheic zone [6,13] and from remobilisation of previously deposited contaminated overbank sediment [2,9,14]. Because of the diffuse nature of the contaminant source and in stream transport, metal contaminants can be deposited in particulate form on riverbanks and floodplains several hundreds of kilometres from the main mining area [15]. As a result thousands of tons of trace metals can be stored along river banks and floodplains [15,16] and can remain in the sediment for hundreds of years [17] potentially posing a long term threat to rivers and agricultural land [16]. Metal contaminants buried deep within floodplains could be assigned to long term storage and remain unavailable for uptake by organisms and plants, thus presenting a low environmental risk [9]. However, nearer the active channel where sediment is exposed to variations in river flow, chemical changes (redox potential and pH) brought about through dredging activities [18,19], bioturbation [20], infiltration and exfiltration of river and ground water through the hyporheic zone [6,13,21] and the exposure and submergence of river bank sediment

through flood and drought episodes [22–24], can remobilize stored metals, potentially increasing the bioavailability of these contaminants.

Changes in redox potential and drying (critical processes within the river floodplain environment) have been found to cause the dissolution and precipitation of iron and manganese [20,25–27], sulphur [10] and sulphate [28,29] minerals that are ubiquitous in mining contaminated environments [30–35]. Such changes influence contaminant trace metal mobility [36,37]. Freshly precipitated minerals are generally more reactive than aged forms [38,39] and under dynamic redox potential conditions these more reactive forms could build up over time. However, over prolonged periods of flood and drought other biogeochemical processes may become important and alter mineral composition and reactivity under oxic [31] and reducing [26] conditions, which could in turn affect toxic trace metal mobility.

Climate model predictions based on UKCP09 river basin regions indicate that there will be a shift towards aridity along with a decline in river flow (Q95) by the 2080s in West Wales and North West England [40]. Additionally, the occurrence of localized heavy rainfall events could double by 2080 leading to an increase in the frequency and duration of surface water flooding [41]. Longer dryer antecedent conditions along with more frequent/longer duration floods may alter patterns of submergence and exposure of river bank sediment subsequently changing redox potential conditions over varying temporal scales. This in turn will alter the spatial and temporal patterns of biogeochemical processes within the riverine environment, affecting the mobility and flux of metals into the environment.

The processes found to occur under changing redox potential are highly complex and vary depending on the sorbent, sorbate properties [42], composition of pore water, temperature [43] and geology and mineralogy of the site [19,22]. This paper will attempt to present a comprehensive review of the literature regarding the important biogeochemical processes that control the mobility and partitioning of contaminant trace metals under reducing, oxidising and dry conditions at different temporal scales. Specific reference is made to redox sensitive elements, iron and sulphur, because of their abundance in metal mining contaminated sediments and because minerals containing these elements are most likely to influence trace metal mobility under fluctuating redox conditions. This review is novel in that it draws together the key biogeochemical processes altering iron and sulphur mineral form and reactivity over varying temporal scales under fluctuating reducing, oxidizing and dry conditions. A conceptual model will demonstrate to the reader how dynamic redox potential changes and drying could result in a build-up of reactive forms of iron and sulphur minerals in mining contaminated river bank sediment over time and how that could affect contaminant trace metal mobility.

2. Biogeochemical Processes

2.1. Changes in Mineral Form and Mobility of Trace Metal Contaminants on Submergence of Contaminated Sediment

During a storm event the subsequent high flow and increase in river stage can lead to an infiltration of surface river water laterally through the river bank. This water has been found to carry dissolved organic carbon that serves to promote microbial activity [44]. Chemical reduction of sediments can be

a direct consequence of flood wetting and the gradual depletion of oxygen by biogeochemical processes. Aerobic organisms reduce trapped oxygen within hours [45] or days [46] depending on the oxygen concentration of the pore water, sediment grain size [47] and on the constituents important to microbial processes such as availability of labile organic matter [48], microbial species present and temperature [49]. Following depletion of oxygen facultative anaerobes followed by strict anaerobes can proliferate and couple the oxidation of organic matter with the reduction of other electron acceptors that follow a traditionally reported order of chemical reduction: nitrate, manganese and iron oxides and sulphate (reflecting highest to lowest energy efficiency) [26,45]. Table 1 shows redox half reactions for common electron acceptors. The table provides, (i) standard redox potentials (E^o/mV), (ii) pE^o, the negative logarithm of the electron activity at pH 0, $pE^o = E^o(V)/0.0591$ under standard conditions, (iii) pE (w)^c the pE^o at pH 7. The relationship between pE^o at pH 0 and pH 7 has been described by vanLoon and Duffy (pg.363) [50] as: $pE = pE^o$ (w)$^c = pE^o − 7$ ($n1/n2$) where $n1$ = the number of hydronium ions and $n2$ = the number of electrons in the half reaction. It should be noted that natural systems are rarely in equilibrium, the $n1/n2$ ratio has been reported to vary hugely and the contribution of many different redox couples often results in unstable readings [43,50].

Table 1. Redox half reactions for common electron acceptors.

| Redox Half Reaction	E^o/mV	pE^o	pE^o (w)^c	References
$O_{2(g)} + 4H^+ + 4e^-$ — $2H_2O$	+122.9	+20.8	+13.8	[50]
$2NO_3^- + 12H^+ + 10e^-$ — $N_{2(g)} + 6H_2O$	+125	+21.1	+12.7	[50]
$MnO_{2(s)} + 4H^+ + 2e^-$ — $Mn^{2+} + 2H_2O$			+8.9 *	[51]
$FeOOH_{(s)} + 3H^+ + 2e^-$ — $Fe^{2+} + 2H_2O$			−2.7 *	[51]
$SO_4^{2-} + 9H^+ + 8e^-$ — $HS^- + 4H_2O$			−3.4 *	[51]
$CO_2 + 8H^+ + 8e^-$ — $CH_4 + 2H_2O$	+17	+2.87	−4.13	[50]

Note: * pE^o at pH 7.4.

As well as reduction through the oxidation of organic matter, reduced biproducts of microbial metabolism can further participate in chemolithotrophic oxidation reactions if redox potential conditions change or these biproducts are transported to a zone of sufficiently high redox potential [52,53]. Research has shown that as pH declines iron undergoes reductive dissolution at a higher redox potential; Gotoh and Patrick [54] found that under flooded conditions iron reduction occurred at 300 mV at pH 5, 100–300 mV at pH 6 and 7, and −100 mV at pH 8. Manganese solubility is much more sensitive than iron to low pH and redox potential conditions [35,55]. Laboratory studies have demonstrated that manganese can reduce at a higher redox potential (200–300 mV) than iron (0–100) at pH 7 [55] and at a substantially faster rate (1 day to a week) than both iron and sulphate (up to 8 weeks) [48].

Poorly crystalline fine-grained ferrihydrite has been found to reduce more quickly [56] at a higher redox potential [22] than older more crystalline forms such as goethite or hematite. Lovley and Philips [57] reported that iron reduction rates increased up to fiftyfold in the sediment where amorphous ferric oxyhydroxide was substituted for hematite in glucose enrichments and they found areas of incomplete reduction where more crystalline forms were present. Brennan and Lindsay [58] found that a more prolonged and intensive reduction period was required for the reduction of crystalline oxides (hematite) compared to nearly amorphous iron (hydr)oxides. Younger, freshly precipitated iron has a

large (>200 m^2/g) [38,39,59] and complex surface area [60,61]. Grain size is also a major control on the potential for reduction. Langmuir and Whittemore [62] found the relative stability of goethite and hematite changed depending on particle size; goethite is usually more stable than hematite for equal size crystals but less stable than hematite when present at a smaller particle size. The factor that is more important with regards to reduction potential is the amount of reactive surface area [43]. Hydrous oxides, even with the same surface area, can have very different reactivities as a result of different coordination geometry and at a fixed pH, the reactivity is likely to increase with the number of terminal ligands [63].

The dissimilatory reduction of iron and manganese hydr(oxides) occurs through microbial or abiotic transfer of electrons from an electron donor (organic matter or reduced metal) via surface functional groups to the oxidized iron or manganese mineral centre. The electron transfer leads to a change in oxidation state of the metal to reduced iron or manganese. The reduced metal has a more labile bond with oxygen than in its oxidized form and is more easily detached (Scheme 1) [63] leading to the dissolution of iron and manganese (hydr)oxides and the mobilization of any sorbed trace metal contaminants.

Scheme 1. Schematic of a typical redox reaction sequence between a reductant "R" and iron (III) (hydr)oxide, leading to the detachment and dissolution of ferrous iron. The electron transfer and the detachment process may both be rate determining [63]. This material is reproduced with permission of John Wiley & Sons, Inc (Hoboken, NJ, USA) [63].

Surface sites	**Reactants**	**Fast**	**Surface species**
$\equiv Fe^{III}$-OH	+ Reductant R	$\longrightarrow$	$\equiv Fe^{III}R$

Surface species	**Electron transfer**	**Reduced surface species + oxidised reactant**
$\equiv Fe^{III}R$	$\longleftrightarrow$	$\equiv Fe(II) + {}^{\bullet}O$

Reduced Surface species	**Slow** $\longrightarrow$ **Detachment** of Fe(II)	**Fe(II) (aq) + surface site**
$\equiv Fe^{II}$		
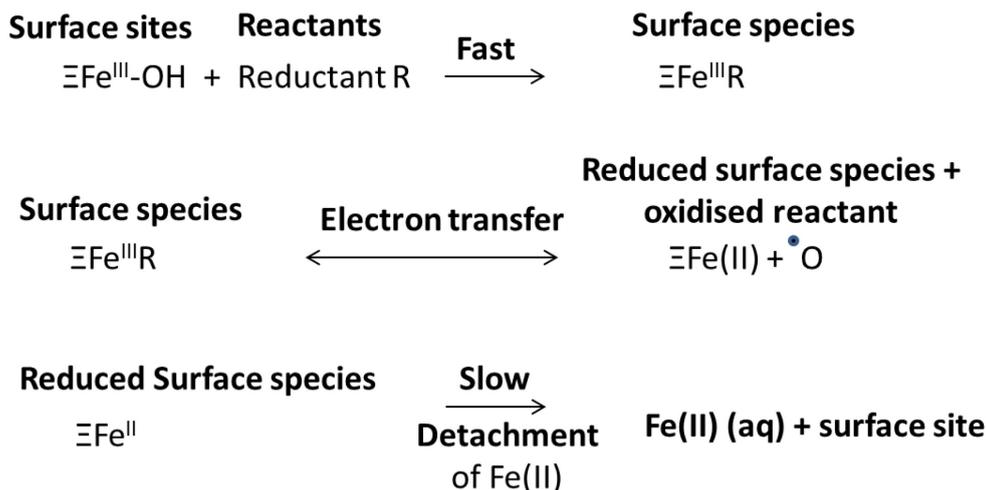
Lesven *et al.* [64] reported that rapid depletions of oxygen and a sharp decrease in the redox potential within the first centimetres of the sediment, led to reductive dissolution of manganese and iron (hydr)oxides and the release of trace metals. Similarly Davis and Kent [65] and Charlatchka and Cambier [26] found that the reduction of metal oxides increased the mobility of lead, zinc and cadmium. During prolonged flooding less reactive crystalline forms of iron (goethite, hematite) can undergo reductive dissolution that may serve to mobilize iron, manganese and contaminant trace metals further: Du Laing *et al.* [66] found a steady increase in dissolved iron and manganese concentrations during prolonged flooding. However over extended flood periods where environmental conditions are suitable for the precipitation of metal sulphides [67,68] and/or sorption of metals onto carbonates and hydroxides [26] the attenuation of dissolved iron and trace metals may occur (Section 2.2).

2.2. Changes in Mineral Form during Prolonged Flooding: Sulphate Reduction and Metal Sulphide Precipitation

Evidence suggests that an increase in the frequency or/and magnitude of flood events can extend the residence time of pore water within the river bank and increase nutrient cycling, although the biogeochemical implications of this are poorly understood [44]. For sulphate reduction, conditions must be anoxic, although reported redox potentials vary (−120 mV [69], −150 mV [47], −220 mV [70]). Sufficient labile organic carbon must be available for sulphate reduction and is a key rate limiting factor [71,72]. Sulphate concentrations must be high enough: A model developed by Lovley and Klug [73] predicted that if sulphate concentrations fell below 30 μM, methanogenic bacteria could out-compete sulphate reducers for substrate. However, sulphate concentrations are likely to exceed this value in mining polluted systems characterized by high concentrations of sulphur [43]. The reduction of sulphate yields hydrogen sulphide (H_2S) that can rapidly react with dissolved metal contaminants and precipitate as insoluble metal sulphide phases [74,75]. Iron is generally the predominant metal generating solid phase sulphides [43], although the rate of iron mono-sulphide production can be severely retarded in environments where availability of easily reducible iron is low, for example in marine environments [71,76–78] and in salt marshes where the slow reductive dissolution of more residual forms of iron can limit the rate of monosulphide formation [79]. Even in mining contaminated sediments high in total iron concentrations, the availability of easily reducible iron may be limiting. Further research would be required to determine whether in such environments, processes occurring at the oxic-anoxic interface could serve to promote the production of easily reducible iron, and whether this influences the rate of iron mono-sulphide formation.

Precipitation of metal sulphides can act as a sink for trace metal contaminants [43]. Metals such as lead, zinc, copper can adsorb to or co-precipitate with iron mono-sulphide and they can also precipitate directly as discrete phases [67]. Although generally insoluble, the relative solubility of discrete metal sulphides varies and is reported as: manganese sulphide > iron mono-sulphide (FeS) > nickel sulphide (NiS) > sphalerite (ZnS) > cadmium sulphide (CdS) > Galena (PbS) > copper sulphide (CuS) > pyrite (FeS_2)—reflecting the highest to lowest solubility [43,66]. Metal sulphides are highly resistant to desorption effects of chlorides (zinc, copper and cadmium), hydroxides and bicarbonates (zinc) [22] under anoxic conditions. However, when sediment is re-exposed to dissolved oxygen, metal sulphide oxidation could constitute a secondary source of trace metal contamination, as will be discussed further in Section 2.3.

Pyrite is reported to be more thermodynamically stable [80] and more resistant to oxidation than amorphous mono-sulphide precipitates [81], although the environmental consequences on oxidation are more severe [74]. The mechanisms of pyrite formation are poorly understood [82,83] and reported processes vary. In general studies indicate pyrite can form under anoxic [82] and mildly reducing conditions [80] and amorphous iron monosulphide (FeS), poorly crystalline Macinawite (FeS_{1-x}) and greigite (Fe_3S_4) are considered as precursors to pyrite formation [67]. Proposed reactions include:

Direct reaction of FeS with H_2S [82]:

$$FeS + H_2S \leftrightarrow FeS_2 + 2H^+$$

Reaction of iron monosulphides or other pyrite pre-cursors with intermediate sulphur or polysulphur species [82]:

$$FeS + \frac{1}{8}S_8 \leftrightarrow FeS_2$$
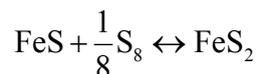
Wilkin and Barnes [80] describe a process where, under weakly oxidizing conditions, aqueous sulphide species are oxidized to produce sulphur and polysulphides and that reacted with mackinawite to form greigite. Transformation from greigite to pyrite could then occur through sulphur addition [80]:

$$Fe_3S_4 + 2S^o \leftrightarrow 3FeS_2$$

Giblin [84] reported that mild oxidation events in a salt marsh oxidized sulphides to polysulphides that were able to precipitate directly with reduced iron to form pyrite [83]:

$$Fe^{2+} + S_2^{2-} \leftrightarrow FeS_2$$
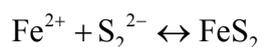
Schoonen and Barnes [83] found direct pyrite formation from reaction between polysulphides and ferrous iron difficult to prove. Studies show that metastable polysulphide species S_8^{2-}, S_6^{2-} and HS_2^- are most important around the sulphate/sulphide redox boundary at pH 5–9 (within the range of natural environmental systems) and, although concentrations remain low compared to total dissolved sulphide, polysulphide activity has been reported to reach a maximum at the oxic–anoxic boundary in natural systems. Hydrodisulphide ion, HS_2^- is the relatively stable over pH 6–8 and S_2^{2-} is present at more alkaline pH [53].

Lord and Church [79] noted that a readily available reactive iron source including both reactive ferric oxides and dissolved iron seemed to be key for pyrite formation in salt marsh sediment. The reaction was described as [79]:

$$FeOOH + \frac{3}{2}HS^- + \frac{1}{16}S^0_8 + \frac{3}{2}H^+ \leftrightarrow FeS_2 + 2H_2O$$
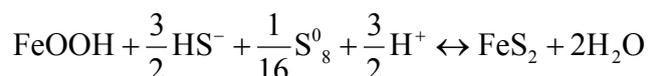
In addition to a reactive iron source (i) sulphate reduction, to supply dissolved sulphide and (ii) proximity to an oxidative zone to allow for the partial oxidation of sulphide compounds to form elemental sulphur and polysulphides, were proposed requirements for rapid pyritization [79]. The authors were unsure of the biogeochemical pathway for pyrite formation although the requirement for an iron monosulphide precursor was hypothesized. Similarly, reactive iron has been found to be a rate limiting factor for iron monosulphide formation and degree of pyritization in marine environments [78]. Whether a build-up of more reactive forms of iron under dynamic redox potential conditions could influence the rate of monosulphide formation and perhaps pyritization in mining impacted sediment is unclear.

Other attenuation mechanisms for trace metal contaminants in anoxic sediment may take place alongside metal sulphide precipitation [85]. Pore water composition and pH directly influence metal precipitate composition and resulting minerals. Most divalent cations (lead copper, zinc) can be present as dissolved uncomplexed aquo species or as hydroxides, bicarbonate or chloride species at pH < 7. At pH ≥ 7 dissolved carbonate species and hydroxide species may form [50]. In systems where bicarbonate concentrations exceed sulphide concentrations and saturation is reached, the precipitation of siderite ($FeCO_3$) [45,86] and manganese carbonate ($MnCO_3$) [26] has been observed and although

most trace metals are capable of forming pure carbonate phases, copper, lead, zinc and cadmium have been reported to substitute for calcium, magnesium and iron in calcite ($CaCO_3$), aragonite ($CaMg(CO_3)_2$), ankerite ($Ca(Fe,Mg)(CO_3)_2$) and siderite ($FeCO_3$) [87].

Although the reduction of sulphate consumes protons and generates alkalinity, the precipitation of metal sulphides such as iron monosulphides consumes alkalinity [85]. The processes may be net-neutralizing in mine water with high sulphate to iron ratios because the number of moles of sulphate reduced would exceed the number of moles of iron precipitated [74]. Some laboratory studies report an initial fall in pore water pH at the start of a flood and propose that oxidation of organic matter coupled to microbial reduction result in production of CO_2 and organic acids [26,64]. The pH of the water is clearly important with regards to surface charge: at very low pH competition between protons and positive metal cations for negative surface sites can lead to the mobility of trace metal contaminants. The influence of pH on metal sorption behaviour will be discussed further in Section 2.4.

The precipitation of metal sulphides may serve only as a temporary sink for contaminants whilst conditions remain anoxic. Re-oxidation of anoxic sediment and the subsequent oxidation of metal sulphides could result in the rapid release of trace metal contaminants into pore water during the early stages of oxidation [88].

2.3. Changes in Mineral Form and the Release of Trace Metal Contaminants during Oxidation of Reduced Sediments: Sulphide Oxidation and Iron and Manganese Mineral Precipitation

When flood water subsides, a decline in river stage follows and pore water may exfiltrate from the river bank. The subsequent exposure of reactive sediment surface sites to the flow path of oxidized water and the diffusion and convection of oxygen have been found to influence the rate of metal sulphide oxidation [43]. The oxidation of pyrite through reaction with aqueous ferric iron is known to be an important biogeochemical pathway in the pH range of 2–9 [89] and could be a significant metal sulphide oxidation mechanism under moderately reducing conditions. Aqueous ferric iron can rapidly oxidize pyrite at low pH ($\leq$4) although oxygen would be required to replace ferric iron used up in the process [43]. Under less acidic conditions the decreased solubility of ferric iron is likely to mean that pyrite oxidation rate becomes more dependent on the iron recycling process to replenish the supply of aqueous ferric iron [89]. Microbes have been reported to accelerate the oxidation of sulphide minerals by an average of thirty four times relative to the abiotic rate [10]. Adhesion and biofilm formation have been described as key factors for microbial oxidation of sulphides: bacteria preferentially attach to poorly crystallized minerals or minerals with defects or fractures. Such adhesion can form an interfacial microenvironment between the outer membrane of a bacterial cell and the surface of a sulphide mineral [10]. Other reports relating to the oxidation of pyrite indicate that free-floating iron oxidizing bacteria contribute more efficiently to pyrite oxidation through an indirect mechanism [43].

Freshly precipitated amorphous fine-grained metal sulphides and framboidal pyrite have been reported to oxidize more rapidly than older more crystalline forms [74,90]. Moreover the metals that have been freshly sorbed to iron and manganese monosulphides are particularly labile and when exposed to oxygen can oxidize in minutes [19,68]. Solubilisation kinetics have been reported to differ between metal suphides: Caille *et al.* [88] found lead and copper sulphides were released more rapidly than zinc. Whilst Domenech *et al.* [91] noted that sphalerite (ZnS) oxidized faster than pyrite (FeS_2)

and galena (PbS) and chalcopyrite ($CuFeS_2$) had similar oxidation rates to pyrite. Furthermore the rate of galena dissolution was enhanced at low pH, an effect not apparent for sphalerite or chalcopyrite. Sulphate and trace metal contaminants may be released into solution on oxidation of metal sulphides. However, the fate of these dissolved elements is poorly understood. The formation of metal sulphate complexes could serve to keep metals dissolved and mobile under hydrologically saturated conditions [87], although not all metal sulphate complexes are highly soluble and in high sulphur systems the formation of anglesite ($PbSO_4$) could provide a solubility control for lead under oxidising conditions [34,92].

The oxidation of iron based sulphides, pyrite, chalcopyrite and arsenopyrite present in mining contaminated sediments could bring about very low pH (2.5–4.5) conditions that may serve to mobilize trace metal contaminants [74,93,94]. Iron tends to have the highest metal concentration at coal mines [95]. However in metal mining systems trace metals such as lead, zinc, copper and cadmium may be present at high concentrations in the form of metal sulphides. The oxidation of sphalerite (ZnS) and galena (PbS) would not directly generate acidity although, hydrolysis of trace metals once they enter solution could serve to increase acidity [74]. The effect of regional lithology can be important with regards to the buffering capacity of pore water. Where sediment is high in carbonates the dissolution of calcite can provide an important buffering mechanism that can maintain *circum* neutral pH conditions [96] although the dissolution of metal carbonates can also serve to mobilize trace metal contaminants [2,97]. Many UK metal mining contaminated systems however are underlain by Lower Paleozoic shales and mudstones with low concentrations of base metals [95,98] and that could make these systems more susceptible to periodic acidic episodes.

On exposure to oxygen, reduced (dissolved) iron and manganese oxidize and undergo hydrolysis [99,100]. Iron would be expected to oxidize more rapidly at a lower redox potential and pH than manganese [55,101], although some of the oxidized iron could then act to oxidize reduced manganese [100]. Whitney [102] found that manganese and iron formed discrete oxide phases in different micro-environments because iron was able to precipitate under conditions of lower redox potential and pH than manganese. The precipitation of iron and manganese on oxidation and sorption of contaminant trace metals are likely to be key biogeochemical processes controlling the mobility of trace metal contaminants under dynamic redox potential conditions and will be discussed in detail in Section 2.4. However, if sediment conditions remained wet and oxidized, the aging and crystallization of iron minerals could serve to alter mineral reactivity (sorption capacity and susceptibility to dissolution when redox potential conditions change): Iron first precipitates as a poorly crystalline hydrous ferric oxide or ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$ or $Fe_2O_3 \cdot 2FeO(OH) \cdot 2.6H_2O$) [43,62]. The formation of simple iron hydrolysis species has been reported to occur very rapidly [99]. However, after that a slower re-crystallization of the iron mineral has been reported to occur with aging [43,99]. During the aging process ferrihydrite has been found to convert to hematite between pH 7–9. Outside of that range ferrihydrite may dissolve and re-precipitate as goethite [103]. The processes involved in the crystallization of ferrihydrite to more stable forms in heterogeneous sediments are poorly understood, although with increasing crystallinity the solubility and surface reactivity of iron minerals has been found to decrease [38,99] and more crystalline forms of iron may be less sensitive to redox potential changes. Crystallization of iron minerals however may be retarded under mildly acidic conditions [38] and through the chemi-sorption of organic [104] or inorganic [105] species. Anderson and Benjamin [105] reported that crystallization of ferrihydrite to goethite occurred in

twenty four hours in the absence of silicate, however non-crystalline forms of iron remained for at least 1–2 weeks in its presence. Baltpurvins *et al.* [103] proposed that sulphate could form relatively strong complexes with ferric iron compared to nitrate and chloride and the adsorption of sulphate onto the surface of ferrihydrite may act as a chemical glue to suppress dissolution and formation of goethite, thereby reducing the rate of transformation of ferryhydrite. In this way poorly crystalline forms of iron (hydr)oxide could persist within the sediment.

Iron (hydr)oxides precipitated in the presence of sulphate results in surface characteristics unique from pure ferrihydrite or more crystalline iron (hydr)oxides [106,107] which could alter sorption properties of trace metal contaminants as will be reviewed (Section 2.4).

2.4. Sorption of Trace Metals onto Iron (Hydr)Oxides

On precipitation, iron and manganese (hydr)oxides can rapidly (minutes to hours) scavenge dissolved trace metal contaminants [18,108]. Freshly precipitated iron (hydr)oxides have an adsorption capacity ten times that of aged oxides and that has been found to correspond to a tenfold difference in (i) cation exchange capacity (CEC), 354 meq/100 g (freshly precipitated) compared to 8 meq/100 g (goethite) and (ii) surface area 303 m^2/g (freshly precipitated) compared to 29 m^2/g (goethite) [39]. Very little freshly precipitated iron and manganese may be needed to sorb high concentrations of trace metals such as copper, cadmium [109] lead and zinc [110].

Sorption of trace metals onto iron (hydr)oxides is pH dependent and has been reported as follows at circum-neutral pH: lead > copper > zinc > cadmium [43]. This order is often in line with the reported affinity of trace metals for iron (hydr)oxide surfaces [110–113]. Desbarats and Dirom [114] found that metals were sorbed preferentially to ferric iron in the order (lead > copper > zinc > cadmium) and, as freshly precipitated ferric iron concentrations increased, trace metals were sorbed with greater efficiency, Burton *et al.* [115] on the other hand, found that zinc had a greater affinity for iron and manganese (hydr)oxides than lead and copper. Zinc and cadmium have a higher sorption edge, the pH at which fifty percent sorption occurs, than lead and copper so are more sensitive to low pH conditions [116]. These trace metals are often noted as being more mobile than lead and copper under oxic conditions [12,42,117]. Lead and copper have been reported to out-compete zinc for sorption sites: Hamilton-Taylor *et al.* [118] found that competition with lead and copper for sorption sites altered the zinc sorption edge and zinc remained dissolved, available for scavenging by planktonic algae. Metal aquo-complexes that form can affect sorption capacity; for example cadmium was found to remain mobile in solution far longer than other metals due to complexation with oxyanions that served to inhibit sorption to iron (hydr)oxide surfaces [19]. Moreover, other factors can influence sorption characteristics such as concentration of reactive iron and pH: Carroll *et al.* [42] found at low (<0.044 ppm) iron concentrations where pH > 7, lead, cadmium and zinc partitioned preferentially with carbonate and hydroxide phases (zinc), however, in sediments higher in iron (176.9 ppm), zinc and lead sorbed predominantly to iron (hydr)oxides. Mineral surface composition and structure has been reported to influence trace metal sorption characteristics: In mining contaminated environments the formation of hydroxysulphate minerals at low pH < 4 results in surface characteristics that are unique from pure ferrihydrite minerals [35] that can alter sorption characteristics and influence sorption edge properties for copper and zinc. Webster *et al.* [107] found that copper and zinc had a

lower sorption edge for iron hydroxysulphate than for pure ferrihydrite. Factors proposed to enhance sorption were (i) formation of ternary complexes between the metal oxide, sorbed sulphate and metal cation and (ii) a microbially mediated precipitation. Moreover sorption of zinc by phosphate enriched iron (hydr) oxides has been found to increase markedly at lower pH compared to pure iron phases. Ghanem and Mikkelsen [119] concluded that the phosphate increased the net negative charge on the oxide surface and served to lower the iron (hydr)oxide point of zero charge. The sorption of trace metals with both pure and mixed iron (hydr)oxide phases can act as a sink for trace metals. Although, where conditions become reducing, the subsequent dissolution of these minerals could serve to release these contaminants back into the water column [120]. Accurately predicting sorption of trace metal contaminants would be of use when determining the potential for toxic trace metal release when environmental conditions change. However contaminant trace metal sorption processes occurring within heterogeneous sedimentary environments are highly complex and can be influenced by a variety of factors. Further laboratory study is recommended to try to identify key mechanisms of solute interaction within mining polluted sediment.

The fate of contaminant trace metals sorbed to iron (hydr) oxides over time where conditions remain oxic and wet is poorly understood. In general, studies indicate that trace metal sorption onto a metal hydro(oxide) is a two-step process: (i) rapid external surface sorption followed by (ii) a slow diffusion into internal sorption sites that are not readily accessible by the bulk solution [38,106]. At low trace metal sorbate concentrations surface complexation may dominate, however at high sorbate concentrations metal precipitation may be a more important mechanism and result in a new solid phase less readily dissolved or desorbed when conditions change (Scheme 2) [38,63]. The stability of the sorption complex with ageing has been found to vary depending on trace metal contaminant: Ford *et al.* [38,121] found that as iron aged, lead was unable to incorporate into the crystal structure and as a result formed a more labile sorption complex than nickel. Nickel however was taken into the crystal structure although that led to the retardation of iron crystallization rates. Majzlan *et al.* [122] reported that although ferrihydrite was an excellent material for sorption of arsenic, as the iron (hydr)oxide samples aged arsenic became more easily leachable. They proposed that increasing polymerization of the iron octahedra led to fewer adsorption sites.

Iron mineral crystallization and incorporation of trace metals into the iron crystal structure could be key factors that retard the rate of reductive dissolution of iron minerals and limit the extent of contaminant trace metal release when reducing conditions return. It is possible however that crystallization processes may be retarded through sorption of trace metals and amorphous forms of iron may persist. Moreover some contaminant trace metals may not be incorporated into the crystal structure and remain in a potentially bioavailable form. It is clear that more reactive forms of iron could pose an environmental risk with regards to toxic trace metal mobilization under changing redox potential conditions. However further research is necessary to understand how the reactivity of minerals may change and how that influences trace metal release over time when metal mining contaminated sediment is exposed to dynamic redox potential conditions.

As discussed below other processes can control the mobilization of trace metal contaminants in metal mining contaminated sediments subjected to long dry periods.

Scheme 2. Schematic representation of surface complex formation (**a**) and surface precipitation (**b**) on hydrous ferric oxide ($Fe(OH)_3(S)$). This material is reproduced with permission of John Wiley & Sons, Inc [63]. (**a**) At low surface coverage with Me^{2+}, surface complex formation dominates. (**b**) With progressive surface coverage, surface precipitation may occur. The surface precipitate is looked at as a solid solution of $Fe(OH)_3(S)$ and $Me(OH)_2(S)$.

$FE(OH)_3(S)$ $)$—$OH + Me^{2+}$ $\rightleftharpoons$ $Fe(OH)_3(S)$ $)$—$O Me^+ + H^+$

a) Surface complex formation

$FE(OH)_3(S)$ $)$—$O Me^{2+} + Me^{2+} + 2H_2O$ $\rightleftharpoons$ $\left\{ \begin{array}{c} Fe(OH)_3(S) \\ Me(OH)_2(S) \end{array} \right\}$ $)$—$O Me^+ + 2H^+$

'Solid solution'

b) Surface precipitation
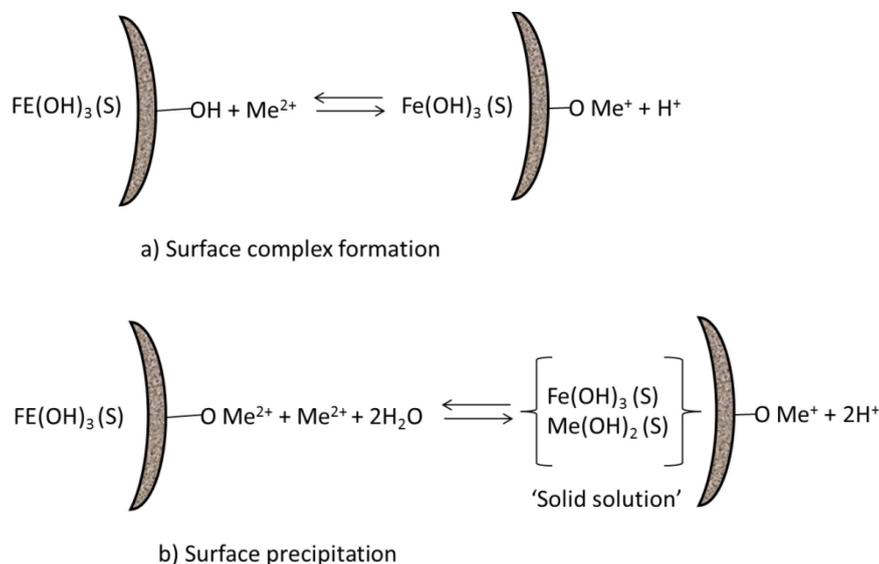
2.5. Effects of Long Dry Episodes on Mineral Form and Reactivity

Over long dry periods, evaporation of pore water and chemical saturation of solutes can promote the formation of soluble iron sulphate salts [24,28,29,123]. These hydrated iron sulphate salts are generally formed from the products of pyrite oxidation and include melanterite ($Fe^2 SO_4 \cdot 7H_2O$) and copiapite ($Fe^2 Fe^3 4(SO_4)6(OH)_2 \cdot 20H_2O$). They are highly soluble and present a temporary store of metals and acidity and in the case of rhomboclase ($H_3 0)Fe^3(SO_4)_2 \cdot 3H_2O$ have been described as a solid form of sulphuric acid [43]. Contaminant trace metals such as copper and zinc can substitute for ferric and ferrous iron in these minerals [124]. Buckby *et al.* [28] found that hydrated iron sulphate minerals were able to transiently store on average 10% and 22%, zinc and copper respectively, of the total discharge of the Rio Tinto over the summer period. The most abundant iron sulphate salt was from the copiapite group precipitated directly from the iron sulphate rich water, although salt composition was found to reflect the local variations in the water composition. Salts that accumulate in riverbanks and waste piles over extended dry periods can be rapidly dissolved when wet conditions return and result in a sharp increase in dissolved metals and acidity [24,28]. In the case of rhomboclase it can result in severely acidic (pH < 1) waters [43]. Seasonal variations in the concentration of copper have been reported because copper is partitioned preferentially to zinc into melanterite over dry periods, however when wet conditions return, the dissolution of melanterite can cause the rapid release of copper [124]. Hudson-Edwards *et al.* [125] describe the mobilization of arsenic, copper, zinc and lead that likely arise from the dissolution of yellow-white precipitates on the contaminated alluvium of the Rio Tinto area, south West Spain, during periods of high rainfall. It is clear that these episodic flushing effects [24] present a serious environmental risk to aquatic biota [126].

2.6. Simplified Conceptual Model

In order to visualize the cyclical nature of the processes described above under dynamic redox potential conditions in mining contaminated river bank sediment, a simplified conceptual model (Figure 1) was designed. This model is a re-statement of the processes described above. It theorizes the changes in mineral form and trace metal release on a temporal scale in response to submergence and exposure of river bank sediment.

Figure 1. Simplified conceptual model to show changes in iron and sulphur species and effects on contaminant trace metal release in response to changes in redox potential and drying at different temporal scales. The red star indicates a process rate limited by the availability of easily reducible iron.
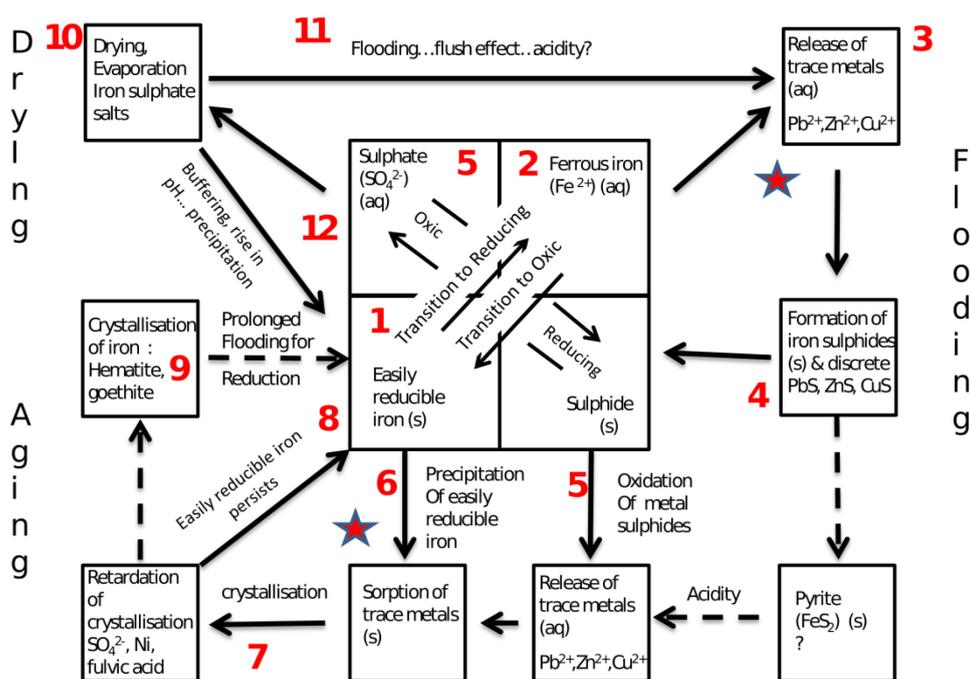
(1) During a storm event the rise in river stage can lead to the inundation of surface river water into the river bank. Oxygen could rapidly deplete through microbial respiration leading to the reductive dissolution of easily reducible iron.

(2) Resulting in the release of ferrous iron.

(3) And the mobilization of trace metal contaminants that were partitioned with easily reducible iron (Section 2.1).

(4) Where increased frequency and magnitude flow events result in extended pore water residence times iron and toxic trace metals may react with dissolve sulphide to form metal sulphides. This can serve to attenuate trace metals under reducing conditions and could result in the formation of pyrite. Although the mechanisms are not well understood easily reducible iron is an important rate-limiting factor for both iron monosulphide and pyrite formation (Section 2.2). Metal sulphides are insoluble and often resistant to desorption where redox potential conditions remain reducing.

(5) When flood conditions subside water exfiltrates from the river bank and the oxidation of metal sulphides could lead to the release of toxic trace metal contaminants and, although more

thermodynamically stable than monosulphides, oxidation of pyrite could lead to highly acidic conditions that could promote trace metal mobilization (Section 2.3).

(6) On oxidation, the precipitation of poorly crystalline ferric iron could serve to attenuate high concentrations of trace metal contaminants. The extent of trace metal sorption depends on the concentration of easily reducible iron as well as trace metal behaviour, pH and mineral surface characteristics (Section 2.3).

(7) Where conditions remain stable over time, iron may age, crystallize and become less reactive.

(8) Sorption of organic or inorganic substances may retard this process and easily reducible iron may persist in the sediment (Section 2.3).

(9) With aging and crystallization of iron minerals, trace metals may be incorporated into or desorbed from the crystal structure (Section 2.4). Crystalline forms of iron are more resistant to reductive dissolution, however, over a prolonged flood period reduction of more crystalline, less reactive, forms of iron could serve to mobilize iron and trace metal contaminants and (1) could result in an increase in the concentration of easily reducible iron when sediments are re-oxidized (Section 2.1).

(10) Over, long dry periods, water could evaporate from the sediment and iron sulphate salts could precipitate. They store metals and acidity and are highly soluble.

(11) When wet conditions return, these salts can dissolve and release trace metal contaminants and acidity that could serve to mobilize trace metals (Section 2.5).

(12) Where buffering occurs the rise in pH could result in (1) the precipitation of easily reducible iron (6) that could sorb high concentrations of contaminant trace metals.

The model highlights key biogeochemical processes that can lead to changes in mineral reactivity as a result of flood drought cycles and the impact on contaminant trace metal mobility over varying temporal scales. It could therefore provide a high level indication of the potential environmental risk metal mining river bank sediment may pose as a result of fluctuations in the variation and frequency of flood and drought cycles predicted as a result of climate change.

The authors note that the processes and trends above would clearly alter depending on riverbank sediment environment. Although not included in this review further study focused on investigating how these effects alter within different geomorphological and hydrological environments is recommended.

3. Conclusions

Changes in redox potential can alter the composition of secondary iron and sulphur minerals and this can influence the sorption of toxic trace metals and susceptibility to dissolution when further redox potential changes occur. It is, however, unclear how different duration and frequency of wet and dry cycles would influence the dissolution and precipitation of iron and sulphur minerals in mining contaminated river bank sediment, what the long term effects of different wet and dry cycles on iron and sulphur mineral reactivity are, and whether more reactive forms of iron could build-up in the sediment over time. This is important because this form of iron could potentially increase contaminant trace metal mobility and serve as a rate-limiting factor in monosulphide and potentially pyrite formation under dynamic redox potential conditions.

Further work is needed to determine (i) how different duration and frequency of wetting and drying of mining contaminated river bank sediment influences redox potential; and (ii) whether that affects

mineral reactivity over time (sorption capacity and susceptibility to dissolution); (iii) the key biogeochemical processes controlling the mobility of contaminant trace metals and whether those processes alter over time in response to these dynamic redox potential changes.

It is therefore recommended that:

- Mesocosm experiments are undertaken that simulate river bank environment in a controlled environment under different frequency and duration of wet and dry cycles.
- Characterization of the sediment under these conditions: sequential extractions that target reactive iron minerals (ferrihydrite), in addition to more crystalline forms (goethite and hematite) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) analysis to identify mineralogical changes.
- Techniques such as Diffusive Gradients in Thin Film (DGT) and Diffusive Equilibrium in thin films (DET) are applied to understand the interactions between solutes. Measurements made passively in the sediment at high spatial resolution could prevent mixing of larger pore water samples and avoid averaging of concentrations and chemical reactions during sampling that could confound results. These techniques could promote a greater understanding of the mechanisms that control trace metal mobility in mining contaminated sediment under dynamic redox potential conditions.

Acknowledgments

Conflicts of Interest

The authors declare no conflict of interest.

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