Copper dynamics under alternating redox conditions is influenced by soil properties and contamination source

Ramona Balint [a,b,*], Daniel Said-Pullicino [a], Franco Ajmone-Marsan [a]

[a] Dept. of Agricultural, Forest and Food Sciences — Agricultural Chemistry and Pedology, University of Turin, Largo Paolo Braccini 2, 10095 Grugliasco, Italy
[b] Geological Institute of Romania, Str. Caransebes nr. 1, Sector 1, 012271 Bucuresti, Romania

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ABSTRACT

Understanding the effect of soil redox conditions on contaminant dynamics is of significant importance for evaluating their lability, mobility and potential transfer to other environmental compartments. Under changing redox conditions, soil properties and constituents such as Fe and Mn (hydr)oxides and organic matter (OM) may influence the behavior of associated metallic elements (MEs). In this work, the redox-driven release and redistribution of Cu between different soil pools was studied in three soils having different contamination sources. This was achieved by subjecting soil columns to a series of alternating reducing and oxidizing cycles under non-limiting C conditions, and assessing their influence on soil pore water, leachate and solid phase composition. Results showed that, in all soils, alternating redox conditions led to an increase in the distribution of Cu in the more labile fractions, consequently enhancing its susceptibility to loss. This was generally linked to the redox-driven cycling of Fe, Mn and dissolved organic matter (DOM). In fact, results suggested that the reductive dissolution of Fe and Mn (hydr)oxides and subsequent reprecipitation as poorly-ordered phases under oxic conditions contributed to the release and mobilization of Cu and/or Cu-containing organometallic complexes. However, the behavior of Cu, as well as the mechanisms controlling Cu release and loss with redox cycling, was influenced by both soil properties (e.g. pH, contents of easily reducible Fe and Mn (hydr)oxides) and source of Cu contamination.

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1. Introduction

The mechanisms governing metallic element (ME) release from soils subjected to changing water contents may be directly or indirectly related to variations in soil redox potentials. The release of MEs may be linked to redox-driven processes such as the reductive dissolution of Fe and Mn (hydr)oxides (Du Laing et al., 2009; Frohne et al., 2011), or to the degradation of soil organic matter (SOM) with which they are often linked (Reddy and DeLaune, 2008).

Among the divalent transition metals, Cu is considered to be the one most tightly bound to organic matter (OM) and strongly associated with Fe and Mn (hydr)oxides and clay minerals (Phillips, 1999; Zhao et al., 2007). Apart from intrinsic soil and ME properties, the release of Cu from soils may depend on the mechanisms involved in the retention of Cu on soil constituents, and consequently on the source of Cu.

Copper is a contaminant diffused in the soil–water system by a range of anthropic activities and its release may pose a significant threat to environmental and human health. The use of Cu-containing pesticides in agriculture may result in the transfer of substantial amounts of Cu to arable soils. Vineyard topography and intense rainfalls may cause pesticide losses by surface runoff and leaching, potentially resulting in surface and groundwater contamination (Barrett and McBride, 2006; Huguenot et al., 2010). In mining areas, soils may have high

* Corresponding author at: Di.S.A.F.A. — Chimica Agraria e Pedologia, University of Turin, Largo Paolo Braccini 2, 10095 Grugliasco (TO), Italy. Tel.: +39 0116708519; fax: +39 0116708692.
E-mail address: ramona.balint@unito.it (R. Balint).

concentrations of MEs either due to the mining activities, incorrect disposal of mine waste and flotation residue, or to the bedrock itself (Nimirciag, 2012). Since this mainly occurs in mountainous river valleys, the increasing possibility of flash floods may influence soil redox conditions (EEA, 2008; Popescu et al., 2013a). Urban soils may also present high contaminant concentrations, especially MEs, exceeding threshold values (Ajmone-Marsan and Biasioli, 2010; Charlesworth et al., 2011) due to anthropic activities, such as traffic, industry and waste disposal. Rapid land use changes occurring in urban areas may often lead to soil compaction and extensive sealing (Biasioli and Ajmone-Marsan, 2007; Scalenghe and Ajmone-Marsan, 2009). Consequently, urban soils may be subject to water saturation for short periods of time following intense storms, therefore leading to changes in soil redox conditions.

Most research on Cu dynamics in soils has focused on the stability, release and mobility of Cu associated with Fe and/or Mn (hydr)oxides (Davranche and Bollinger, 2000; Loomer et al., 2011; Matocha et al., 2005), or OM (Amery et al., 2008; Businelli et al., 2009; Hernandez-Soriano and Jimenez-Lopez, 2012). Only few studies assessed the interdependence between these soil constituents in the attempt to identify the key processes controlling Cu release (Grybos et al., 2007; Parat et al., 2002). Moreover, most studies have thoroughly evaluated the behavior of Cu under permanently oxic or anoxic environments, showing that Cu release may be either promoted or inhibited as a result of water saturation with respect to unsaturated conditions, as a function of soil mineral composition, quantity and quality of OM, and contamination source (Lindsay et al., 2011; Matocha et al., 2005; Wang and Staunton, 2006). However, our understanding of the effect of changing soil redox conditions on Cu behavior and its potential environmental threat is still limited. Based on these considerations, we aimed at elucidating the influence of alternating reducing and oxidizing conditions on Cu release, mobilization and redistribution in soils with different sources of Cu contamination. We also evaluated the interactions between Cu dynamics and redox-driven Fe, Mn and dissolved organic matter (DOM) cycling.

2. Materials and methods

2.1. Soil characterization

Three topsoils (0–20 cm) were sampled from areas exposed to different sources of Cu-containing contaminants: (i) a non-calcareous agricultural soil sampled from a vineyard (VIN) where Cu-containing phytochemicals, such as $CuSO_4$ in combination with glyphosate, were extensively applied for the control of mildew (Alessandria, Italy; 44.680601°N, 8.622292°E); (ii) a mine-impacted soil (MIN) located within pastures affected by Cu-containing mine tailings (Popescu et al., 2013b), and sampled in the vicinity of a flotation plant (Balan, Romania; 44.672789°N, 25.796523°E); and (iii) a compost-amended urban soil (IND) collected from an area affected by mass production automobile industry (Torino, Italy; 45.089939°N, 7.672155°E). Each soil sample was composed of a series of subsamples (~1 kg each) and adequately homogenized. These 3 soils were selected for their similar Cu contents, which would provide a better understanding of the contamination source effect on the behavior of Cu under redox conditions.

Soil physical and chemical properties were determined in duplicate using standard methods (MIPAF, 2000) and reported in Table 1. Soil samples were air-dried, gently crushed and sieved to pass through a 2 mm sieve. Soil pH was measured potentiometrically in a 1:2.5 soil:KCl (1 M) suspension. Total C and N were measured by a dry combustion method (elemental analyzer, NA2100, CE Instruments, Italy). Particle-size analysis was performed by the sieve–pipette method, using sodium hexametaphosphate as a dispersant (Gee and Bauder, 1986). Reducible and poorly crystalline Fe (hydr)oxides as well as associated Cu and Mn were extracted with dithionite–citrate–bicarbonate (DCB) and ammonium oxalate (AO), as described by Mehra and Jackson (1958) and Schwertmann and Cornell (1991), respectively. Although generally employed for Fe fractionation, DCB and AO extraction procedures could also be used to evaluate the dynamics of metals associated with Fe (hydr)oxides (Adamo et al., 2006). Metal distribution in progressively less labile metal pools was assessed in triplicate using the modified BCR sequential extraction described by Rauret et al. (2000). This procedure aims at extracting four ME fractions using: 0.11 M acetic acid (F1), 0.5 M hydroxylammonium chloride (F2), 8.8 M hydrogen peroxide and 1 M ammonium acetate at pH 2 (F3), and *aqua regia* (F4). Small aliquots of soil were further ground (<0.5 mm) to determine pseudo-total (PT) metal concentrations by microwave-assisted (Start D, MILESTONE, U.S.A.) *aqua regia* ($HCl:HNO_3$, 3:1) digestion. Total contents of Cu, Fe and Mn in all extracts were analyzed by flame atomic absorption spectrometry (FAAS, AAnalyst 400, Perkin Elmer, U.S.A.). Recoveries of the BCR procedure were calculated as the sum of metal concentrations extracted in each step normalized to the results of the PT metal digestion. In all soils, the BCR extraction yielded Fe, Mn and Cu recoveries ranging between 91 and 106, 96 and 116, and 88 and 108%, respectively.

2.2. Column mesocosm experiment

Soil columns (70 cm in height and 7 cm in diameter) were setup and subjected to alternating reducing and oxidizing conditions as previously described in Balint et al. (2013). Briefly,

Table 1
Main physico-chemical properties of the studied soils.

	VIN	MIN	IND
pH_{KCl}	6.7	5.1	8.5
C_{tot} (g kg^{-1})	26.3	38.4	34.1
C_{org} (g kg^{-1})	26.3	38.4	16.8
N_{tot} (g kg^{-1})	2.2	3.7	0.6
Fe_{PT} (g kg^{-1})[a]	39.8	38.2	37.8
Fe_{DCB} (g kg^{-1})[b]	12.8	12.8	11.6
Fe_{AO} (g kg^{-1})[c]	1.1	5.2	2.2
Mn_{PT} (mg kg^{-1})	963	1140	1029
Mn_{DCB} (mg kg^{-1})	685	623	657
Mn_{AO} (mg kg^{-1})	578	517	446
Cu_{PT} (mg kg^{-1})	90	101	100
Cu_{DCB} (mg kg^{-1})	14	16	1
Cu_{AO} (mg kg^{-1})	45	56	34
Clay (g kg^{-1})	298	40	70
Silt (g kg^{-1})	381	320	280
Texture (ISSS)	Light clay	Loam	Sandy loam/loam

[a] Pseudo-total.
[b] Dithionite–citrate–bicarbonate.
[c] Ammonium oxalate.