Canadian Journal of Soil Science
Revue canadienne de la science du sol

Flooding-Induced Mobilization of Potentially Toxic Trace Elements from Uncontaminated, Calcareous, Agricultural Soils

Journal:	<i>Canadian Journal of Soil Science</i>
Manuscript ID	CJSS-2017-0077.R1
Manuscript Type:	Article
Date Submitted by the Author:	10-Oct-2017
Complete List of Authors:	Indraratne, Srimathie; University of Winnipeg, Environmental Studies and Sciences; University of Peradeniya, Department of Soil Science Kumaragamage, Darshani; University of Winnipeg, Environmental Studies and Sciences
Keywords:	Anaerobic conditions, Calcareous soils, Flooded soils, Potentially toxic trace elements, Pore water

SCHOLARONE™
Manuscripts

Flooding-Induced Mobilization of Potentially Toxic Trace Elements from Uncontaminated, Calcareous, Agricultural Soils

Indraratne, S.P. and Kumaragamage, D.

Department of Environmental Studies and Sciences, The University of Winnipeg, Winnipeg, MB
Canada R3B 2E9

Short title: Flooding-induced trace element release from uncontaminated soils

***Corresponding author d.kumaragamage@uwinnipeg.ca**

Abbreviations: CEC, Cation exchange capacity; Eh, Redox-potential; ICP-AES, inductively coupled plasma atomic emission spectroscopy; OM, Organic matter; PCA, Principal component analysis, PTTE, Potentially toxic trace elements

ABSTRACT

Enhanced mobilization of potentially toxic trace elements (PTTE) is well documented for contaminated floodplains, wetlands and rice paddies. Limited information is available on flooding-induced PTTE release from uncontaminated, agricultural soils from temperate regions. We conducted an incubation study with simulated flooding using calcareous, uncontaminated agricultural soils to assess the release dynamics of a few PTTE and identify the controlling factors. Packed soils were flooded, and soil Eh, pH, total dissolved metals and S concentrations in pore water and floodwater were measured for eight weeks. Pore water arsenic (As) and nickel (Ni) concentrations were initially low, but significantly increased with flooding by 12- and 6-fold, respectively. Copper (Cu) concentration declined with flooding, while zinc (Zn) showed no consistent trend. Arsenic and Ni concentrations correlated negatively with Eh, and positively with other redox-sensitive elements, while Cu behaved in a manner opposite to that of As and Ni; however, correlating positively with S. Pore water Zn correlated negatively with pH and Ca, and positively with Al. Principal component analysis confirmed the role of Eh on As, Ni and Cu release from flooded soils and the pH dependency on Zn release. Prolonged flooding released environmentally significant quantities of some PTTE from uncontaminated, agricultural soils.

Key Words: Anaerobic conditions, Calcareous soils, Flooded soils, Flood water, Pore water, Potentially toxic trace elements, Principal component analysis

INTRODUCTION

Contamination of surface and groundwater by potentially toxic trace elements (PTTE) is an environmental problem worldwide (Förstner and Wittmann 1981; Schwarzenbach et al. 2006). Accumulation of PTTE in soils poses a long-term risk to ecosystem health, since they can be transported with water in the soluble phase or associated with mobile particulates, contaminating ground water and surface water bodies. Various biogeochemical factors and processes influence the retention and release of these elements in soils, which, in turn, influences their availability and mobility (Carrillo-González et al. 2006; Balint et al. 2014; Frohne et al., 2014). Total element concentration in soils, presence of clay minerals, organic matter and oxide surfaces, sulfur (S) chemistry, pH and redox (Eh) processes largely influences the mobility of PTTS in soils (Frohne et al., 2014).

Prolonged flooding has been shown to profoundly influence biogeochemical cycles of PTTE in soils from contaminated sites, wetlands and rice fields (Balint et al. 2014; Shaheen et al. 2014a, 2014b) resulting in greater concentrations of PTTE released to floodwater. A considerable body of information has now been documented on the various factors influencing the behavior of PTTE under flooded conditions. Release of PTTE had been associated with soil redox potential (Eh) and pH changes, increased dissolved organic carbon, and reductive dissolution of Fe and Mn oxide minerals releasing sorbed metals (Shaheen et al. 2014b, 2014c; Nakamaru and Altansuvd 2014; Williams et al. 2014). However, reaction of metals with sulfide (produced through microbial reduction of sulfate at low Eh) can suppress the solubility and mobility of some metals under severely anaerobic conditions (Gambrell 1994; Du Laing et al. 2009a, 2009b).

In recent years, weather-related hazards such as flooding have become more frequent and acute as a result of global climate change. In the northern great plains of North America, snowmelt flooding and flash flooding for varying periods of times is a common occurrence in agricultural soils because of the relatively flat landscape and poorly permeable soils (Bedard-Haughn 2009). Even though agricultural soils usually contain relatively low PTTE concentrations, they may still release environmentally significant quantities of PTTE under prolonged flooded conditions, when changes in soil hydrologic regime makes the surface soil layer anaerobic with a sharp decrease in Eh.

Previous research investigating PTTE release from soils under flooded, anaerobic conditions were often limited to contaminated floodplain soils (Frohne et al. 2014; Balint et al. 2014; Shaheen et al. 2014 a), wetlands (Gambrell 1994, Nakamaru and Altansuvd 2014) and rice paddy soils (Williams et al. 2014; Rinklebe et al., 2016; Martin and Jalali 2017). Less information is available on uncontaminated agricultural soils of temperate regions, that are prone to spring snowmelt flooding and summer flooding and has the potential to release environmentally significant quantities of PTTE to floodwater. Research focusing on phosphorus (P) release from calcareous, uncontaminated agricultural soils documented significant and large increases in pore water and floodwater Fe and Mn concentrations in some of the studied soils (Amarawansa et al. 2015; Jayarathne et al. 2016), the magnitude of increase varying depending on soil properties.

We hypothesized that the development of anaerobic conditions under prolonged flooding of soils changes soil Eh and pH, altering the chemistry of redox-sensitive elements such as Fe, Mn, and S, which in turn, affect the release dynamics of other metal pollutants. Our focus was mainly on uncontaminated, calcareous, agricultural soils typical of the northern great plains of

North America, where bioavailable PTTE concentrations are relatively low. This hypothesis was tested with two objectives: (1) to assess the release dynamics and mobilization of a few PTTE from 12 uncontaminated, agricultural soils with varying properties under flooded, anaerobic conditions and (2) to assess the impact of the main controlling factors such as Eh, pH, Fe, Mn and S on the release of PTTE from these soils to pore water and floodwater.

MATERIALS AND METHODS

Incubation Experiment with Simulated Flooding

An incubation experiment with simulated flooding was conducted using 12 uncontaminated, agricultural soils collected from different locations in Manitoba. Composite soil samples collected from surface depth (0-15 cm) were analyzed for soil particle size, pH (1:2 soil: water ratio), cation exchange capacity (CEC), and soil organic matter (loss-on-ignition). Detailed information on soil collection and analysis are described in Jayarathna et al. (2016). In addition to the above properties, Mehlich-3 extractable calcium (Ca), magnesium (Mg), Fe, Mn, aluminum (Al), cadmium (Cd), lead (Pb), arsenic (As), nickel (Ni), copper (Cu), zinc (Zn) and selenium (Se) were determined by shaking 2.5 g soil with 25 mL of Mehlich-3 extracting reagent (Mehlich 1984) for 5 min, filtering the extract through Whatman No. 42 filter paper and analyzing for Ca, Mg, Fe, Mn, Al, Cd, Pb, As, Ni, Cu, Zn and Se concentrations using inductively coupled plasma atomic emission spectroscopy (ICPAES; Thermo iCAP 6500 Duo, Cambridge, UK).

The laboratory incubation study was conducted in triplicate using a randomized complete block design. Field moist soil samples were packed into incubation vessels, installing a redox potential probe with a platinum (Pt) sensor (Paleo Terra ®, Amsterdam, The Netherlands) and a Rhizon-flex pore water sampler (Rhizosphere Research Products, Wageningen, The Netherlands)

at a depth of 5 cm. Soils were flooded using reverse osmosis water and incubated for a period of 8 weeks at room temperature ($20 \pm 5^\circ \text{C}$). On the day of the flooding and thereafter every week for 8 weeks, pore water and floodwater samples were taken. The redox potential of flooded soils was measured using permanently installed Pt electrodes coupled with a temporally installed reference electrode. More detailed information on the incubation treatment and setup, and extraction of pore water and floodwater samples are described elsewhere (Jayarathna et al. 2016).

Pore water samples were immediately analyzed for pH using a Fisher Accumet AB15 pH meter. Floodwater samples were filtered through $0.45 \mu\text{m}$ membrane filters prior to analysis. Samples of floodwater and pore water were analyzed for total As, Ni, Cu, Zn, Pb, Cd, Se, S, Fe and Mn concentrations using ICP-AES within 48 h. Spikes, blanks and duplicates were analyzed with each analytical batch for quality control purposes.

Statistical Data Analysis

PROC MIXED procedure of SAS version 9.2 (SAS institute 2008) was used for analysis of variance (ANOVA) of soil Eh, pore water pH and metal concentrations of pore water and floodwater. When metal concentrations were below detection limits, a value corresponding to half of the detection limit of the element was assigned (Wong et al. 2002). Residuals of pore water and floodwater metal concentrations and soil Eh did not follow a normal distribution according to the Shapiro-Wilks test from Proc UNIVARIATE ($W < 0.9$) procedure. Therefore to meet the assumption of normality of residuals, raw data of these variables were natural log-transformed prior to analysis and back-transformed. The two-way ANOVA was performed keeping soils as fixed effect and time (days after flooding) as the repeated measure factor with mean comparison using the Tukey-Kramer test. Pearson product moment correlation coefficient was calculated to investigate correlations between As, Ni, Cu, Zn, Pb, Cd, and Se concentrations

with Eh, pH, and concentrations of Fe, Mn, and S. Principal Component Analysis (PCA) was carried out using statistical package IBM ® SPSS ® 19.0 (Chicago, Illinois, USA, 2010) to reduce the original set of raw data into a number of principal components to identify possible clusters between variables and factors influencing the release of PTTE to pore water and floodwater. All data were natural-log transformed (except for pH and Eh) before correlation analysis and PCA were carried out. We applied Varimax normalized rotation which minimizes the number of variables with a high loading on each component and facilitate the interpretation of results (Micó et al. 2006). The Kaiser criterion was used to determine the number of retained principal components (PCs). For all statistical analyses, significance was determined at $P < 0.05$.

RESULTS AND DISCUSSION

Initial Soil Properties

The surface soils used in the study varied in texture (clay % from 11 to 74), OM (3.3 to 17%) and CEC (15.2 to 50.9 cmol_c kg⁻¹). Soil pH was in the alkaline range for all except Osborne soil (Table 1). More information on initial soil characteristics are provided elsewhere (Jayarathne et al. 2016). Based on the bioavailable metal concentrations in soils extracted by Mehlich 3 extractant (Table 1), all soils are uncontaminated with As, Ni, Cu, Zn, Pb and Cd (Caridad-Cancela et al. 2005; Fayiga and Ma, 2005; Sahoo et al., 2010; Morse et al., 2016).

Change in Pore Water and Floodwater Trace Element Concentrations with Flooding Time

Pore water and floodwater concentrations, in general, were above detectable levels for total As, Ni, Cu, Zn, S, Fe, Mn, Al, Se, Mg and Ca. Both pore water and floodwater concentrations were below detection limits for Pb (<5.6 µg L⁻¹) and Cd (< 0.1 µg L⁻¹), during the entire flooding period (data not shown). Cadmium and Pb concentrations in uncontaminated soils are generally low, especially in alkaline soils (Chaney 2010; Hough 2010). Pore water Se

concentrations, which were below detection limit ($5.8 \mu\text{g L}^{-1}$) during the early stages of flooding increased to above detection limit at 56 days of flooding in most soils (data not shown).

The initial As concentrations ranged from <3.0 (detection limit) to $6.9 \mu\text{g L}^{-1}$, and the concentrations increased with flooding time, reaching maximum concentrations ranging from 5.0 to $64.4 \mu\text{g L}^{-1}$ (Fig. 1a). The pore water total As concentrations observed in this study were often within ranges reported previously for paddy soils (Williams et al. 2011; Roberts et al. 2011). Floodwater total As concentrations were two- to three- fold less than pore water As concentration (Fig. 2a, Supplemental Table S1) and the response to flooding was less pronounced, and not statistically significant. The concentrations of total As in both pore water and floodwater were well below the threshold concentration for irrigation water ($100 \mu\text{g L}^{-1}$) but exceeded the threshold for livestock ($25 \mu\text{g L}^{-1}$) in some soils, at the latter stages of flooding (Canadian Council of Ministers of the Environment 2007). In some soils, floodwater concentrations exceeded the maximum permissible As concentration ($10 \mu\text{g L}^{-1}$) for drinking water (World Health Organization 2011), (Fig. 2a), while the pore water As concentrations exceeded the limit in all soils except Scantebury (Fig. 1a).

Initial total Ni concentration in pore water ranged from 1.5 to $7.4 \mu\text{g L}^{-1}$ while the concentrations in floodwater were below detection limit ($1.3 \mu\text{g L}^{-1}$) in all soils (supplemental Table S2). Pore water Ni concentration increased with time of flooding in most soils (Fig. 1b) with significant main effects of soil and time, as well as interaction of soil $\times$ time. Enhanced release of Ni had been previously reported from contaminated floodplain soils (Rennert and Rinklebe 2010; Rennert et al. 2010; Antić-Mladenović et al. 2011). The floodwater Ni concentrations in most soils remained below detectable limits for almost the entire flooding period (Fig. 2b, Supplemental Table S2). In both pore water and floodwater, the total Ni

concentrations did not exceed the WHO guideline for drinking water ($70 \mu\text{g L}^{-1}$; World Health Organization 2011), or the recommended threshold for irrigation use ($200 \mu\text{g L}^{-1}$; Canadian Council of Ministers of the Environment 2007) at any time of flooding.

Copper behaved differently to As and Ni, and did not show an enhanced release with the time of flooding (Fig. 1 c). The initial pore water Cu concentrations on the day of flooding (7 to $15 \mu\text{g L}^{-1}$; Supplemental Table S3) are in the range of previously reported values for floodplain soils and intertidal sediments (Du Laing et al. 2009b). The main effects of soil and time as well as interaction effect of soil $\times$ time were significant for pore water Cu concentration (Fig. 1c) and showed a decreasing trend with time of flooding. Since sulfate gets reduced to sulfide at Eh values around -100 to -150 mV at pH 7, CuS formation would have been responsible for the significant decline in Cu concentration in soils with low Eh values (Fig 3a), as previously reported for floodplain soils (Du Laing et al. 2009a).

Concentrations of Cu in floodwater were lower than in pore water (Fig. 2c) on the day of flooding in all soils (Supplemental Table S3). In contrast to the pore water concentrations, floodwater Cu concentrations significantly increased in most soils with time of flooding. It appears that the effect of precipitation or other reactions/ processes responsible for removing Cu from pore water was less effective for floodwater, suggesting that these reactions/ processes may be redox-sensitive. Rinklebe et al. (2016) also observed higher Cu concentrations in floodwater under oxidized condition. Concentrations of Cu in both pore water and floodwater were much lower than the WHO ($2000 \mu\text{g L}^{-1}$; World Health Organization 2011) standards, and for irrigation use (200 - $1000 \mu\text{g L}^{-1}$; Canadian Council of Ministers of the Environment 2007) in all soils at all periods of flooding.

Pore water Zn concentrations ranged from 3 – 11 $\mu\text{g L}^{-1}$ on the day of flooding. The change in pore water Zn concentration with time of flooding was inconsistent. The main effect of soil was significant, with Osborne soil showing a significantly greater pore water Zn concentrations (Fig 1d, Supplemental Table S4) probably due to its low pH. Thus, flooding and the development of anaerobic conditions seem to have had no influence on Zn release to pore water (Supplemental Table S4) in these uncontaminated agricultural soils.

Floodwater Zn concentrations increased significantly by the 7th day of flooding, and then the concentration decreased with time of flooding (Fig 2d). Zinc has low toxicity to man and is not a health concern at levels found in drinking water (World Health Organization 2011). In all soils at all flooding times, pore water and floodwater Zn concentrations were much lower (≈ 100 -fold less) than the threshold concentrations for irrigation use (1000-5000 $\mu\text{g L}^{-1}$; Canadian Council of Ministers of the Environment 2007).

Pore water Se concentrations increased from below detection limit (5.8 $\mu\text{g L}^{-1}$) to above detection limit at 56 days of flooding in all soils with the exception of Osborne and Scanterbury soils (data not shown). The results suggest the release of Se with the development of anaerobic conditions. Pore water Se concentrations did not exceed the irrigation use (20 $\mu\text{g L}^{-1}$; Canadian Council of Ministers of the Environment 2007) in any soil at all times of flooding. None of the soils released detectable concentrations of Se to floodwater.

Dynamics of Eh, pH, and pore water concentrations of Fe, Mn and S with flooding

In all soils, Eh steadily decreased with time of flooding, but the magnitude of decrease varied among soils (Fig. 3a). The change in Eh with flooding in these soils had been previously described in detail (Jayarathne et al. 2016). In summary, a rapid decline in Eh was observed within the first week of flooding in all soils, and thereafter Eh values remained stable around

+200 mV with further time of flooding for varying periods (14 to 42 days), depending on the soil. Thereafter, Eh values declined with further flooding time. At 56 days of flooding most soils had negative Eh values (from -12 to -92 mV) with the exception of Osborne and Scanterbury soils, which had Eh values of +53 and +21 mV, respectively.

Soil pore water pH values of different soils on the day of flooding were in a narrow range of 7.4 to 7.8, with the exception of Osborne soil which had an acidic pH of 6.1. The effect of flooding time on pH was not significant ($P>0.05$) and inconsistent during the flooding period (Fig. 3b) as described in detail previously (Jayarathne et al. 2016). Unlike in acidic soils, where flooding tend to increase soil pH, flooding of alkaline soils tend to decrease soil pH through increasing partial pressure of CO₂ (Ponnamperuma et al. 1966; Ponnamperuma 1972), which reacts with water to form carbonic acid.

Increased concentrations of Fe and Mn in soil pore water under anoxic conditions have been documented for a wide range of soils (Du Laing et al. 2007; Amarawansha et al. 2015). In the present study, the pore water Fe and Mn concentration significantly increased with flooding in all soils with the exception of Scanterbury clay, as previously described by Jayarathne et al. (2016). It was also shown that the magnitude of increase was larger for Mn than Fe. Decrease of Eh due to flooding can lead to the reduction of insoluble Fe and Mn (hydr)oxides to soluble Mn²⁺ and Fe²⁺ and PTTE that are associated with these (hydr)oxides can be released from the solid phase (Frohne et al 2014). In par with this mechanism, the opposite, i.e., immobilization of these elements due to co-precipitation with or adsorption to Fe and Mn (hydr)oxides, is possible at high Eh.

Pore water total S concentration increased in all soils during the first two weeks of flooding and then showed a rapid decline, with lowest total S concentrations at 56 days of

flooding (Supplementary Table 5). Under severely reducing conditions, sulfate gets reduced to sulfide, which may react with metal ions (such as Fe, Mn, Ni, Cu, Zn, Cd) to form insoluble metal sulfide precipitates (Du Laing et al. 2007; Frohne et al. 2010), thus decreasing total S concentration in pore water.

Evaluating factors controlling As, Ni, Cu and Zn release from flooded soils

Correlation analysis was conducted to determine the extent of the relationships among the concentrations of four metals (As, Ni, Cu and Zn) in pore water and floodwater and some key factors controlling their release such as pH, Eh, and pore water concentrations of Ca, Mg, P, Al, Fe, Mn and S (Table 2). Pore water As concentration was negatively correlated with Eh, but positively correlated with Fe, Mn, S, Al, Ca and Mg concentrations, and was not significantly correlated with pH. Negative correlation between As and Eh indicates higher release of As in more reduced soils. Thus it is clear that with increasing severity of anaerobiosis (decreasing Eh), more As is released to the pore water from most soils, increasing As concentrations with time of flooding. Greater soluble As under reduced conditions than under oxidized conditions had been previously observed for rice soils and contaminated floodplain soils (Shaheen et al. 2014a, b; Williams et al. 2014; Rouwane et al. 2015). The dominant forms of arsenic in soils are arsenate (+5) and arsenite (+3). In drained and air-dried soils more than 90% of total As was present as arsenate (Matera et al. 2003), which has a greater affinity for sorption by soil minerals than arsenite (Zhu et al. 2013), thus, less mobile in soils. In flooded paddy soils however, arsenite was found to be the predominant species (Williams et al. 2011; Roberts et al. 2011) because of the reducing conditions. The increase in As concentration with time of flooding in the present study could be mainly attributed to the transformation of arsenate to arsenite under reducing

conditions, which has a lower affinity for sorption by soil minerals and thus more inclined to partition into solution (Yamaguchi et al. 2011).

Pore water Ni concentration showed highly significant negative correlation with Eh and positive correlations with Fe, Mn, P and Al, similar to As. Significant negative correlation with Eh indicates that reduced conditions increased Ni concentration in pore water. Nickel exists in soil pore water as free ionic form (Ni^{2+}) and as complexed forms with organic and inorganic ligands. Negative correlations between Eh and soluble Ni concentrations have been previously reported (Antić-Mladenović et al. 2011; Shaheen et al. 2014c) consistent with the findings of this study. They attributed the increase in Ni concentration with soil reduction mainly to reductive dissolution of Fe/Mn oxyhydroxides, and displacement of Ni^{2+} by Fe^{2+} and Mn^{2+} from exchange sites. In contrast to As, Ni showed a significant negative correlation with pH and Ca, but not with S and Mg (Table 2). Significant negative correlations with pH and Ca imply that higher pH and greater Ca concentrations result in lower Ni concentrations in pore water.

Pore water Cu concentrations, which generally decreased with flooding were positively correlated with Eh and S, and negatively correlated with Fe, Mn and P (Table 2). Thus flooding and development of reducing conditions decreased pore water Cu concentration unlike most other PTTE, as previously reported with flooded acidic soils (Balint et al. 2014).. It is documented that reduced forms of Cu may form insoluble Cu^+ -humic acid complexes or Cu_2O (Biasioli, et al. 2010; Fulda et al. 2013). Shaheen et al (2014c) observed a significant positive correlation between Cu and SO_4^{2-} in short term flooded soils and concluded that pore water Cu concentrations were controlled by the chemistry of SO_4^{2-} . Since our soils were mostly alkaline, the reduction of Cu^{2+} with subsequent complexation / precipitation may have played a major role in reducing pore water Cu concentration with flooding, particularly through CuS precipitation.

Pore water Zn correlated negatively with pH and Ca, and positively with Al, and did not show significant correlations with Eh or other elements (Fe, Mn, S, P) that showed enhanced concentrations with flooding. In contrast to As and Cu that did not correlate with pore water pH (Table 2), both Ni and Zn showed significant negative correlations with pore water pH.

Unlike pore water, floodwater is exposed to the atmosphere and therefore soil Eh does not directly influence floodwater element concentrations; rather, the effect of Eh is indirect through its impact on pore water metals which diffuses to floodwater. Floodwater As, Ni, and Cu concentrations showed significant positive correlations with pH and floodwater concentrations of S, P, Ca and Mg, while Zn behaved differently showing significant negative correlation with these parameters. Correlations between floodwater As, Ni, Cu and Zn with Fe, Mn and Al were inconsistent. It should be however noted that in comparison to pore water, floodwater PTTE concentrations were very low; thus, drawing conclusions based on floodwater data should be done with caution.

Behavioral similarities and differences among As, Ni, Cu and Zn dynamics

Varimax-rotated principal component analysis reveals possible association between pore water PTTE concentrations (Table 3) and their controlling factors. Results showed that three principal components had statistically significant Eigen values (>1). These three principal components (PC) accounted for 66.9% of the total variance of metal release to pore water from these soils. The PC1 accounting for 35.4% of the total variance, revealed that pore water Fe, Mn, Cu, P, As, Ni, Al, and Se, are associated with Eh, displaying high loadings to PC1 (0.894, 0.864, -0.686, 0.677, 0.606, 0.604, 0.592, 0.569 and -0.881, respectively), thus confirming Eh dependent release of those elements from flooded soils to pore water. While pore water As and

Ni concentrations increased under anaerobic (low Eh) conditions along with Fe, Mn, P, Al and Se supporting our earlier explanations, Cu concentrations decreased with low Eh.

Concurrent release of As and Ni with mobilization of Fe/Mn in flooded soil had been previously observed in contaminated soils and paddy soils (Masscheleyn et al. 1991; Yamaguchi et al. 2011; Antić-Mladenović et al. 2011). Under reducing conditions, the reductive dissolution of $\text{Fe}^{3+}/\text{Mn}^{4+}$ oxyhydroxides can rapidly release the elements that are associated with them to the soil solution, thus simultaneously increasing the pore water concentrations of Fe/Mn and other metals (Carbonell-Barrachin et al. 2000; Antić-Mladenović et al. 2011). The increased concentrations of Fe^{2+} and Mn^{2+} in soil solution may displace cationic elements such as Ni from exchangeable sites (Antić-Mladenović et al. 2011), further increasing their concentration in pore water. The decrease in pore water Cu concentrations with flooding and decreasing Eh can be best explained by significant positive correlations between pore water Cu and S concentration (Table 2), suggesting CuS precipitation, as previously observed in floodplain soils (Frohne et al. 2010). Preferential precipitation of sulfides with metals has been reported (Du Laing et al. 2007) where formation of metal sulfides with lower solubility (such as CuS) is preferred to those with higher solubility (such as NiS).

The second component (PC2), accounting for 18.8% of the variance, was correlated with S, Mg and Ca (0.812, 0.806 and 0.742, respectively), while the third component (PC3), accounting for 12.7% of the variance, was correlated with Zn and pH (0.804 and -0.669, respectively), confirming the strong pH dependence on pore water Zn concentration.

Conclusions

Pore water and floodwater concentrations of As and Ni increased with increasing severity of anaerobic conditions, at times exceeding the maximum permissible limit for drinking and for

irrigation use. Concurrent release of Fe, Mn, S and P through reductive dissolution also played a role in increasing pore water As and Ni concentrations with flooding time. Pore water Cu concentrations decreased with flooding, suggesting sulfate reduction to sulfide and possible precipitation of CuS. Changes in Zn concentrations in both pore water and floodwater with flooding time did not show a consistent trend, but correlated negatively with pH. Principal component analysis confirmed the role of Eh on As, Ni and Cu release from flooded soils and the pH dependency on Zn release. Anaerobic conditions with flooding promotes dissolution of Fe, Mn, P, As, Ni, Al and Se, while oxidizing conditions promotes Cu release into the pore water. Our results demonstrate that even uncontaminated, calcareous, upland (non-paddy) agricultural soils may release potentially toxic trace elements in environmentally significant quantities when subjected to prolonged flooding.

ACKNOWLEDGEMENTS

The authors acknowledge the funding provided by Environment Canada through Lake Winnipeg Basin Stewardship Fund. We also thank our farm co-operators and our colleagues in Manitoba Agriculture, Food and Rural Development and Agriculture and Agri-Food Canada for their assistance in providing the soils for this study, and Kumudu Jayarathne for technical help.

REFERENCES

- Antić-Mladenović, S., Rinklebe, J., Frohne, T., Stärk, H.-J., Wennrich, R., Tomić, Z., and Ličina, V. 2011. Impact of controlled redox conditions on nickel in a serpentine soil. *J. Soils Sediment.* **11**: 406-415.
- Amarawansa, E.A.G.S., Kumaragamage, D., Flaten, D., Zvomuya, F., and Tenuta, M. 2015. Phosphorus mobilization from manure-amended and unamended alkaline soils to overlying water during simulated flooding. *J. Environ. Qual.* **44**: 1252–1262.

- Balint, R., Nechifor, G., and Ajmone-Marsan, F. 2014. Leaching potential of metallic elements from contaminated soils under anoxia. *Environ. Sci. Process. Impacts*. **16**: 211-219.
- Bedard-Haughn, A., 2009. Managing excess water in Canadian prairie soils: A review. *Can. J. Soil Sci.* **89**:157-168.
- Biasioli, M., Kirby, J.K., Hettiarachchi, G.M., Ajmone-Marsan, F., and McLaughlin, M.J. 2010. Copper lability in soils subjected to intermittent submergence. *J. Environ. Qual.* **39**: 2047–2053.
- Carbonell-Barrachina, A.A., Jugsujinda, A., Burlo, F., De Laune, R.D., and Patrick, W.H. 2000. Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH. *Water Res.* **34**: 216-224.
- Caridad-Cancela, R., Paz-González, A., and de Abreu, C.A., 2005. Total and extractable nickel and cadmium contents in natural soils. *Communications in soil science and plant analysis*. **36**:241-252.
- Carrillo-González, R., Šimůnek, J., Sauvé, S., and Adriano, D. 2006. Mechanisms and pathways of trace element mobility in soils. *Adv. Agron.* **91**: 111-178.
- Canadian Council of Ministers of the Environment. 2007. Canadian water quality guidelines for the protection of aquatic life: Summary table. Updated December, 2007. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- Chaney, R.L. 2010. Characteristics and behavior of Cadmium and zinc. pp 409-440, In *Trace Elements in soils* (Ed. P.S. Hooda), Blackwell Publishing Ltd, West Sussex, United Kingdom

- Du Laing, G., Rinklebe J., Vandecasteele B., Meers E., and Tack F.M.G. 2009a. Trace metal behavior in estuarine and riverine floodplain soils and sediments: Review. *Sci. Total Environ.* **407**: 3972-3985
- Du Laing G., Meers, E., Dewispelaere, M., Vandecasteele, B., Rinklebe, J., Tack, F.M.G., and Verloo, M.G. 2009.b Heavy metal mobility in intertidal sediments of the Scheldt estuary: field monitoring. *Sci. Total Environ.* **407**: 2919–2930
- Du Laing, G., Vanthuyne, D.R.J., Vandecasteele, B., Tack, F.M.G., and Verloo, M.G. 2007. Influence of hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil. *Environ. Pollut.* **147**: 615-625.
- Fayiga, A.O., and Ma, L.Q., 2005. Arsenic uptake by two hyperaccumulator ferns from four arsenic contaminated soils. *Water, Air, & Soil Pollution.* **168**:71-89.
- Förstner, U., and Wittmann, G.T.W. 1981. *Metal Pollution in the Aquatic Environment.* Springer-Verlag. Berlin.
- Frohne, T., Rinklebe, J., and Diaz-Bone, R.A., 2014. Contamination of floodplain soils along the Wupper River, Germany, with As, Co, Cu, Ni, Sb, and Zn and the impact of pre-definite redox variations on the mobility of these elements. *Soil Sediment Contam. Int. J.* **23**:779–799.
- Frohne T, Rinklebe J, Diaz-Bone, R.A., and Du Laing, G. 2010. Controlled variation of redox conditions in a floodplain soil: impact on metal mobilization and biomethylation of arsenic and antimony. *Geoderma.* **160**: 414-424.
- Fulda, B., Voegelin, A., Maurer, F., Christl, I., and Kretzschmar, R. 2013. Copper redox transformation and complexation by reduced and oxidized soil humic acid. 1. X-ray absorption spectroscopy study. *Environ. Sci. Technol.* **47**: 10903-10911.

- Gambrell, R.P. 1994. Trace and toxic metals in wetlands: a review. *J. Environ. Qual.* **23**: 883-891.
- Hough, R. L. 2010. Characteristics and behavior of copper and lead. pp. 441-460. In *Trace Elements in soils* (Ed. P.S. Hooda), Blackwell Publishing Ltd, West Sussex, United Kingdom.
- Jayarathne, P.D.K.D., Kumaragamage, D., Indraratne, S., Flaten, D., and Goltz, D. 2016. Phosphorus release to floodwater from calcareous surface soils and their corresponding subsurface soils under anaerobic conditions. *J. Environ. Qual.* **45**: 1375–1384.
- Martin, N.H., and Jalali, M. 2017. The effect of waterlogging on electrochemical properties and soluble nutrients in paddy soils. *Paddy Water Environ* **15**: 443-455.
- Masscheleyn, P. H., Delaune, R.D., and Patrick, W.H. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* **25**: 1414–1419.
- Matera, V., Le Hecho, I., Laboudigue, A., Tellier, S., and Astruc, M. 2003. A methodological approach for the identification of arsenic bearing phases in polluted soils. *Environ. Pollut.* **126**: 51-64.
- Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* **15**: 1409 – 1416.
- Micó, C., Recatalá, L., Peris, M., and Sánchez, J. 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere.* **65**: 863–872.
- Morse, N., Walter, M.T., Osmond, D. and Hunt, W., 2016. Roadside soils show low plant available zinc and copper concentrations. *Environmental Pollution.* **209**:30-37.

- Nakamaru, Y.M., and Altansuvd, J. 2014. Speciation and bioavailability of selenium and antimony in non-flooded and wetland soils: A review. *Chemosphere*. **111**: 366-371.
- Ponnamperuma, F.N., Martinez, E., and Loy, T. 1966. Influence of redox potential and partial pressure of carbon dioxide on pH values and the suspension effects of flooded soils. *Soil Sci.* **101**:421–431.
- Ponnamperuma F.N. 1972. The chemistry of submerged soils. *Adv. Agron.* **24** :29-96.
- Rennert T., and Rinklebe, J. 2010. Release of Ni and Zn from contaminated floodplain soils under saturated flow conditions. *Water Air Soil Pollut.* **205**: 93-105.
- Rennert T., Meißner, S., Rinklebe, J., and Totsche, K.U. 2010. Dissolved inorganic contaminants in a floodplain soil: comparison of in situ soil solutions and laboratory methods. *Water Air Soil Pollut.* **209**: 489-500.
- Rinklebe, J., Shaheen, S.M. and Yu, K. 2016. Release of As, Ba, Cd, Cu Pb and Sr under pre-definite redox conditions in different rice paddy soils originating from the USA and Asia. *Geoderma*. <http://dx.doi.org/10.1016/j.geoderma.2015.10.011>
- Roberts, L. C., Hug, S.J., Voegelin, A., Dittmar, J., Kretzschmar, R., Wehrli, B., Saha, D.C., Badruzzaman, A.B.M., and Ali, M.A. 2011. Arsenic dynamics in porewater of an ntermittently irrigated paddy field in Bangladesh. *Environ. Sci. Technol.* **45**: 971–976.
- Rouwane, A., Rabiet, M., Grybos, M., Bernard, G., and Guibaud, G. 2015. Effects of NO_3^- and PO_4^{3-} on the release of geogenic arsenic and antimony in agricultural wetland soil: a field and laboratory approach. *Env. Sci. Poll. Res.* **23**: 4714-4728.
- Sahoo, P.K., Bhattacharyya, P., Tripathy, S., Equeenuddin, S.M. and Panigrahi, M.K., 2010. Influence of different forms of acidities on soil microbiological properties and enzyme

- activities at an acid mine drainage contaminated site. *J. hazardous materials*. **179**:966-975.
- Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., Gunten, U.V., and Wehrli, B. 2006. The Challenge of Micropollutants in Aquatic Systems. *Science*. **313**: 1072-1077.
- Shaheen, S.M., Rinklebe, J., Frohne, T., White, J.R., and De Laune, R.D. 2014a. Biogeochemical Factors Governing Cobalt, Nickel, Selenium, and Vanadium Dynamics in Periodically Flooded Egyptian North Nile Delta Rice Soils. *Soil Sci. Soc. Am. J.* **78**: 1065–1078.
- Shaheen, S.M., Rinklebe, J., Rupp, H., and Meissner, R. 2014b. Lysimeter trials to assess the impact of different flood–dry-cycles on the dynamics of pore water concentrations of As, Cr, Mo and V in a Contaminated floodplain soil. *Geoderma* **228-229**: 5-13.
- Shaheen, S.M., Rinklebe, J., Rupp, H., and Meissner, R. 2014c. Temporal dynamics of pore water concentrations of Cd, Co, Cu, Ni, and Zn and their controlling factors in a contaminated floodplain soil assessed by undisturbed groundwater lysimeters. *Environ. Pollut.* **191**: 223-231.
- World Health Organization. 2011. Guidelines for Drinking Water Quality. 4th Edition. WHO. Geneva, Switzerland.
- Williams, P. N., Santner, J., Larsen, M., Lehto, N.J., Oburger, E., Wenzel, W., Glud, R.N., Davison, W., and Zhang, H. 2014. Localized Flux Maxima of Arsenic, Lead, and Iron around Root Apices in Flooded Lowland Rice. *Environ. Sci. Technol.* **48**: 8498-8506.
- Williams, P.N., Zhang, H., Davison, W., Meharg, A.A., Hossain, M., Norton, G.J., Brammer, H., and Islam, M.R. 2011. Organic Matter- Solid Phase Interactions Are Critical for

- Predicting Arsenic Release and Plant Uptake in Bangladesh Paddy Soils. *Environ. Sci. Technol.* **45**: 6080-6087.
- Wong, S.C., Li, X.D., Zhang, G., Qi, S.H., and Min, Y.S. 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Pollut.* **119**: 33-44.
- Yamaguchi, N., Nakamura, T., Dong, D., Takahashi, Y., Amachi, S., Makino, T. 2011. Arsenic release from flooded paddy soils is influenced by speciation, Eh, pH, and iron dissolution. *Chemosphere.* **83**: 925-932.
- Zhu, J., Pigna, M., Cozzolino, V., Caporale, A.G., and Violante, A. 2013. Higher sorption of arsenate versus arsenite on amorphous Al-oxide, effect of ligands. *Environ. Chem. Lett.* **11**: 289-294.

Table 1. Initial properties^a of 12 surface soils (arranged in the order of increasing clay content)

Soil Series	Clay %	pH	OM %	CCE	EC	CEC	Mehlich-3 extractable ion concentrations (mg kg ⁻¹)											
							Al	Ca	Mg	Fe	Mn	Cd	Pb	As	Ni	Cu	Zn	Se
Reinland	11	7.6	3.4	15	0.70	15.2	1148	3241	197	90	153	0.08	0.24	0.051	4.20	1.42	7.19	0.013
Almasippi	13	8.2	3.3	56	0.95	15.6	276	4554	497	85	82	0.06	0.18	0.073	7.14	1.53	10.81	0.021
Long Plain	13	7.7	4.0	36	1.22	20.4	257	5146	201	128	87	0.09	0.26	0.039	2.67	1.85	7.65	0.015
Sprague	16	7.7	3.8	102	1.11	16.5	636	4376	261	191	50	0.07	0.21	0.042	2.24	1.56	7.83	0.012
Newdale	27	7.6	6.0	52	0.74	18.5	1934	4794	323	97	241	0.08	0.24	0.041	5.08	1.76	9.91	0.014
Lakeland B	32	7.9	8.5	169	1.06	29.3	422	8257	656	131	82	0.12	0.36	0.078	5.79	2.24	9.46	0.021
Niverville	37	7.7	7.8	189	1.39	33.7	102	8044	609	89	116	0.08	0.24	0.161	6.20	2.23	9.44	0.014
Fyala	42	7.7	17.0	210	1.53	43.1	556	8810	715	274	34	0.16	0.48	0.178	6.24	2.87	10.67	0.016
Lakeland I	42	7.7	11.0	207	1.33	40.9	363	8462	700	86	50	0.18	0.54	0.030	4.27	1.87	9.32	0.014
Osborne	58	6.4	8.4	32	1.24	46.3	3112	5083	516	220	53	0.20	0.60	0.026	9.31	2.09	17.99	0.012
Arborg	67	7.4	6.4	60	1.82	37.6	3598	6315	647	263	49	0.22	0.66	0.107	6.94	1.89	5.60	0.015
Scanterbury	74	7.6	5.6	42	1.21	50.9	2576	8620	648	168	45	0.28	0.84	0.020	3.96	1.77	5.65	0.012

OM- Organic matter; CCE- Calcium carbonate equivalent; EC- Electrical conductivity (1:2, Soil: solution); CEC- Cation exchange capacity (cmol kg⁻¹)

^a Mean of two replicates

Table 2. Pearson's correlation coefficients for pore water and floodwater concentrations of studied elements and some selected parameters controlling their release (natural log-transformed data, except for pH and Eh).

Parameter	As	Ni	Cu	Zn
Pore water				
Eh	-0.481***	-0.482***	0.578***	-0.042
pH	0.173	-0.317**	0.049	-0.385***
Fe	0.510***	0.545***	-0.569***	0.048
Mn	0.491***	0.441***	-0.569***	0.139
S	0.357***	-0.054	0.426***	-0.026
P	0.664***	0.486***	-0.245*	0.144
Al	0.308**	0.504***	-0.141	0.309**
Ca	0.243*	-0.270***	0.060	-0.220*
Mg	0.403***	0.058	0.076	-0.104
Floodwater				
pH	0.511***	0.238*	0.362***	-0.560***
Fe	0.278***	0.092	0.129	-0.031
Mn	0.336***	0.296**	0.225*	-0.182
S	0.624***	0.565***	0.653***	-0.415***
P	0.598***	0.471***	0.509***	-0.514***
Al	-0.253**	-0.130	-0.183	0.374***
Ca	0.531***	0.427***	0.562***	-0.613***
Mg	0.616***	0.509***	0.579***	-0.615***

*, **, ***, correlation is significant at 0.05, 0.01 and 0.001, respectively

Table 3. Rotated component Matrix resulting from Varimax rotation with Kaiser Normalization for pore water metals and relevant properties. Natural log-transformed data were used, except for pH, Eh and Zn.

	PC1	PC2	PC3	Communalities
Fe	.894			.809
Eh	-.881			.785
Mn	.864	.411		.751
Cu	-.686	.354	.387	.790
P	.677	.518	.273	.658
As	.606		.118	.649
Ni	.604		.531	.647
Al	.592		.461	.567
Se	.569	.206		.374
S	-.223	.812	.115	.722
Mg	.248	.806	-.215	.758
Ca	.103	.742	-.307	.655
Zn			.804	.647
pH			-.669	.548
Initial Eigen value	4.952	2.624	1.783	
% variance	35.38	18.75	12.74	
Cumulative %	35.38	54.12	66.86	

FIGURE CAPTIONS

Fig. 1. Pore water concentrations (geometric LS means) of toxic metals in different soils with time of flooding; (a) As (b) Ni (c) Cu and (d) Zn

Fig. 2. Floodwater concentrations (geometric LS means) of toxic metals in different soils with time of flooding; (a) As (b) Ni (c) Cu and (d) Zn

Fig. 3. Changes in (a) redox potential and (b) soil pore water pH, during 56 day of flooding in different soils (arithmetic means).