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Factors affecting metal mobilisation during oxidation of sulphidic, sandy wetland substrates

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ABSTRACT

Most metals accumulate as sulphides under anoxic conditions in wetland substrates, reducing their bioavailability due to the solubility of metal sulphides. However, upon oxidation of these sulphides when the substrate is occasionally oxidised, metals can be released from the solid phase to the pore water or overlaying surface water. This release can be affected by the presence of carbonates, organic matter and clay. We compared changes of Cd, Cu and Zn mobility ($CaCl_2$ extraction) during oxidation of a carbonate-rich and a carbonate-poor sulphidic, sandy wetland substrate. In addition, we studied how clay with low and high cation sorption capacity (bentonite and kaolinite, respectively) and organic matter (peat) can counteract Cd, Cu and Zn release during oxidation of both carbonate-rich and carbonate-poor sulphidic sediments. $CaCl_2$-extractability of Cu, a measure for its availability, is low in both carbonate-poor and carbonate-rich substrates, whereas its variability is high. The availability of Cd and Zn is much higher and increases when peat is supplied to carbonate-poor substrates. A strong reduction of Cd and Zn extractability is observed when clay is added to carbonate-poor substrates. This reduction depends on the clay type. Most observations could be explained taking into account pH differences between treatments, with kaolinite resulting in a lower pH in comparison to bentonite. These pH differences affect the presence and characteristics of dissolved organic carbon and the metal speciation, which in turns affects the interaction of metals with the solid soil phase. In carbonate-rich substrates, Cd and Zn availability is lower and the effects of peat and clay amendment are less clear. The latter can also be attributed to the high pH and lack of pH differences between treatments.


KEYWORDS: Cadmium, Copper, Zinc, Sulphides, Mobilisation

1. Introduction

Wetland soils and sediments consist of a mixture of organic and inorganic compounds. In the pore water, metals can be present as free ion, or as organic or inorganic complex. In the solid phase, adsorption sites for metals can be clay minerals, Fe-, Mn- or Al-(hydr)oxides, organic matter and carbonates. Metals can also be included in the mineral structure or precipitate with formation of metal carbonates and metal sulphides. Sulphide formation is mediated by sulphate reducing bacteria in anoxic conditions. Accordingly, they are normally found in sulphate-rich wetland substrates. According to e.g. Kornicker & Morse (1991), Morse & Arakaki (1993), Huerta-Diaz et al. (1998) and Billon et al. (2001), iron monosulphide (FeS) is often considered the most reactive of the sulphide phases in sediments. Trace metals entering anoxic sediment environments can be expected to react to form sulphide phases according to: $M^{2+} + FeS(s) \leftrightarrow MS(s) + Fe^{2+}$, where M = e.g. Cd, Cu, Ni, Pb, Zn, Co, Hg (Simpson et al., 2000). Because the solubility of these metal sulphides is very low, sediments with an excess of reactive sulphide to trace metals will exhibit very low dissolved metal concentrations in their pore water. The reactive sulphide fraction may be estimated by measuring the acid-volatile sulphide (AVS) content of the sediment, whereas the simultaneously extracted metal (SEM = $\sum$ Cd, Cu, Ni, Pb, Zn) content approximates the reactive trace metal fraction (Di Toro et al., 1992; Allen et al., 1993).

When sulphide-containing wetland substrates are oxidised upon contact with water containing dissolved oxygen or with air, the sulphides will tend to be gradually oxidised to sulphate, and metals will be released into the pore water. This can occur occasionally in constructed wetlands used for wastewater treatment or more frequently in tidal marshes, and result in an increased mobility and bioavailability of metals retained within the system (Du Laing et al., 2009b). Once the reactive sulphide phase, which is determined as AVS (predominantly FeS), has been exhausted in the absence of other binding phases, the metals are expected to appear in the pore waters in order of

decreasing metal sulphide solubility, that is Ni, Zn, Pb, Cd and then Cu (Di Toro et al., 1992). Berry et al. (1996) provided evidence for this relationship for each of the metal ions Cd, Cu, Ni, Pb and Zn (Simpson et al., 2000). Next to the direct release of metals precipitated as sulphides, the pH can decrease during sulphide oxidation due to the following reaction (presented for FeS):

$$4 \, FeS_{(s)} + 9 \, O_2 + 10 \, H_2O \rightarrow 4 \, Fe(OH)_{3(s)} + 4 \, SO_4^{2-} + 8 \, H^+.$$
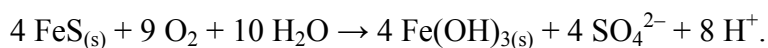
For each molecule of FeS oxidized, two protons are produced. In unbuffered sediments, these reactions will cause a drop in pH which will limit transfer of trace metals from the water phase to the wetland substrate and/or causing a desorption from the soils or sediments (e.g. Salomons et al., 1987; Gambrell et al., 1991b; Calmano et al., 1993).

The presence of carbonates in calcareous wetland substrates constitutes an effective buffer against such pH decrease and thus hampers metal release (Satawathananont et al., 1991; Tack et al, 1996). Moreover, carbonates may also directly precipitate metals (e.g. Gambrell, 1994; Guo et al., 1997; Charlatchka & Cambier, 2000). They can be geochemically or biogenically formed and be deposited as part of the sediments in tidal flats, floodplains or marshes. However, decalcification occurs as carbonates are consumed upon oxidation of sulphides and concurrent release of protons: $CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$. Evidently, the intensity of decalcification due to sulphide oxidation varies with the amount of sulphide previously formed in the wetland substrate, and thus on the duration of waterlogging, and the availability of sulphate and organic matter. Also the increased Ca concentrations in the pore water during partial decalcification can cause an enhanced release of metals in the calcareous wetlands' substrate layer (Du Laing et al., 2007b).

The SEM/AVS ratio is used to assess potential sediment toxicity. Some authors (Di Toro et al., 1992; van den Hoop et al., 1997) state that no lethal toxic effects on organisms should be expected if the SEM/AVS ratio is smaller than one. Di Toro et al. (1990) initially showed that lethal toxic effects of cadmium spiked marine sediment on amphipods can successfully be predicted by

considering the Cd/AVS ratio, whereas estimation of the toxicity based on the total metal content of the sediment failed. Lethal toxic effects were found to be absent for Cd/AVS ratios smaller than one, but appeared to be present at Cd/AVS ratios exceeding one. Comparable results were afterwards also observed for freshwater sediments (e.g. Ankley et al., 1991), sediments contaminated with Cu, Pb, Ni and Zn (e.g. Di Toro et al., 1992; Ankley et al., 1993; Casas & Crecelius, 1994), and also for other organisms (Carlson et al., 1991; van den Hoop et al., 1997). However, simultaneously extracted metals may also include metals which are associated with alternative binding phases when these are present, e.g. metals associated with carbonates, organic matter or clay. When metals are associated with these compounds, the risk for metal toxicity and bioavailability may be much lower than expected from the fact that SEM exceeds AVS.

To assess the importance of the presence of carbonates in determining metal mobility and availability when SEM starts to exceed AVS during oxidation of sulphidic sediments, we monitored Cd, Cu and Zn mobility ($CaCl_2$ extraction) during oxidation of both a carbonate-rich and a carbonate-poor sulphidic, sandy wetland substrate. In addition, the effects of clay with low and high cation sorption capacity (bentonite and kaolinite, respectively) and organic matter (peat) on counteracting Cd, Cu and Zn release were studied.

2. Materials and methods

A carbonate-poor, metal-contaminated sulphidic sand was sampled from the bottom of the river Dommel (Belgium). A carbonate-rich sand consisted of commercially available estuarine sand which was enriched in sulphides by waiting for 7 weeks after addition of a growth medium for sulphate-reducing micro-organisms. This induced reduction of sulphates to sulphides. Meanwhile, metals were regularly spiked to the substrate, inducing metal sulphide precipitation. Parts of the carbonate-rich and the carbonate-poor sulphidic sand were also mixed with peat (2% w/w), bentonite (10% w/w) and kaolinite (10% w/w). This resulted in 8 different substrates to be tested.

Glass recipients (Ø = 15 cm, height = 6 cm) were filled with 525 g of each substrate type. The initially wet substrates were left to dry and oxidise at room temperature (20 °C). Every 2 days, the substrates were mixed well with a spoon to eliminate the gradient caused by drying and oxidation. The experiment was conducted in triplicate. Dry weight percentage, pH, AVS contents, HCl- and $CaCl_2$-extractable metal contents of the substrates were measured regularly. In the beginning of the experiment, measurements were conducted daily, and less frequently afterwards.

To measure dry weight percentage, 10 g of substrate was dried in an oven at 200°C for 16h. The pH was measured with a pH electrode in a suspension of substrate in distilled water (1:5 ratio) after equilibration for 18 h. Acid volatile sulphide (AVS) was determined on fresh substrate samples by conversion of sulphide to H_2S and absorption in a Zn-acetate solution, followed by back titration (Tack et al. 1997). Therefore, three pyrex gas washing bottles were connected in series. The first bottle was filled with 100 mL of deionized water, whereas the next two bottles were filled with 95 mL of deionized water. All flasks were deoxygenated by bubbling N_2 through for 30 minutes. Five mL of 2 M ZnOAc was added to each of the second and third bottles. Subsequently, 10 g of substrate and 20 mL of 6 M HCl were added to the first bottle and N_2 was re-bubbled through it for 30 minutes. The acid induced the conversion of sulphides to H_2S in the first bottle, which was transported by the N_2 carrier gas to the second and third bottle and absorbed in the Zn-acetate solution. The Zn-acetate solution was subsequently acidified, and KI and KIO_3 were added, which induced the formation of I_2. As a result, the collected sulphides (S^{2-}) were oxidized to elemental sulphur (S^0) by an equivalent amount of I_2, which was reduced to I^-. The excess I_2 was titrated with $Na_2S_2O_3$. HCl-extractable metals were defined as the metals released from the substrate upon addition of the HCl during AVS analysis (also defined as the simultaneously extracted metals or SEM). To measure $CaCl_2$-extractable metal contents, 50 mL of 0.01 mol L^{-1} $CaCl_2$ was added to 10 g of substrate and shaken for 2 h. The suspension was filtered over a 0.45 μm filter (Chromafil RC 45/25, Macherey – Nagel) and the filtrate was analysed using ICP-MS (Elan DRC-e, Perkin Elmer

SCIEX). Trace metal speciation changes in the extracts as function of pH were modelled using the software Visual MINTEQ ver. 2.40 (http://www.lwr.kth.se/English/OurSoftware/vminteq/) using as input data: pH measured in water extract, 0.01 mol L^{-1} Ca^{2+} and 0.02 mol L^{-1} Cl^{-} (i.e. background cation and anion concentrations in 0.01 mol L^{-1} CaCl$_2$ extractans) and Cd, Cu and Zn concentrations measured in the CaCl$_2$ extract (assumed to be present as Cd^{2+}, Cu^{2+}, Zn^{2+}). Absence of dissolved organic carbon was assumed.

3. Results and discussion

3.1. Carbonate-rich versus carbonate-poor substrate

The dry weight percentage of the substrates increased from between around 96.5 % in the beginning of the experiment to around 100 % from day 7 onwards. The carbonate-rich substrate had a higher initial dry weight and reached its maximum dry weight percentage slightly faster compared to the carbonate-poor substrate. The initial pH was very high (around 10) in the carbonate-rich substrate. This should probably be attributed to the presence in both substrates of carbonates and/or sulphides which remove protons released into solution, in combination with a lack of other compounds and processes which may release these protons into solutions (e.g. organic matter). The presence of carbonates constitutes an effective buffer against a decrease in pH. Whereas the pH of the carbonate-poor substrate decreased from 6.3 to below 5 during the first 5 days of drying and oxidation (Fig. 1, blank), the pH of the carbonate-rich substrate fluctuated within the range 9.5-10.5 (data not shown).

Figure 1

Due to oxidation of sulphides to sulphates, AVS contents decreased from above 7 mmol kg^{-1} DM to below 1 mmol kg^{-1} DM during the first 3 days (Fig. 2, blank). Minimum values were reached faster in the carbonate-rich substrate, which also reached its maximum dry weight percentage a bit faster.

From the moment AVS contents decreased below 1 mmol kg^{-1} DM, CaCl$_2$-extractable Cd and Zn contents, indicating a very mobile metal fraction, started to increase (Fig. 3, blank). They reached their maximum from around day 7 onwards, which coincided with reaching the minimum moisture content. The CaCl$_2$-extractable levels mostly persisted afterwards, indicating minimum readsorption of the metals to the solid sediment phase. When CaCl$_2$-extractable contents were expressed relative to HCl-extractable contents (Table 1), it is clear that the metals are more mobile in the carbonate-poor substrate. This can be attributed to the lower pH, which prevents transfer of most trace metals from the water to the solid phase or causes desorption from the wetland soil and sediments (Calmano et al., 1993). At low pH, the negative surface charge of organic matter, clay particles and Fe and Al oxides is reduced, and various compounds such as carbonates and sulphides become more soluble. Carbonates may also directly precipitate metals (Charlatchka & Cambier, 2000). Presence of carbonates can result in CuCO$_3$, CdCO$_3$ and ZnCO$_3$ occurring in solution. CuCO$_3$ is most easily formed, but especially ZnCO$_3$ is expected to precipitate. Compared to Cd and Zn, Cu is less mobile and also less affected by the presence of carbonates. Copper mobility, represented by the CaCl$_2$-extractable contents in relation to the HCl-extractable contents, is initially low. In contrast to Cd and Zn, CaCl$_2$-extractability of Cu also does not increase much during oxidation of the sulphides (e.g., data for day 7 presented in Table 1). This points towards a strong association of Cu to the solid phase before as well as after oxidation of the sulphides.

Table 1

Figure 2

3.2. Role of organic matter and clay

Both at low and high carbonate contents, the variability of CaCl$_2$-extractable Cu contents was high. At low (Fig. 3) and high (Fig. 4) carbonate contents, Cu was somewhat more mobile when peat was

applied due to its affinity to form complexes with soluble organic molecules (Ashworth and Alloway, 2008; Du Laing et al., 2009a), released from the peat. After oxidation of the sulphides, the mobility was slightly lower in the presence of kaolinite or bentonite as compared to the blank (Fig. 3, Table 1). Bentonite reveals a lower capacity to reduce Cu mobility as compared to kaolinite, although bentonite has a higher cation exchange capacity (CEC). The CEC is expected to be especially high as the pH of the bentonite-amended substrate did not decrease below 9 during the oxidation (Fig. 1). Moreover, speciation modelling indicated that tenorite (CuO) also starts to precipitate above pH 7.7, so additional removal of Cu from solution could be expected at these higher pH levels. However, the differences in pH between substrates amended with kaolinite and those amended with bentonite may have affected the speciation of Cu in solution which might explain the apparent anomaly that sorption is weaker on bentonite than on kaolinite. According to thermodynamical equilibrium calculations, Cu^{2+} is expected to be the main species in solution at pH 6, whereas $Cu(OH)^+$ and $Cu(OH)_2$ are most abundant in solution at a pH of about 9. The speciation shift from Cu^{2+} in solution at pH 6 to $Cu(OH)^+$ and $Cu(OH)_2$ in solution at pH levels close to 9 may have reduced the affinity of Cu for sorption to the clay. Moreover, the pH-dependent presence and characteristics of organic compounds in solution probably have affected Cu concentrations in solution, especially due to the strong association of Cu with organic matter as previously reported in literature (Du Laing et al., 2009a). When pH increases from 6 to above 8, the negative charge on organic molecules is increased. The negatively charged molecules are repelled into the soil solution, thereby increasing dissolved organic matter concentrations and Cu concentrations in solution (Ashworth and Alloway, 2008). Moreover, the negative charge promotes additional association between these dissolved organic molecules and metals, such as Cu. In the carbonate-rich substrates, clear differences in Cu extractability between bentonite and kaolinite cannot be observed, which may be attributed to the quite stable pH, not depending on the type of amendment and varying between 9.4 and 10.5 (data not shown).

Figure 3

Extractability of Cd and Zn by $CaCl_2$ is affected to an important extent by the supply of bentonite, kaolinite and peat in the carbonate-poor substrates (Fig. 3, Table 1). Peat increases Cd and Zn extractability, which should be attributed to the presence of dissolved organic molecules in the extracts. The effect is slightly higher for Cd. A strong reduction of Cd and Zn extractability is observed when kaolinite and bentonite are added. Bentonite results in the lowest extractability, probably due to its higher cation exchange capacity. Differences between bentonite and kaolinite are smaller for Cd (factor 5) as compared to Zn (factor 15). This may again be due to pH differences between these treatments (Fig. 1) and the effect of pH on the speciation of Cd and Zn. At a pH below 7.5 (kaolinite amended substrate), almost all Zn occurs as Zn^{2+} in solution whereas Cd occurs as Cd^{2+} or $CdCl^{+}$ (both about 48%) in solution. At pH 9 (bentonite amended substrate), 80% of the Zn is present as neutral $Zn(OH)_2$ in solution, whereas less than 20% is still positively charged (Zn^{2+} or $Zn(OH)^{+}$ in solution). This speciation shift may have changed the tendency of Zn to adsorb onto solid phases. In comparison to Cu, organic matter is expected to play a lesser role as the affinity of Zn for dissolved organic matter at higher pH is lower (Ashworth and Alloway, 2008). Moreover, at the observed Zn concentration, Zn was found to start precipitating as zincite (ZnO) when pH 8.7 is exceeded. By contrast, Cd still mainly occurs as Cd^{2+} or $CdCl^{+}$ (both about 47%) and only 0.1% occurs as $Cd(OH)_2$ at pH 9. No precipitation occurs and the formation of $Cd(OH)_2$ only starts to become significant (>5%) at pH 10. Accordingly, differences in Cd and Zn mobility between amendments are not observed in the amended carbonate-rich substrates (Fig. 4), as they do not differ significantly in pH. The extractability of Cd and Zn by $CaCl_2$ is highly variable in these substrates, probably due to I) the impact of Ca released from the solid soil phase upon dissolution of the carbonates on the Ca and CO_3^{2-} concentration in the liquid phase and II) the heterogeneous distribution of small shells, and thus carbonates, in the solid phase of the estuarine sand used as substrate.

Figure 4

4. Conclusion

CaCl$_2$-extractability of Cu, a measure for its availability, is low in both carbonate-poor and carbonate-rich substrates, whereas its variability is high. The availability of Cd and Zn is much higher and increases when peat is supplied to carbonate-poor substrates. A strong reduction of Cd and Zn extractability is observed when clay is added to carbonate-poor substrates. This reduction depends on the clay type. Most observations could be explained taking into account pH differences between treatments, with kaolinite resulting in a lower pH in comparison to bentonite. These pH differences affect the presence and characteristics of dissolved organic carbon and the metal speciation, which in turns affects the interaction of metals with the solid soil phase. In carbonate-rich substrates, Cd and Zn availability is lower and the effects of peat and clay amendment are less clear. The latter can also be attributed to the high pH and lack of pH differences between treatments.

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TABLE CAPTIONS

Table 1. CaCl$_2$ – extractable Cd, Zn and Cu contents (mg kg^{-1} DM) relative to HCl-extractable

contents (%) in the carbonate-poor and carbonate-rich substrates as affected by amendment at day

7 of the experiment (n = 3)

FIGURE CAPTIONS

Figure 1. pH during drying and oxidation of a sulphidic, carbonate-poor sandy substrate to which

bentonite, kaolinite and peat are added (blank = no amendment)

Figure 2. Acid-volatile sulphide (AVS) contents (mmol kg^{-1} DM) during drying and oxidation of a

sulphidic, carbonate-poor (A) and carbonate-rich (B) sandy substrate to which bentonite, kaolinite

and peat are added (blank = no amendment)

Figure 3. CaCl$_2$ – extractable Cd, Cu and Zn contents (mg kg^{-1} DM) during drying and oxidation of

a sulphidic, carbonate-poor sandy substrate to which bentonite, kaolinite and peat are added (blank

= no amendment)

Figure 4. CaCl$_2$ – extractable Cd, Cu and Zn contents (µg kg^{-1} DM) during drying and oxidation of

a sulphidic, carbonate-rich sandy substrate to which bentonite, kaolinite and peat are added (blank =

no amendment)

Table 1. CaCl$_2$ – extractable Cd, Zn and Cu contents (mg kg^{-1} DM) relative to HCl-extractable contents (%) in the carbonate-poor and carbonate-rich substrates as affected by amendment at day 7 of the experiment (n = 3)

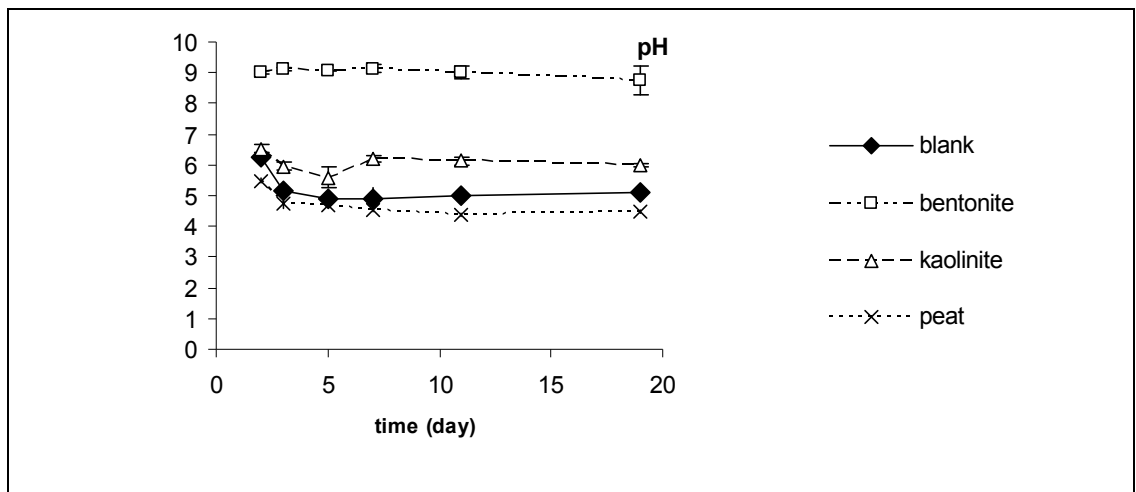|	Cd	Zn	Cu
Carbonate-poor			
Blank	12.3 ± 5.6	37.6 ± 6.1	0.38 ± 0.08
Peat	31.4 ± 3.4	42.3 ± 7.5	1.77 ± 1.05
Kaolinite	0.7 ± 0.1	10.3 ± 1.0	0.29 ± 0.09
Bentonite	0.1 ± 0.0	0.7 ± 0.2	0.58 ± 0.66
Carbonate-rich			
Blank	2.6 ± 2.3	1.6 ± 0.7	0.58 ± 0.39
Peat	1.7 ± 1.4	2.9 ± 1.5	0.70 ± 0.54
Kaolinite	1.5 ± 1.9	4.1 ± 3.5	0.32 ± 0.17
Bentonite	1.8 ± 1.0	2.0 ± 0.8	0.70 ± 0.42

Figure 1. pH during drying and oxidation of a sulphidic, carbonate-poor sandy substrate to which bentonite, kaolinite and peat are added (blank = no amendment)
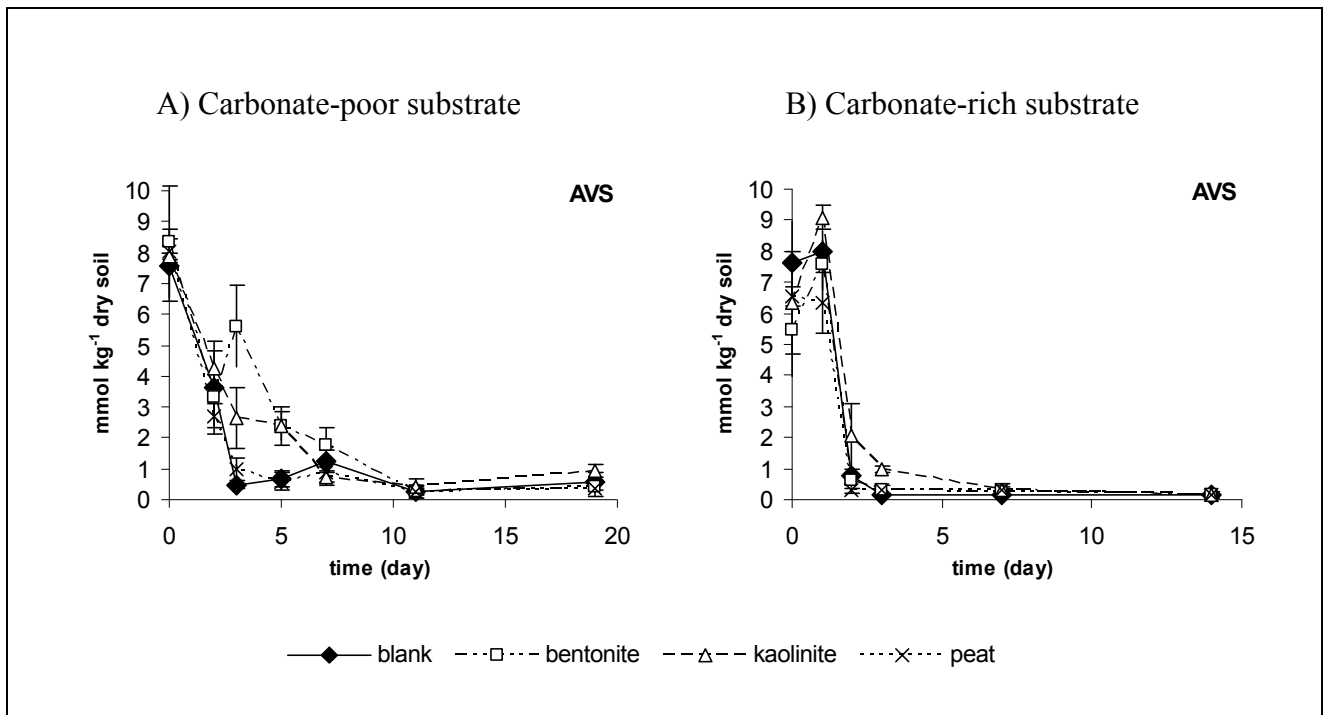
Figure 2. Acid-volatile sulphide (AVS) contents (mmol kg^{-1} DM) during drying and oxidation of a sulphidic, carbonate-poor (A) and carbonate-rich (B) sandy substrate to which bentonite, kaolinite and peat are added (blank = no amendment)
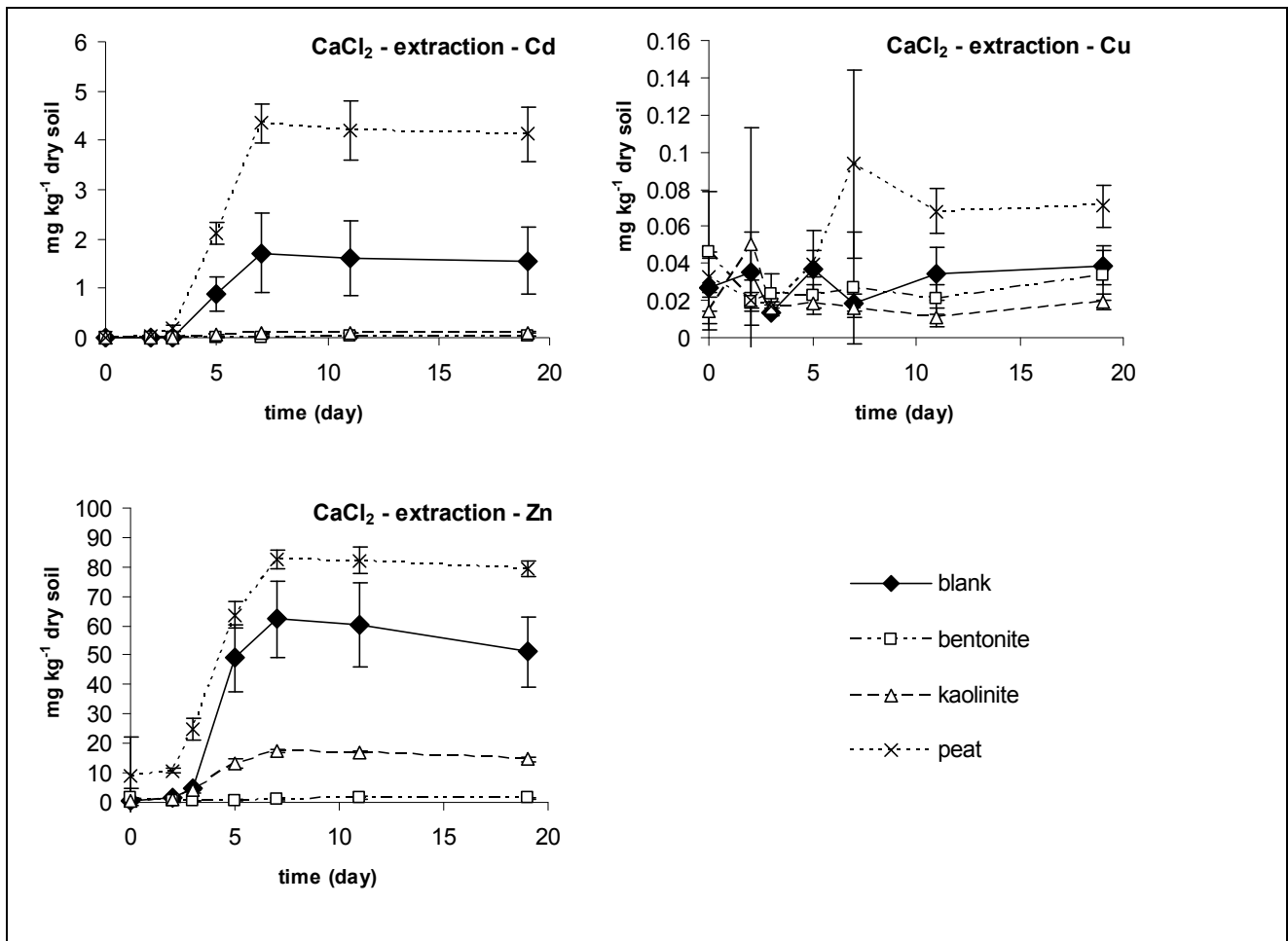
Figure 3. CaCl$_2$ – extractable Cd, Cu and Zn contents (mg kg^{-1} DM) during drying and oxidation of a sulphidic, carbonate-poor sandy substrate to which bentonite, kaolinite and peat are added (blank = no amendment)
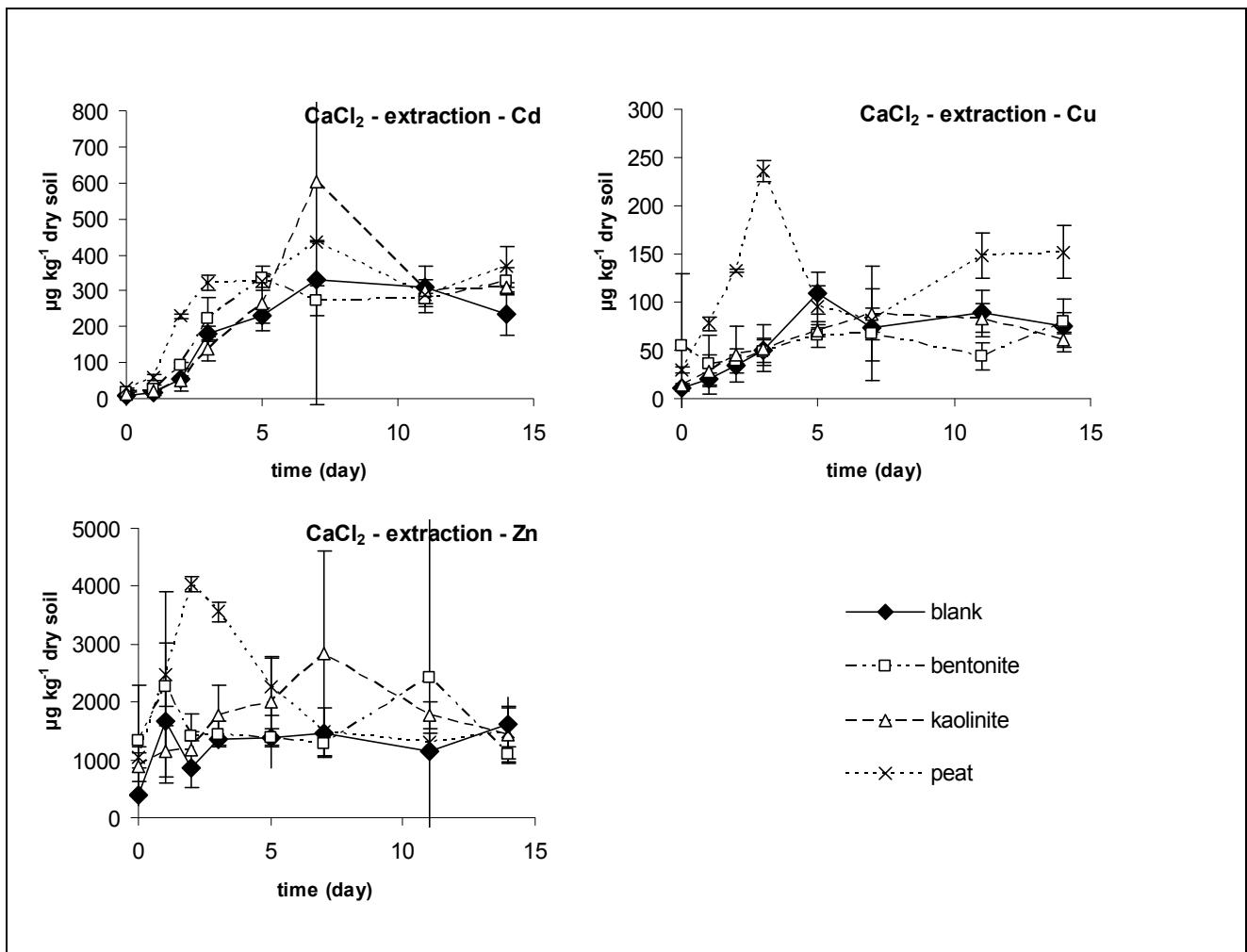
Figure 4. CaCl$_2$ – extractable Cd, Cu and Zn contents (μg kg^{-1} DM) during drying and oxidation of a sulphidic, carbonate-rich sandy substrate to which bentonite, kaolinite and peat are added (blank = no amendment)