

The mobilization of metals and inorganic compounds during resuspension of anoxic sediment

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ABSTRACT

Resuspension events, such as dredging, can cause anoxic sediments to be exposed to oxic conditions. In this study, the release of heavy metals (Ni, Co, Cu, Zn, Pb and Cd) and inorganic compounds (As) from initially anoxic sediments and the sources and fate of the released metals are investigated. After 1-2 days aeration, significant amounts of heavy metals (Mn, Zn, Cd, Ni, Co) are released to the aqueous phase with decreasing pH, primarily due to the oxidation of acid volatile sulfide (AVS) and pyrite (FeS₂). In a well-buffered system, oxidation of iron sulfides alone does not induce heavy metal release. While the release of Zn, Co, Cd and Ni needs to be initiated by the oxidation of iron sulfide minerals, we believe that carbonates and oxides are the primary sources of the released metals. Among the heavy metals and inorganic compounds investigated, it appears that there are three distinct categories: 1. Mn, Zn, Cd, Ni, and Co; 2. Fe, Pb and As; and 3. Cu, with respect to their release profiles. The different profiles are believed to be related to their sources and the relative affinity of these compounds to iron and/or manganese oxyhydroxides and/or organic matter after oxidation. A new dredge elutriate test is being developed to better measure bioavailability.

INTRODUCTION

In industrialized countries, many water bodies are polluted with contaminants like metals. And many of these contaminants are associated with suspended matter (1). Particulate matter has sorptive behavior, which can cause sediments to act as a sink for metals in aquatic environments (1,2). In anoxic sediments, sulfides are often believed to be the major solid phase regulating the mobility and bioavailability of heavy metals. The ratio of Σ SEM (simultaneously extracted metals) /AVS (acid volatile sulfide) has been proposed by the EPA as a measure in evaluating the quality of sediments contaminated with heavy metals such as Cd, Pb, Ni, Zn and Cu. At Σ SEM/AVS < 1, sediments are interpreted as non-toxic because the reactive sulfide present exceeds the extractable sediment metal concentrations. Nevertheless, "non-toxic" sediments can also act as potential sources for heavy metal release to aquatic biota. Changing the aquatic conditions and exposing the anoxic sediment to an oxic environment can cause the sulfide material to be reoxidized and metals released. This can turn into a consequential pollution source. The aquatic conditions can be changed through physical and chemical properties. These changes can occur by natural events such as storms, by human activity such as dredging, or prop wash. The mobilization and bioavailability of these metals can be influenced by changes in the pH, redox conditions, and organic complexation (1). Some of the effects are kinetically limited or some are dominated by equilibrium. According to the U.S. Army Corps of Engineers, approximately 380 million cubic yards of sediment are dredged every year in the U.S. (3). The environmental risks of these dredging activities have become a major concern and a better understanding of the potential environmental impact of resuspension event on the mobility of toxic metals is greatly needed.

When the anoxic sediment is introduced to oxic conditions two main reactions happen. First, the oxidation of sulfides causes the release of the metals. Second, the oxidation of iron and manganese cause the precipitation of iron and manganese oxyhydroxides. These oxyhydroxides have very strong adsorptive surfaces. In turn, the newly freed metals will adsorb to the oxyhydroxides. So the question lies in how fast each process proceeds. According to measurements done, the rate of oxidation of iron and manganese is faster than sulfides (4) so there are ample surfaces available for sorption. So, during resuspension events the precipitated metals can switch to adsorb species. This can form a top layer of pollutants on the sediment when sedimentation occurs. So frequent resuspension events could cause continuous desorption. When the metals are in the adsorb state they can be released rather quickly if the pH were to drop. If the adsorbent is transported back to anoxic conditions then the metals will be transferred back to stable sulfides.

Previous resuspension experiments have been performed either under controlled pH-Eh conditions (3-5,16) or without any pH control (6,7). It has been reported that resuspension of sulfide-rich anoxic sediments tend to decrease the solution pH, primarily due to the oxidation of AVS and pyrite. Significant release of toxic metals to the aqueous phase and the enhanced mobility and bioavailability of these metals, therefore, are expected with increased acidity. Degtiareva and Elektorowicz (6) conducted a computer simulation of metal release following resuspension of contaminated sediment and they concluded that the fate of toxic metals during resuspension depended on the calcite concentration in the sediment. Although considerable release of heavy metals due to the increased acidity during resuspension has been reported extensively, the nature of metal release, especially the sources and mechanism of the release, is still unclear. In this study, the resuspension of anoxic Trepangier Bayou sediments will be

conducted under controlled and uncontrolled pH conditions and the results will be evaluated on both long-term (6-7 days) and short-term (24 hours) time scales. The sources of the released metals will also be investigated by comparing sequential extraction results of the sediments before and after resuspension experiments.

The importance of microbial activities has long been studied (8-11). Singer and Stumm (8) reported that the iron-oxidizing bacteria, *Thiobacillus ferrooxidans*, catalyzed pyrite oxidation about 10^6 times faster than abiotic oxidation. Likewise, Pugh et al. (10) showed that the oxidation rate of pyrite and marcasite was about nine-fold greater for the same treatment inoculated with *T. ferrooxidans*. Although the importance of microbial catalysis in sulfide oxidation has been well established, little is known about their effect on heavy metal release during resuspension of anoxic sediments. During resuspension, when anoxic sediments are exposed in well-oxygenated overlying waters, intensified microbial activities would be expected with the adequate supply of oxygen. In this study, we will examine the effect of microbial activity on heavy metal mobilization by comparing their release pattern in the presence and absence of microbial population.

MATERIALS AND METHOD

Sediments

Sediments from Trepangier Bayou, Norco, LA were chosen for this study because of the potential for serious heavy metal contamination problems. Samples were collected from a soft-bottom shallow-water area and the organic carbon content of this sediment is 8.1%. To maintain its anoxic character, Trepangier sediment was stored in a N_2 gas filled glove box. Subsampling and sediment transfer were carried out under N_2 condition. The total metal concentration in the sediment was determined by ICP and ICP/MS after the sediment was digested with nitric acid reflux (1:1) and hydrogen peroxide oxidation (30%) following the EPA SW-846 method 3050. Trepangier Bayou sediments contain significant concentration of Zn, Cu, Ni, Pb and As. A detailed characterization for the sediments including total metal concentrations, AVS, total reduced sulfide and organic carbon analyses are summarized in Table 1.

Sequential extractions

The sequential extraction method of Tessier et al. (12) was adopted to study the metal distribution in various fractions. The extraction released metals sequentially in the following four operationally defined fractions: 1: exchangeable, 2: bound to carbonate; 3: bound to iron and manganese oxides; and 4: bound to sulfides/organic matter. The extraction procedure was conducted on wet Trepangier Bayou sediments preserved under N_2 conditions. Sample handling was also conducted in N_2 gas-filled glove box but the extractions were performed outside the glove box in a closed centrifuge tube and the oxidation of anoxic sediments during the extractions was assumed to be negligible. Similar sequential extractions were also performed on Trepangier sediments aerated for 7 days.

Resuspension experiment

Laboratory scaled resuspension experiments were run where pH, Eh, dissolved oxygen (DO), and microbial activities were either monitored or controlled and the release of heavy metals in solution and suspended solids were analyzed. Trepangier sediment slurries (4 - 40 g dry weight) were resuspended in one liter of either 0.01 M NaCl or artificial river water (0.01 M NaCl + 0.86 mM NaHCO₃ and 0.33 mM CaCl₂) solutions were resuspended by an overhead propeller stirrer. Water samples were collected as a function of time (0, 2, 5, 15, 30 min followed by 1, 3, 5, 24, 72 h and 1 week). Most experiments were stopped after one week's stirring except for one resuspension experiment was monitored for one month. In the first 15 minutes, water samples were taken while stirring and the solution drawn from the suspension was not replaced. In subsequent samplings, the samples were taken from the supernatant solution (~ 20 ml) and the amount of solution withdrawn was replaced by an equivalent volume of artificial river water to maintain a constant solid/solution ratio. The stirrer was stopped for 2 to 3 minutes to allow solids to settle before sampling and the supernatant solutions were withdrawn with a syringe and filtered through 0.45 µm Nalgene™ syringe filters (SFCA). The pH, Eh and DO of each solution were recorded immediately before each sampling. An Orion- Ross combination glass electrode and a platinum redox electrode with an expandable ion analyzer EA 920 (Orion Research) were used for the pH and Eh measurements. The glass electrode was calibrated at 25°C using buffers at pH of 4.0, 7.0 and 10.0 and the Eh electrode was checked using a redox buffer at +476 mv, following Standard method 2580. The filtered samples were then acidified with 1% nitric acid and analyzed for Fe, Mn, Zn, Cd, Cu, Ni, Co, S, As and DOC concentrations.

The microbial activity was controlled by addition of 0.01M NaN₃ as a bacterial inhibitor and the anaerobic condition was controlled by purging the sediment suspension with N₂. Similar resuspension experiments were also conducted with the addition of calcite (5% Ca) and EDTA (0.1 mM). To summarize, our resuspension experiments were conducted under the following widely different pH, Eh conditions: 1. aerated (varying both Eh and pH); 2. anaerobic (low Eh and neutral pH); 3. no microbes (varying Eh, neutral pH); 4. anoxic and pH adjusted (Low Eh, varying pH); and 5. buffered with the addition of calcite (varying Eh, neutral pH).

Reagent-grade or better chemicals were used to make all solutions. Water used in this research was prepared by passing deionized water (Continental Water Co., Bedford, MA) through a Barnstead Ultrapure Mixed Bed Cartridge (Barnstead Co., Boston, MA) to remove silica and CO₂. The water was further purified with an Amberlite XAD-2 resin (Rohm & Hass Co., Philadelphia, PA) column to remove trace organic materials. Solution metal concentrations were measured on a Perkin Elmer Optima 4000 DV ICP-OES or an Elan 9000 ICP-MS. The RSD of three replicate analyses was generally below 3%. For selected samples, the dissolved organic carbon (DOC) content of the solution was analyzed. DOC concentrations were measured using a total organic carbon analyzer TOC-5050A (Shimadzu Corporation) and the relative standard deviation (RSD) of five experiments was generally below 2%.

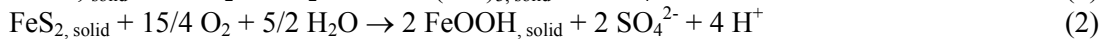
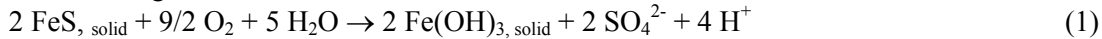
RESULTS AND DISCUSSION

Resuspension under aerobic conditions - the kinetics of metal release

The results of aerated resuspension experiments of Trepangier sediments conducted without controlling pH are presented in Figure 2. In Fig. 2, the change in solution pH and Eh at a

sediment concentration of 20 g/l is plotted in a Eh-pH diagram for Fe speciation and the reactions and equations used to draw this diagram are summarized in Table 2. During the 6 days aeration period, the solution pH decreases from 7.2 to 3.8 and Eh increases from -320 to +390 mV. The Eh-pH diagram of Fe is adopted here because it not only presents the progressive changes in the solution pH and Eh, but also shows the relationship between these changes and Fe speciation through the dissolution and precipitation of Fe solid phases. It is important to note that this and the following Eh-pH diagrams are constructed for one set of conditions, and any changes in these concentrations will shift the position of the boundaries between the stability fields. The solution DO concentration increases sharply within the first 3 hours of resuspension (from 1 to 8.1 mg/L) and stays above 8.1 throughout the whole experiment. Accompanied by pronounced pH and Eh changes, dissolved S and metal concentrations increase considerably between 24 to 48 hours of aeration and the metal release is proportional to the sediment concentration. As shown in Fig. 3, the solution S concentration increases during day 1 to 3 and reaches a plateau after 3 days aeration. We measured the AVS content in the Trepangier sediment after resuspension and the results indicate that more than 99% of AVS is oxidized after 6 days aeration. Based on the results of the solution S concentration, total sulfides and AVS analyses before and after resuspension, we estimate that ~ 40% of the total released S is from the oxidation of AVS and 60% is from pyrite. At the end of the 6 days resuspension experiment, the percent release of Fe and Mn is 0.03 % and 62.6 % respectively, whereas the total release of S is 71.0% (Fig. 4). The order of trace element total release from the Trepangier sediment is Cd (58.2%) > Zn (57.6%) > Co (36.5%) > Ni (21.2%) > Cu (3.6%) > As (1.2%) > Pb (0.35%). A similar order of metal release (Cd > Zn > Cu > Pb) has been reported by Calmano et al. (4), even though their resuspension experiments were performed at controlled neutral-pH values.

Similar to the findings of this study, many investigations (6,7,13) have shown a distinct pH drop after exposing the anoxic sediments to oxygenated overlying waters and it is suggested that the oxidation of AVS and pyrite is the primary source of the increased acidity, according to the following reactions:



As shown in these two equations, 1 mol of AVS can produce 2 mol of H⁺ whereas 1 mol of pyrite can produce 4 mol of hydrogen ions. Equations 1 and 2 also predict the subsequent precipitation of Fe-oxyhydroxides. Interestingly, the last two data points (day 5 and 6) in Fig. 2 sit right on the phase boundary between Fe²⁺ and Fe₂O₃ indicating the possible precipitation of iron oxyhydroxides, which may explain the dramatic decrease of solution Fe concentration after day 3 in Fig. 3.

In this study, the release of heavy metals and the inorganic compound from Trepangier sediment are evaluated on both long-term (6-7 days) and short-term (24 hours) time scales. For the short-term resuspension, the solution pH drops from 7.2-7.3 to 6.7-6.8 and Eh changes from -330 to -160 mv (Fig. 1). Unlike the long-term resuspension, where the dramatic changes in solution pH and Eh and significant metal release are observed, the mobilization of metals within the first 24 hours is insignificant. After 24 hours aeration, the percent release of Ni, Co, Zn, Cd, Pb and Cu can be seen in Fig. 4 and no relationship between metal release and sediment concentration is observed.

The results of our aerated resuspension experiments suggest that the kinetics of metal release during resuspension of an anoxic sediment is fairly slow and appreciable metal release

typically occurred between one to two days aeration. However, Saulnier and Mucci (14) reported a significant release of Fe, Mn and As in the first hour of resuspension of anoxic sediment in seawater. The kinetics of metal release during the resuspension of anoxic sediments is likely related to the oxidation rate of sulfide minerals and different sulfide minerals exhibit different oxidation rates. For instance, it is reported that AVS is usually oxidized during a few hours of exposure of an anoxic sediment to oxic waters whereas a major portion (20% - 50%) of pyrite can oxidize in a day (15). Nicholson and Scharer (13) demonstrated that the rate of pyrrhotite oxidation at atmospheric concentration of O₂ and 22°C was 100 times faster than that measured for pyrite. Compared to AVS and pyrite, metal sulfides including CdS, Cu₂S, PbS and ZnS appear to be more resistant to oxidation and it was reported that the oxidation of these minerals could take more than 24 hours resuspension (16).

Aerated vs. anoxic resuspension

Figure 5 compares the solution pH and Eh changes during resuspension under aerated and anoxic conditions (N₂) at a sediment concentration of 10 g/l. When the Trepangier sediment is resuspended under aerated conditions, the solution pH decreases from 7.0 to 4.8 and Eh changes from -210 to -16 mv after 5 days aeration. In contrast, the solution pH increases from 7.0 to 7.4 and Eh is maintained at ~-300 mv when the sediment is resuspended under anoxic conditions. As seen in Fig. 5, pyrite appears to be stable during the anoxic resuspension (open symbols) while the oxidative dissolution of FeS₂ is expected to occur under aerated conditions (closed symbols). The percent release of Fe, As, Mn, Co, Ni, Cd, Zn, Pb and Cu under anoxic, aerobic and acidic anoxic conditions is compared in Fig. 6. The release of these metals is negligible when resuspended under N₂. However, the release of Mn, Co, Ni, Cd, and Zn are significantly greater in the aerated samples. Meanwhile, the remobilization of Cu, Pb and As in both systems is similar, presumably due to the readsorption to the newly formed iron oxyhydroxides under aerated conditions and the strong complexation with dissolved organic matter.

Another set of anoxic resuspension experiments, whereby the solution pH was manually lowered by the addition of HCl, was compared with the aerated resuspension when the solution pH was naturally reduced by the oxidation of sulfide minerals. Clearly, under anoxic conditions, when the solution pH is manually lowered to 4.6, the precipitation of iron oxyhydroxides as well as their scavenging for As and Pb is minimized. It is proposed the increased acidity, instead of redox changes during resuspension, is the direct trigger to the dramatic increase in the release of Mn, Co, Ni. In the case of Zn and Cd, besides the pH effect, redox potential could also be an important factor. Cu is released to a similar extent in the solution of both systems suggesting that the mobilization of Cu is probably less strongly influenced by pH and redox changes.

Resuspension in well-buffered systems

The effect of calcite on solution pH and Eh changes during Trepangier sediment resuspension is presented in Fig. 7. Similar to the resuspension experiments conducted at 10 and 20 g/l, dramatic changes in solution pH and Eh are observed when the sediment suspension is aerated for 7 days without the addition of calcite. In contrast, little changes in pH and moderated changes in Eh occur in the system with the addition of calcite. Consequently, significant release of metals is observed without the addition of calcite but no or little release is found after the addition of calcite (Fig. 8). These findings are consistent with our Eh-pH plot (Fig. 7) where the

oxidative dissolution of FeS_2 and FeCO_3 was predicted with no addition of calcite whereas possible phase transformation from FeS_2 to $\text{FeCO}_3/\text{Fe}_2\text{O}_3$ is suggested in the presence of calcite.

It is interesting to note that, while the release of all the metals are quenched by the addition of calcite, the release of S, primarily due to the oxidation of AVS and FeS_2 , is similar in both systems. There are two explanations for this finding. For metals initially bound with sulfide minerals, the release of these metals are masked by the precipitation of metal carbonates and/or oxides, or by their readsorption onto newly formed iron carbonate and oxyhydroxides. For metals originally bound with carbonate or oxide phases, they will not be released since carbonate/oxides are stable at neutral pH. Therefore, again we conclude that the increased acidity is the direct cause of the significant mobilization of most heavy metals.

In agreement with these observations, Saulnier and Mucci (14) reported that the resuspension of oxic sediments did not lead to the release of Fe, Mn and As, whereas the resuspension of anoxic sediments in an oxygenated water can induce a significant release of these elements. Likewise, Degtiareva and Elektorowicz (6) demonstrated that the fate of toxic metals during resuspension depended on the calcium content in the sediment. In contrast, Calmano et al. (4) reported a continuous increase in dissolved Cu, Cd and Zn concentration following sediment resuspension at pH 7.5. This discrepancy could be explained by two possibilities. Firstly, the resuspension experiments by Calmano et al. (4) were performed on a long-term scale and the highest release rate occurred after 200 hours resuspension. In our study, resuspension experiments at neutral pH are conducted for 168 hours and significant release of metals might not occur in the time scale of our experiments. Secondly, the concentration of total Fe in our sediment is about 7 times greater than that in the sediment studied by Calmano et al. (4) and the pH of resuspension experiment was controlled by the addition of calcite. Consequently, the chances for the precipitation of metal carbonate minerals and the readsorption by iron oxyhydroxides and calcite in our system is much higher and the great scavenging ability of these phases may explain the lack of metal release in this study.

Resuspension in the presence and absence of microbial activities

Figure 9 compares the changes in the solution pH and Eh during the resuspension of Trepanzier sediment in the presence and absence of microbial activities. As shown in Fig. 9, when the sediment suspension is aerated in the presence of a bacterial inhibitor, NaN_3 , little changes in pH and moderate changes in Eh are observed (open symbols). After 6 days resuspension, the percent release of metals and inorganic compounds are compared in Figure 10. Clearly, the release of Mn, Zn, Ni, Co and Cd is much greater without NaN_3 and therefore in the presence of microbes. For instance, the percent release of Zn and Cd is ~2 orders of magnitude greater in the presence of a microbial population and the induction time for the microbial activity is between one to two days. It is evident that the presence of microbes catalyzes the oxidation of AVS and pyrite during aeration, which consequently accelerates the production of solution acidity as well as the simultaneous release of Mn, Zn, Ni, Co and Cd to the aqueous phase. Contrary to these metals, the percent release of Pb and As remains almost unaffected by the addition of NaN_3 possibly due to their readsorption onto the newly formed iron oxyhydroxides.

In contrast to all the other metals, more Cu is released to the solution in the absence of microbes (Fig. 11). Given that Cu is known to form strong complexes with dissolved organic

carbon (DOC), the solution concentration of DOC was also measured in these experiments. Figure 11 plots the concentration of DOC as a function of aeration time in the presence and absence of microbes. As shown in Fig. 11, the concentration of DOC increases in the first 14 hours and then decreases with time in the presence of microbes. In contrast, the concentration of DOC increases gradually with time throughout the whole experiment without microbes. The DOC concentration in the suspension likely reflects a balance between the production of DOC from the decomposition of high molecular weight organic matter and the consumption of DOC by bacterial activities during resuspension. Although the nature of DOC is not investigated in this study, a fraction of the DOC is certainly able to form strong complexes with heavy metals, especially with Cu. Therefore, we propose that the greater release of Cu to the aqueous phase in the absence of microbes is due to its complexation with dissolved organic matter in the suspension.

During dredging operations, when anoxic sediments are exposed in well-oxygenated overlying waters, the changes in the solution physical and chemical environment may favor the growth of bacteria such as *Thiobacillus ferrooxidans*. The improved incubation environment (more O₂ supply) will thus enhance microbial activities, which is believed to catalyze the oxidation of sulfide minerals and accelerate the release of many toxic metals. The results of this study indicate that, besides the pH and Eh changes, microbial catalysis is essential in regulating metals release during sediment resuspension and this effect may last a long period even after dredging operations are finished. Whereas the importance of pH and Eh has been studied extensively, the effect of microbial activities on metal release during and after a dredging event may be a bigger concern and should not be overlooked.

Sources of the released metals

Figure 12 plots the fractional distribution of Fe, As, S, Mn, Co, Ni, Cd, Zn and Pb in exchangeable, carbonate, oxide and sulfide/organic matter phases, in wet anoxic Trepangier sediments and after 7 days aeration. Comparing Fig. 12 and 1, it is evident that the binding forms of heavy metals and As change significantly before and after the resuspension experiments. For Co, Ni, Zn, Cd and Mn, the dominant fraction is shifted from either carbonate, oxide or sulfide/organic matter phases to the exchangeable phase. In the case of Fe, As and Pb, considerable decrease in the carbonate and sulfide/organic matter fractions confirms the rapid precipitation of iron oxyhydroxides and their strong scavenging ability for As and Pb. The fractionation pattern of Cu remains the same except for a slight increase in the exchangeable phase after aeration confirming the strong complexation between Cu and organic matter, which possibly remain stable during the time scale of our resuspension experiments.

It is clear that the resuspension of an anoxic sediment in oxic waters not only induces heavy metal release to the aqueous phase, but alters their partitioning in the sediment as well. For Zn, Pb, Co, Ni and Cd, the transformation from strongly bound species (oxidic, carbonatic and sulfidic) to more weakly bound species (exchangeable) would increase the mobility and bioavailability of these metals in aquatic environment. Over the extended periods of dredging, the change in the binding forms of the solid phases is likely a bigger concern than that in the solution phase. Therefore, we suggest that, besides the measurements of the total metal concentrations in solution and solid phases, the binding forms of these metals in the sediment also be investigated in any future study.

Sulfide oxidation provides the primary source of metal release (4,14) and the release pattern of Mn, Zn, Ni, Cd and Co in this study is indeed very similar to that of S during our resuspension experiments. Nevertheless, our sequential extraction results indicate that the solution concentration of most metal ions exceeds their total concentration in the sulfide/organic matter phase. For instance, the solution concentration of Zn, at the end of a 6 days resuspension at 20 g/l, is about 2450 $\mu\text{g/l}$, which is 5 times greater than the total Zn associated with the sulfide/organic matter phase. Metal sulfide minerals, therefore, could not be the primary source for Zn. By comparing Figure 12 and 1, we believe that a major portion of released Zn is from the oxides in the sediment because the oxide fraction of Zn decreases sharply after resuspension (from 77% to 28%). Following the same reasoning, we propose that during the resuspension of Trepangier Bayou sediment, oxides are the major source for Zn, Cd and Mn release, carbonates are important for Fe, Mn, Co, Ni, Pb and sulfide/organic matter is the dominant source for Pb and Cu.

In summary, among the heavy metals and inorganic compounds investigated, it appears that there are three distinct categories: 1. Mn, Zn, Cd, Ni, Co; 2. Fe, Pb and As; and 3. Cu, with respect to their release profiles during resuspension. Group 1 metals apparently are associated with Mn carbonate/oxides. They are released to the water column with increased acidity during aerated resuspension and their dramatic release is not affected by the precipitation of Fe oxyhydroxides. In agreement with this study, Stummeyer and Marchig (17) reported that the transition metals Co, Ni and Zn were strongly bonded with Mn oxide phases and were available for incorporation into manganese nodules when the horizontal position of the redox boundary and the surfaces of manganese nodules are located in the same depth. Group 2 elements show strong affinities with Fe oxyhydroxides, which minimize their release to the aqueous phase during resuspension, even under acidic conditions (pH 4). For Group 3 the element Cu, the unique release profile may be determined by its strong complexation with organic matter. Therefore, the different fate of heavy metals and inorganic compounds during resuspension may be related to their sources and the relative affinity of these compounds to iron and/or manganese oxyhydroxides and/or organic matter after oxidation. This classification is consistent with the results of resuspension in the presence and absence of microbial activities and the sequential extractions before and after resuspension.

REFERENCES CITED

1. Petersen, W., Willer, E. and Willamowski, C., "Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water." *Water, Air, Soil Pollution*. **99**, 515-522. (1997).
2. Huang, Sui Liang., "Investigation of Cadmium Desorption from Different-Sized Sediments." *Journal of Environmental Engineering*. **Vol.129**, No.3, 241-247 (2003).
3. Khalid, R. A.; Gambrell, R. P.; Verloo, M. G.; Patrick Jr., W. H. "Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation reduction potential and pH. **Volume I**: literature review," U.S. Army Engineer, (1977).
4. Calmano, W.; Forstner, U.; Hong, J. In *Environmental geochemistry of sulfide oxidation*; Alpers, C. N., Blowes, D. W., Eds.; American chemical society: Washington, DC, (1994), pp 298-321.
5. Hirst, J. M.; Aston, S. R. *Estuarine, Coastal and Shelf Science*, **16**, 549-558 (1983).
6. Degtiareva, A.; Elektorowicz, M. *Water Qual. Res. J. Canada*, **36**, 1-19 (2001).
7. Calmano, W.; Hong, J.; Forstner, U. *Wat. Sci. Tech.*, **28**, 223-235 (1993).
8. Singer, P. C.; Stumm, W. *Science*, **167** (1970).
9. Hong, J.; Forstner, U.; Calmano, W. In *Bioavailability: Physical, chemical and biological interactions*; Hamelink, J. L., Landrum, P. F., Bergman, H. L., Benson, W. H., Eds.; Lewis Publishers, (1994), pp 119-141.
10. Pugh, C. E.; Hossner, L. R.; Dixon, J. B. *Soil Sci.*, **137**, 309-314 (1984).
11. Dubrovsky, N. M.; Cherry, J. A.; Reardon, E. J.; Vivyurka, A. J. *Can. Geotech. J.*, **22**, 110-128 (1985).
12. Tessier, A.; Campbell, P. G. C.; Bisson, M. *Anal. Chem.*, **51**, 844-851 (1979).
13. Nicholson, R. V.; Scharer, J. M. In *Environmental geochemistry of sulfide oxidation*; Alpers, C. N., Blowes, D. W., Eds.; American chemistry society: Washington, DC, (1994), pp 14-30.
14. Saulnier, I.; Mucci, A. *Appl. Geochem.*, **15**, 203-222 (2000).
15. Morse, J. W. In *Environmental geochemistry of sulfide oxidation*; Alpers, C. N., Blowes, D. W., Eds.; American chemical society: Washington, DC, (1994), pp 289-297.

16. Simpson, S. L.; Apte, S. C.; Batley, G. E. *Environ. Sci. Technol.*, **34**, 4533-4537 (2000).
17. Stummeyer, J.; Marchig, V. *Deep-sea Research*, **48**, 3549-3567 (2001).

Table 1 Acid digestion of metals and inorganic compounds from Trepangier Bayou sediments^a.

Metals and other Trepangier parameters		Sediment Quality Guideline ^b	
		(µg/g)	
Ions	Conc. (µg/g)	Conc. (µmol/g)	
Total Fe	86687	1552	
Total Ca	7587	189.3	
Total Mn	983	17.9	
Total Zn	240	3.67	459
Total Co	10	0.17	
Total Ni	22	0.37	48.6
Total Cu	33	0.52	149
Total Pb	257	1.24	128
Total As	19	0.25	33
Total Cd	1.0	0.01	
Total sulfide (%)		1.33	
AVS		125	
calcite		219	
OC (%)		8.1	

^a Sediments were digested with nitric acid reflux (1:1) and hydrogen peroxide oxidation (30%) following the EPA SW-846 method 3050.

^b The values are sediment quality guidelines determined by EPA (EPA 905/R-00/007, June 2000) that reflect probably effect concentrations (PECs, i.e., above which harmful effects are likely to be observed).

Table 2 Reactions and equations used to draw Eh-pH diagram for part of the Fe system.

Phase boundary	Reaction	Equation
FeCO ₃ /Fe ₂ O ₃	2FeCO ₃ + 3H ₂ O = Fe ₂ O ₃ + 2HCO ₃ ⁻ + 4H ⁺ + 2e	Eh = 0.747 - 0.118pH + 0.059log[HCO ₃ ⁻] ^a
FeCO ₃ /Fe ²⁺	FeCO ₃ + H ⁺ = Fe ²⁺ + HCO ₃ ⁻	pH = -0.33 - log[HCO ₃ ⁻] - log[Fe ²⁺] ^a
Fe ²⁺ , H ₂ S/FeS ₂	2H ₂ S + Fe ²⁺ = FeS ₂ + 4H ⁺ + 2e	Eh = -0.057 - 0.118pH - 0.059 log[H ₂ S] - 0.0295log[Fe ²⁺] ^a
Fe ²⁺ , SO ₄ ²⁻ / FeS ₂	FeS ₂ + 8H ₂ O = 2SO ₄ ²⁻ + Fe ²⁺ + 16H ⁺ + 14e	Eh = 0.354 - 0.067pH + 0.0084log[SO ₄ ²⁻] + 0.0042log[Fe ²⁺] ^a
Fe ²⁺ /Fe ₂ O ₃	2Fe ²⁺ + 3H ₂ O = Fe ₂ O ₃ + 6H ⁺ + 2e	Eh = 0.728 - 0.059log[Fe ²⁺] - 0.177pH ^a
FeCO ₃ , H ₂ S/ FeS ₂	FeCO ₃ + 2H ₂ S = HCO ₃ ⁻ + FeS ₂ + 3H ⁺ + 2e	Eh = -0.0472 - 0.0885pH - 0.059 log[H ₂ S] + 0.0295log[HCO ₃ ⁻] ^b
FeCO ₃ , SO ₄ ²⁻ / FeS ₂	FeS ₂ + HCO ₃ ⁻ + 8H ₂ O = 2SO ₄ ²⁻ + 17H ⁺ + FeCO ₃ + 14e	Eh = 0.354 - 0.0716pH + 0.0084 log[SO ₄ ²⁻] - 0.042log[HCO ₃ ⁻] ^b

^aEquations were taken from Garrela and Christ (1965).

^bEquations were derived in this study using the log K values provided by Garrela and Christ (1965).

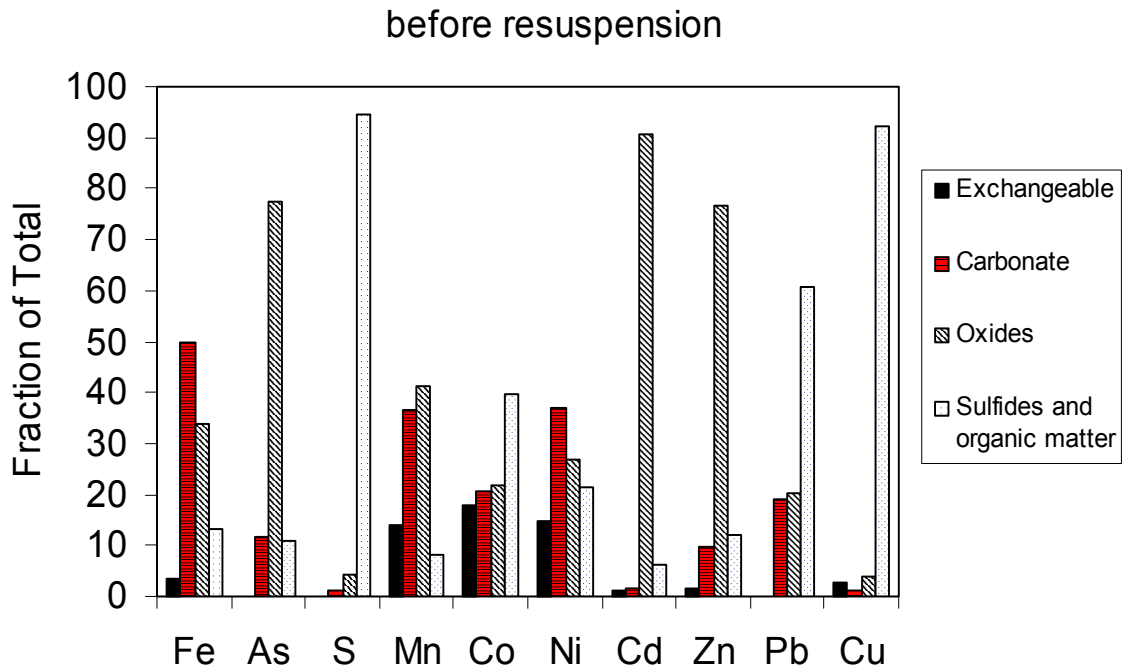


Figure 1. Plot of the fractional distribution of metal ions, sulfur and As in exchangeable, carbonate, oxide, and sulfide/organic matter phases in anoxic Trepangier bayou sediments.

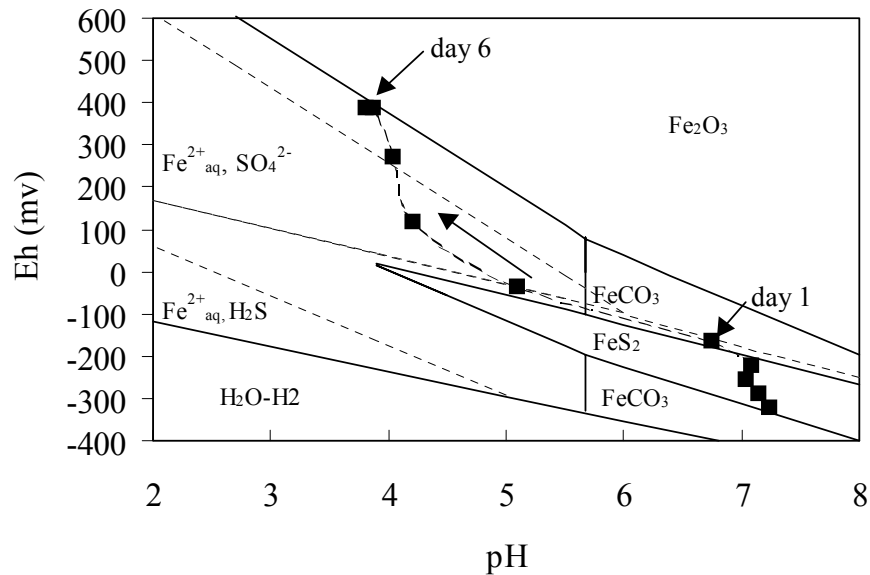


Figure 2. Eh-pH diagram showing phase boundaries for Fe and S species in a 0.01 M NaCl solution following 6 days aeration. For phase boundaries, solid lines are drawn at an activity of total dissolved Fe of 10^{-6} , dissolved S of 10^{-6} and $pCO_2 = 100$. Dashed lines are drawn at $[Fe] = 10^{-4}$, $[S] = 10^{-4}$ and $pCO_2 = 10^{-2}$.

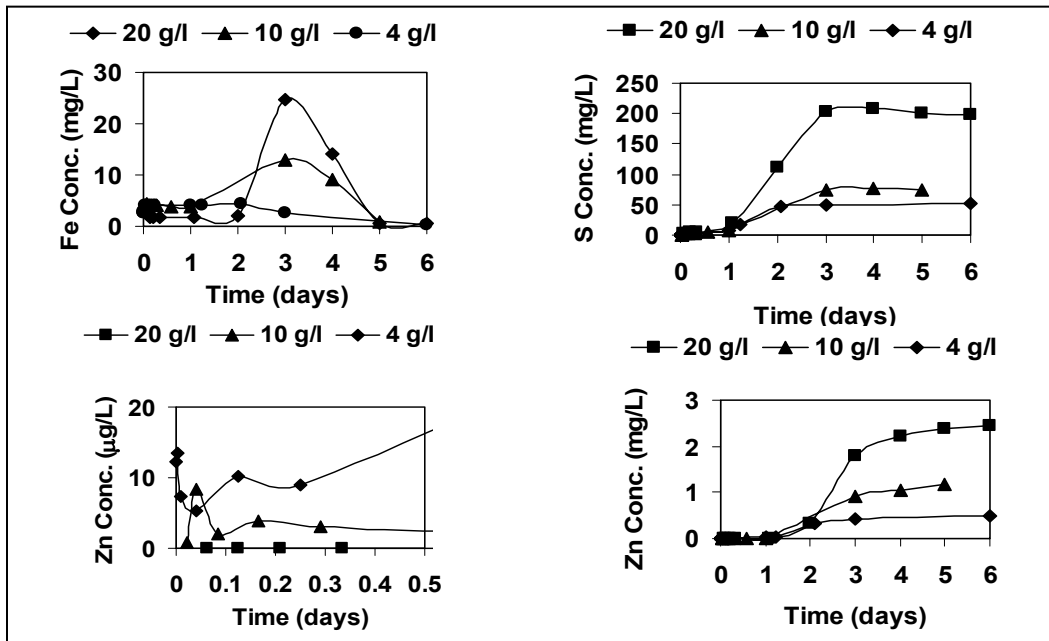


Figure 3. Plots of solution metal and sulfur concentrations as a function of aeration time during resuspension of Trepangier sediment in a 0.01 M NaCl solution.

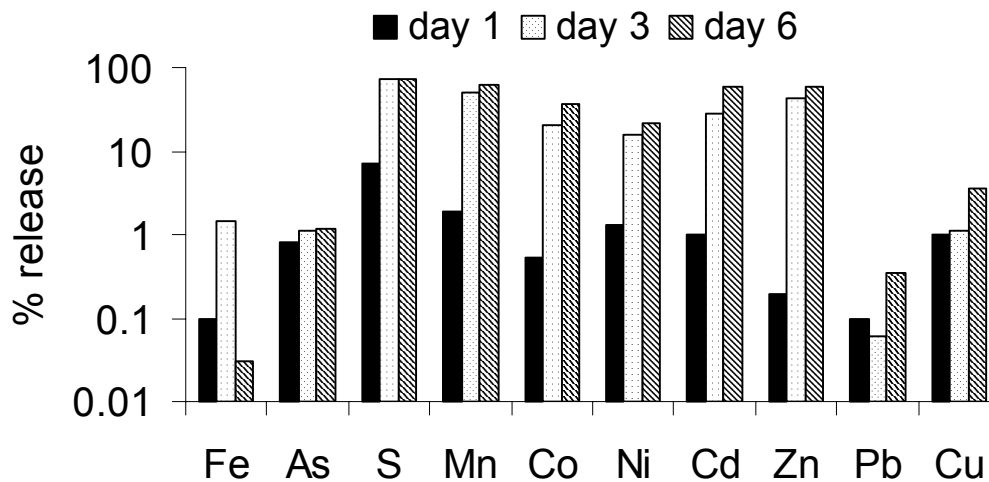


Figure 4. Percent metal release to the water column following 1, 3 and 6 days aeration of Trepangier sediment (20 g/l) in a 0.01 M NaCl solution.

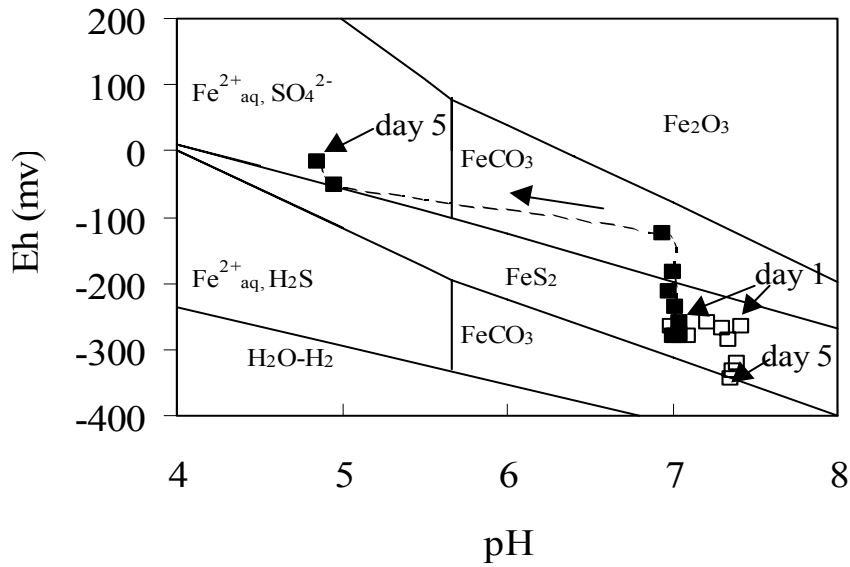


Figure 5. Comparison of Eh-pH plot for Fe species and solid phases for Trepanzier sediment in artificial river water following 5 days aerated (■) and anoxic (□) resuspension. Phase boundaries drawn at assumed activity: $[\text{Fe}] = 10^{-6}$, $[\text{S}] = 10^{-6}$ and $p\text{CO}_2 = 100$

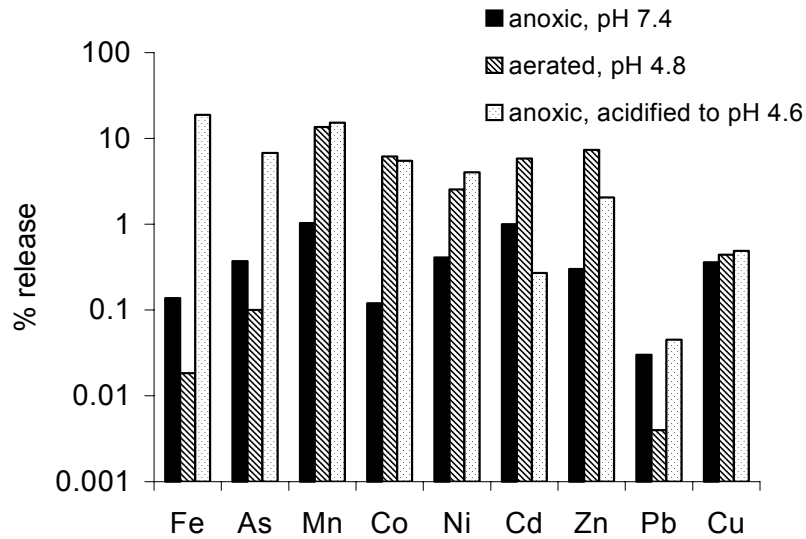


Figure 6. Percent metal release to the water column following 5 days resuspension of Trepanzier sediment (10 g/l) in artificial river water under aerated, anoxic and acidic anoxic conditions.

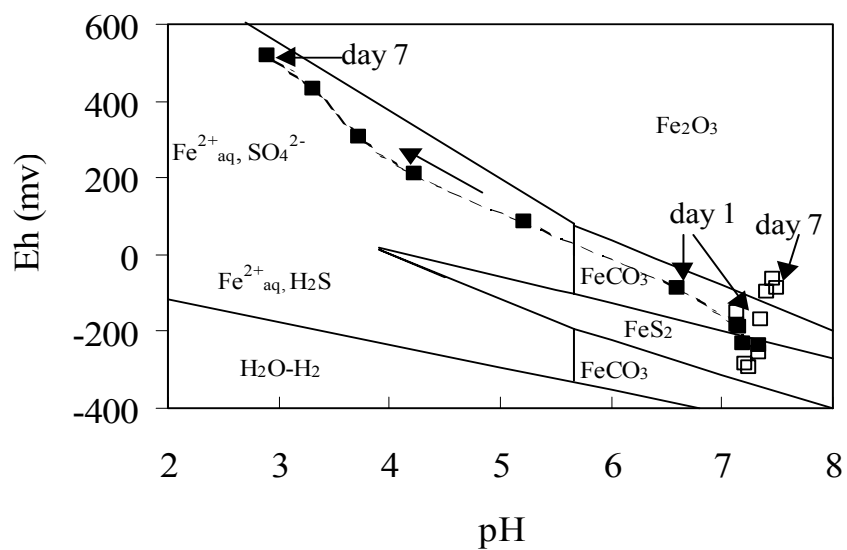


Figure 7. Comparison of Eh-pH plot for Fe species and solid phases for Trepanzier sediment in a 0.01 M NaCl solution following 7 days resuspension in the presence (\square) and absence of calcite (\blacksquare). Phase boundaries drawn at assumed activity: $[Fe] = 10^{-6}$, $[S] = 10^{-6}$ and $pCO_2 = 100$

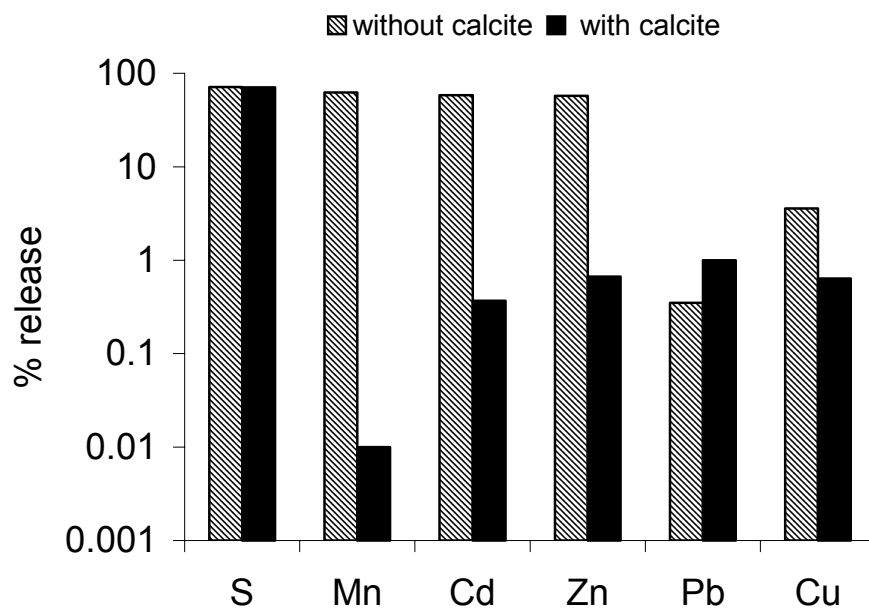


Figure 8. Percent metal release to the water column following 7 days aeration of Trepanzier sediment (40 g/l) in a 0.01 M NaCl solution in the presence and absence of calcite.

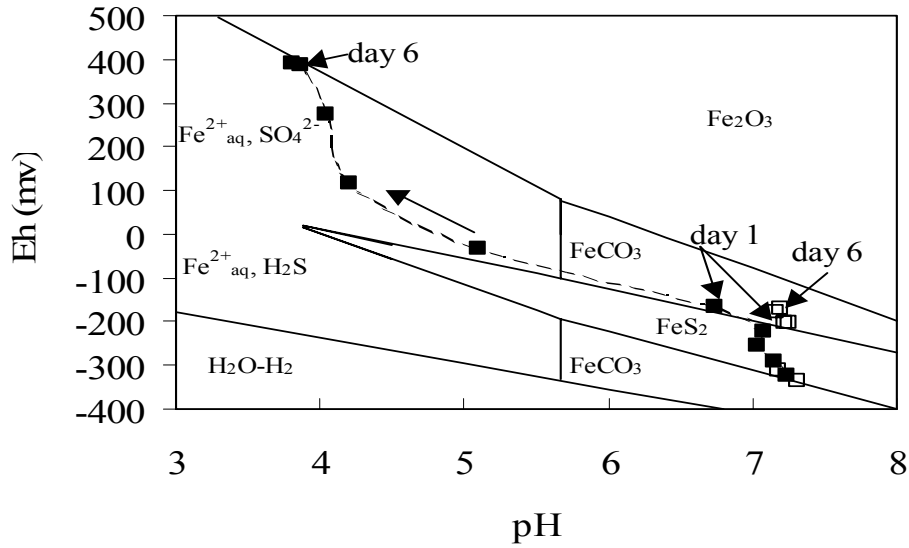


Figure 9. Comparison of Eh-pH plot for Fe species and solid phases for Trepangier sediment in a 0.01 M NaCl solution following 6 days resuspension in the presence (□) and absence of NaN3 (■). Phase boundaries drawn at assumed activity: $[Fe] = 10^{-6}$, $[S] = 10^{-6}$ and $pCO_2 = 100$

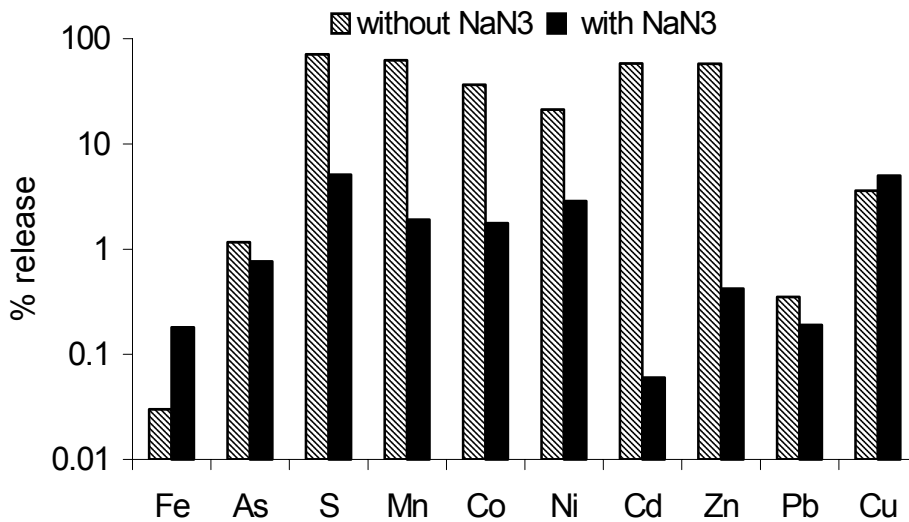


Figure 10. Percent metal release to the water column following 6 days aeration of Trepangier sediment (20 g/l) in a 0.01 M NaCl solution in the presence and absence of NaN3.

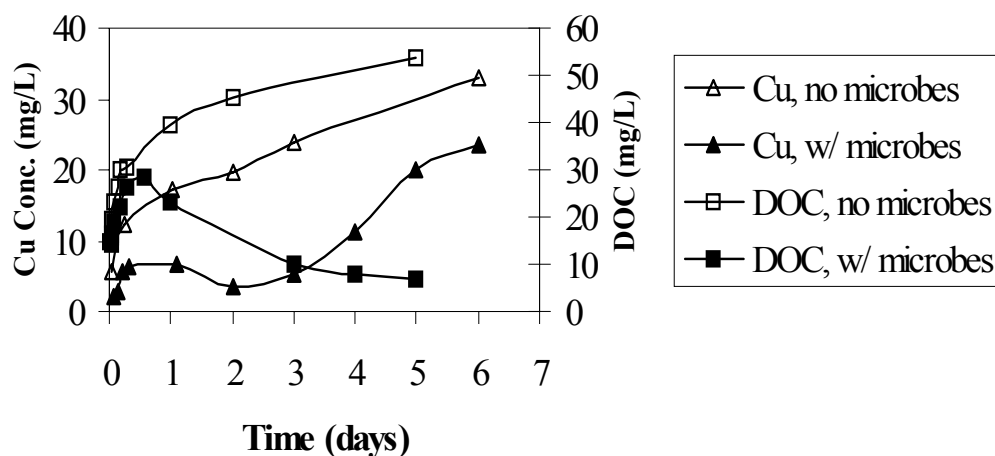


Figure 11. The release profile of Cu and DOC during 6 days aeration of Trepangier sediment (10 g/l) in a 0.01 M NaCl solution in the presence and absence of microbial activities.

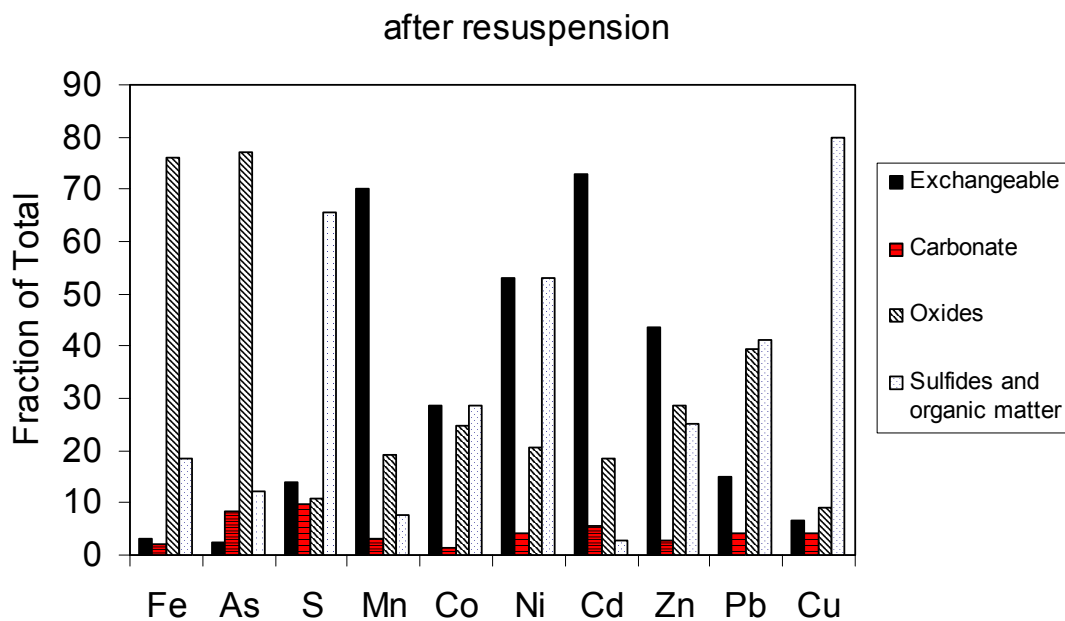


Figure 12. Plot of the fractional distribution of metals ions, sulfur and As in exchangeable, carbonate, oxide and sulfide/organic matter phases in Trepangier sediment, after 7 days resuspension in a 0.01 M NaCl solution.