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Assessment of soil metal distribution and environmental impact of mining in Katanga (Democratic Republic of Congo)

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Abstract

Metal and metalloid (As, Cd, Co, Cu, Pb and Zn) distribution in soils from the Katanga Copperbelt (Democratic Republic of Congo) is investigated in order to characterize the environmental impacts of mining and smelting activities in that area. The concentrations of Cu, Co, As, Zn, Pb and Cd in soils from mining sites are higher than in non metalliferous sites and above permissible metal and metalloid concentrations in soils. Moreover, the fractionation and mobility of Co, and Cu in such environment is assessed using the application of both ammonium acetate-EDTA extraction and speciation modeling (WHAM 6). The resulting data set covers wide range of environmental conditions (pH, trace metals concentration, natural soils and soils affected by mining and ore processing). These extractions show that only a small fraction of Cu and Co is mobile, with variation depending on sites: mobility is higher in soils affected by mining and ore processing. The strong affinity of Mn-oxides for Co may explain lower Co mobility in Mn-rich soils. The high Mn and Fe contents of Cu-Co soils from Katanga may actually exert a protective effect against the toxic effects of Co. Finally, Cu-Co speciation modeling of contaminated sites emphasizes that organic matter strongly sorb Cu whereas Co speciation is mostly by Mn content. This type of study leads to a better understanding of metal fractionation and can guide to define different practices of phytoremediation.

Keywords: metals, Co, Cu, soils, rhizosphere, statistics, Katanga, guide reference

1. Introduction

Mining and smelting operations are coincident with the most important local sources of environmental pollution by metals and metalloids (e.g., Ettler et al., 2014). In particular, soil systems can be affected by mining- or smelting-related dust particles containing metallic contaminants (Candeias et al., 2014; Castillo et al., 2013; Ettler et al., 2014; Jung, 2001; Khalil et al., 2013; Křibek et al., 2010; Lee et al. 2001). In order to study such effects, metals and metalloids have often been studied around mines and smelters (Ettler et al., 2005; Khalil et al., 2013; Křibek et al., 2010; Tembo et al., 2006). A special attention has been paid to the the potential uptake of these elements by plants (Faucon et al., 2009; Lange et al., 2014) and on their bioaccessibility for humans (Banza et al., 2009; Cheyns et al. 2014).

The Katanga Copperbelt (Democratic Republic of Congo) acts as a major producer of copper and cobalt accounting 5% and 47.5% of the world production in 2013, respectively (USGS, 2014). The Katanga is known for copper and cobalt ore deposits, which show enrichment in Cu, Co and other important metals and metalloid such as As, Zn, Pb, U and Cd. Several (world-class) deposits –exploited for these elements are also present in the Katanga Copperbelt, as the Kipushi and the Shinkolobwe deposits (Decrée et al., 2011; Heilen et al., 2008, Kampunzu et al., 2009; Van Wilderode et al., 2013). Over a century, mining has disseminated large quantities of waste in the environment. As a consequence, these activities have created secondary metalliferous substrates with elevated concentrations of metals (Faucon et al., 2011; 2012b). For example, the open pits and underground mines have generated large mine tailings. Copper and Co have been refined in several hydrometallurgical plants and smelters, which also produced As, Zn, Pb and Cd as by-products (Prasad, 1989). In addition, emissions of SO₂ (which causes acid deposition) and metalliferous particles produced by the Cu-smelting industry for over 80 years in the vicinity of the city of

Lubumbashi have degraded woodland and caused its replacement by open grassland and bare soil in the area situated downwind of the copper smelter. Metals are then accumulated mainly in the surface horizons of soils in the surrounding area (Narendrula et al., 2012). These soils have accumulated trace metals due to a single or combined effect(s) of (i) the deposition of atmospheric fall-out from ore-smelter, (ii) the weathering of soil metal-bearing mineral or (iii) the presence of mine deposits. In addition salt efflorescences including various toxic metals can formed and are locally identified as important vectors for the dispersion of metals, as demonstrated in the Likasi area (Mees et al., 2013).

Earlier studies showed that metalliferous soils from the study area have higher total concentrations of Cu, and Co compared to non-metalliferous soils (i.e., Cu and Co concentrations up to 10 to 100 times higher than in non metalliferous soils; Faucon et al., 2009; Narendrula et al., 2012). However, Cu and Co concentrations in soils are very variable from one site to the other. Environmental monitoring and land reclamation initiatives are lacking and only a few studies have already been performed within the mining districts of the Katanga Copperbelt (e.g. Narendrula et al., 2012; 2013; Pourret et al., 2015). These studies primarily focused on the most polluted sites in this area (e.g., Narendrula et al., 2012; 2013). However studies dedicated to metal mobility within individual environmental compartments (soils, mine tailings, smelting waste disposals) and describing the related environmental risks, are still relatively rare (Banza et al., 2009; Cheyns et al., 2014; Pourret et al., 2015). To assess human exposure to pollution in Katanga, which is a real public health concern due to the high population density in the contaminated area, Banza et al. (2009) measured metal concentrations in urine of people living close to mines or smelting plants. Concentrations of Co and other metals were higher in the urine of people living close to mines or smelting plants (including the site contaminated by the Cu-smelter industry of Lubumbashi), exceeding the baseline value of the Centers for Disease Control and Prevention (Shutchka et al., 2010).

Similarly, Elenge et al. (2011), who have investigated metal content in the hair of copper miners in the Katanga, prove the large extent of exposure of artisanal miners in the Katanga Province to chemical components in the exploited ore.

In the present study, metal distribution and Co and Cu chemical fractionation in contrasting soils originating from individual environmental compartments (soils, mine tailings, smelting waste disposals) from the Katanga Copperbelt were investigated. Copper and Co speciation in soil is characterized by modeling to highlight Cu/Co mobility in tropical soils. The resulting data set covers wide ranges of environmental conditions. Such a method will help to identify the factors responsible for metal partitioning, and to predict metal availability. The higher the exchangeable metal concentration is, the higher the metal mobility will be, with subsequent risk of transfer. Indeed, to assess and compare the risk of transfer of metals of different types of habitats and metalliferous soils, fractionation and speciation of Cu and Co in soils have been examined on these types of sites, which have not been clearly incorporated into previous environmental studies.

2. Material and methods

2.1. Study sites

The Katanga Province is located in the South-East of the Democratic Republic of Congo. Its Southern part – the so-called Katanga Copperbelt – is constituted by a number of copper hills from Lubumbashi, in the south-east, to Kolwezi in the north-west, presenting an arc shape. It covers an area estimated at 300 km long and 50 km large (e.g., Cailteux et al., 2005). It is administratively divided in three main areas following the Gécamines subdivision: the South (Lubumbashi), Center (Likasi) and the West (Kolwezi) regions (Fig. 1).

Mineralized rocks mainly appear as rounded hills, typically a few tenths of meters above the level of the surrounding non mineralized area; these hills are relics of a gossan,

(i.e., a weathered part of the copper and cobalt ores; Decrée et al., 2010; De Putter et al., 2010). Copper and Co hills present a gradient of Cu and Co concentrations in soils (about 0.1% Cu total content at the bottom of hill and 5% at the top and about 0.05% Co total content at the bottom of hill and 1% at the top) and are mainly covered by steppic savanna which is characteristic vegetation of Katangan copper outcrops (i.e., old vegetation composed of perennial species with a highly developed underground system) (Séleck et al., 2013). The mineralization is essentially made up of a copper-cobalt ore, which occurs mainly as sulfides, oxides and carbonates. The most abundant primary sulfides are chalcopyrite (CuFeS_2), chalcocite (Cu_2S), and covellite (CuS) for Cu, and carrollite [$\text{Cu}(\text{Co},\text{Ni})_2\text{S}_4$] for Co (Cailteux et al. 2005; Dewaele et al. 2006; El Desouky et al. 2010). The supergene weathering affects significantly these deposits and their host-rocks, leading to oxidation, transport and reprecipitation (at-depth) of the leached metals. The most obvious effect of this weathering event is oxidation in the near-surface orebodies. However, the whole weathering profile varies considerably in depth from one deposit to another. As an example, the supergene weathering affects the deposits of the Tenke-Fungurume district up to 100-200 m depth (Fay and Barton, 2012). This process induced the deposition of sulfides as chalcocite and covellite (El Desouky et al. 2010) in the zone of supergene enrichment of ore deposits, together with the alteration of the sulfide minerals into oxides (cuprite, Cu_2O ; heterogenite, CoOOH ; hematite, Fe_2O_3), carbonates (malachite, $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), silicates [chrysocolla; $(\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{-O}_5(\text{OH})_4\cdot n\text{H}_2\text{O}$] and phosphates [pseudo-malachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$] in the shallower part of the weathering profile (De Putter et al. 2010; Decrée et al. 2010; Dewaele et al. 2006; El Desouky et al. 2010; Fay and Barton 2012). In such profile, Cu is thought to migrate to the water table, where owing to changing redox conditions, it is enriched as Cu sulfides [e.g., chalcopyrite to bornite (Cu_5FeS_4) or chalcocite; De Putter et al., 2010]. On the contrary, Co is quickly oxidized and mostly precipitates as heterogenite, which is often exploited as an earthy and powdery/dusty

black product (Decrée et al., 2010). The weathering process is economically significant because it strongly concentrates metals in the oxidized ore, compared to its content in the primary sulfide ore (e.g., 64% Co for heterogenite vs. 39% Co for carrollite). Economic concentrations of oxidized minerals may also be derived from low grade sulfide mineralization. Through the same processes, other metals and metalloids, such as As, Zn, Pb, U and Cd, present as trace or minor elements in the primary sulfide ore, can be strongly enriched in the oxidized ore (e.g., Decrée et al., 2014), and therefore in the overlying soils. In the present study, non-metalliferous soils, metal rich soils from natural copper hills and soils affected by mining and ore processing were considered (Fig. 2). Three types of soils affected by mining and ore processing have been identified: (i) mine deposits from quarry, (ii) bare soils contaminated by metalliferous fallout from copper smelter and (iii) tailings from hydrometallurgical process (Faucon et al., 2011; Ilunga wa Ilunga et al., 2015).

2.2. Soil sampling

Soil samples (n = 234) were collected from 10 different metalliferous and 3 non-metalliferous sites (Table 1). For each sample, a composite bulk surface soil sample (organic layer; 0-10 cm) was collected in each site by mixing three to four subsamples (100-500 g) taken according a random design (Faucon et al., 2009). The selection of sites was made to integrate samples from non-metalliferous soils (NM), from natural copper hills (i.e., undisturbed by mining activities; Pr) and from soils affected by mining and ore processing metalliferous soils (Fig. 2). Three types of soils affected by mining and ore processing have been identified: mine deposits from quarry (i.e., naturally metalliferous soils disturbed and reworked by mining activities) (S1), bare soils contaminated by metalliferous fallout from copper smelter (S2) and tailings from hydrometallurgical process (S3). Indeed, Baya, Kiswishi and Mikembo soils are miombo soils. Non-metalliferous sites correspond to forest

clearing on lateritic crusts (Duvigneaud and Denaeyer-De Smet, 1963; Faucon et al., 2011). Fungurume 5, Goma 2 and Kolwezi D are natural Cu-Co undisturbed hills from the Tenke-Fungurume region and Kolwezi region, respectively (Fay and Barton, 2012; Cox et al., 2003; Kaya Muyumba et al., 2015; Lange et al., 2014; Schuh et al., 2012). Etoile, Kalabi, Niamumenda and Ruashi are disturbed sites (Malaisse and Grégoire, 1978 ; Faucon et al., 2011 ; Lange et al., 2014, Pourret et al., 2015 ; Ilunga wa Ilunga et al., 2015). Mine de l’Etoile site corresponds to a former Cu-Co hill in the Lubumbashi region whereas Niamumenda and Kalabi sites correspond to two Cu-Co hills locally disturbed by reworked substrate (due to artisanal mining) (Faucon et al., 2012b). The Ruashi site represents mine wastes. Quartier Gécamines and Vallée Karavia sites correspond to bare soils contaminated by metalliferous fallout from the Lubumbashi copper smelter (Prasad, 1989 ; Mpundu Mubemba et al., 2014 ; Pourret et al., 2015). The Lubumbashi smelter is currently in operation. Sulfide concentrate from Kipushi and Kambove along with copper-rich concentrate from Kamoto-Dima with small quantities of dolomite concentrate mainly constitutes the feed for this smelter (Prasad, 1989). Kipushi soils correspond to tailings from hydrometallurgical process in decantation basin near the concentrator (Prasad, 1989; Mees et al., 2013). Twenty soil samples were collected by site except for Kipushi and Kolwezi D (6 and 8, respectively). These 234 soil samples correspond to 60 non-metalliferous soils, 48 undisturbed by mining activities soils, 80 naturally metalliferous soils disturbed and reworked by mining activities, 40 bare soils contaminated by metalliferous fallout from copper smelter and 6 tailings from hydrometallurgical process.

2.3. Analytical procedure

2.3.1. Bulk concentrations

Soil samples were dried at room temperature and sieved (2 mm). The pH (water) was determined on a saturated soil-water paste and Organic Matter (OM) content by loss on ignition (550°C for 12 h). Soil chemical analyses were performed by Acme Analytical Laboratories Ltd. (Vancouver Canada), accredited under ISO 9002. The considered analyzed elements were Al, As, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, U and Zn. Soil samples were digested using a strong multi-acid method that dissolves most minerals. Then, 0.25 g split was heated in HNO₃- HClO₄-HF to fuming and taken to dryness. The residue was further dissolved in HCl and solutions were analyzed using ICP-MS. The precision and accuracy of analysis for element concentrations were determined using standard material (SF-3T). Analyses agreed with values to within 5%.

2.3.2. Selective extractions

The concentrations of plant-available metals (i.e., Co and Cu) were determined using an ammonium acetate-EDTA 1 mol/L (pH 4.65) extraction with stirring for 30 min (1/10 w/v) (Faucon et al., 2011, 2009). Element concentrations were determined by flame atomic absorption spectrometer (Varian 220). All analyses were performed at the Laboratoire de Géopédologie (Université de Liège-Gembloux Agro Bio Tech, Belgium) (Faucon et al., 2011 ; 2009). The precision and accuracy of analysis for element concentrations were determined using in house standards (calibrated with BCR-100 used for plant analysis). Analyses agreed with values to within ±5%.

2.3.3. Mineralogical investigations

The heavy mineral fraction was separated from selected soil samples. The heavy mineral fraction was then washed with ethanol and analyzed by X-ray diffraction analysis

(XRD; Bruker XD8 Advance diffractometer with a monochromatic detector and CuK α radiation). Samples were scanned from 2-70°2 θ and the EVA 2, version 13 equipped with the JCPDS PDF-2 database (ICDD, 2003) was used for qualitative analysis of the powder diagrams. The mineralogical composition of samples was further determined by optical microscopy, scanning electron microscopy (SEM) and energy dispersion spectrometry (EDS). Samples were embedded in resin and prepared as polished thin sections that were examined under a Leica DRM-XP polarizing microscope in transmitted and reflected light and subsequently studied under a Hitachi S3400 SEM equipped with a ThermoNORAN NSS Ultradry EDS (accelerating voltage 10-20 kV and mineral specific beam current and counting time).

2.4. Data treatment

2.4.1. Descriptive statistics

The following statistical parameters were determined for the 13 considered elements and pH and organic matter content, and analyzed: minimum, maximum, mean and median for the central tendency measurement, standard deviation and variation coefficient for the data dispersion measurement; while the data distribution was tested for normality using Shapiro-Wilk test, kurtosis and skewness (Table 2). These parameters will be helpful to compare the datasets, and therefore to summarize the obtained data.

2.4.2. Enrichment factors

In order to select chemical elements that have been enriched in Katanga soils, the enrichment factor (EF) was calculated (Khalil et al., 2012). Based on EF, five categories were recognized: 1) $EF < 2$ states deficiency to minimal enrichment; 2) $2 \leq EF < 5$, moderate

enrichment; 3) $5 \leq EF < 20$, significant enrichment; 4) $20 \leq EF \leq 40$, very high enrichment, and; 5) $EF > 40$, extremely high enrichment. The EF was calculated for the chemical elements using the generalized equation (1):

$$EF_{El} = ([El]_{\text{sample}}/[X]_{\text{sample}}) / ([El]_{\text{crust}}/[X]_{\text{crust}}), \quad (1)$$

where El is the element under consideration, the square brackets indicate concentration (usually in mass/mass units, such as mg/kg), X is the chosen reference element (see below) and the subscripts sample or UCC indicate which medium concentration refers to. Upper Continental Crust (UCC) values were considered (McLennan, 2001). Aluminum was selected to be the reference value. Indeed, Al is the most common reference value used to calculate the EF (e.g., Bourennane et al., 2010; Liénard et al., 2014).

2.4.3. Analyse of variance

The t-test for independent data has been used to assess difference between Co and Cu fractionation. One-way analysis of variance (ANOVA) had been used to assess difference among sites for Co and Cu fractionation. Data from all 234 samples have been used for the t-test and the one-way ANOVA for each sites using XLSTAT. Post-hoc pairwise comparisons were applied after ANOVAs when there was a significant difference.

2.5. Speciation modeling

WHAM 6 (version 6.0.10; <http://www.ceh.ac.uk/services/windermere-humic-aqueous-model-wham>) was used to calculate Cu and Co speciation. Predictions for the equilibrium metal binding by environmental colloids made for the present study were done using the combined WHAM-SCAMP speciation code. WHAM-SCAMP is able to provide a full description of solid-solution speciation by incorporating two main codes: (i) the Windermere

Humic Aqueous Model (WHAM) to calculate the equilibrium solution speciation (Tipping 1994), and (ii) the Surface Chemistry Assemblage Model for Particles (SCAMP) to calculate the binding of protons and metals by natural particulate matter (Lofts and Tipping 1998). The code for the WHAM model incorporates a number of submodels: Humic Ion-Binding Model VI and a description of inorganic solution chemistry, cation exchange by clays, the precipitation of aluminium and iron oxyhydroxides, and adsorption-desorption of humic materials (HM). The SCAMP model consists of three submodels: (i) Humic Ion-Binding Model VI, (ii) a SCM describing proton and metal binding to oxides (e.g., MnOx or FeOx), and (iii) a model describing the electrostatic exchange of cations on clays. Three binding phases were examined: MnOx, FeOx, and HM. The X-Ray diffraction revealed that MnOx and FeOx are respectively pyrolusite and a mix hematite/goethite. The concentration of HM were derived from the experimental OM measurements: 50 % of the OM measured in the field samples was assumed to be HM, themselves being defined as 100 % humic acid. Saturation index and mineral precipitation were not considered; which could be a limitation of this approach (Pourret et al., 2015).

Input data for the Cu and Co speciation determination were total concentrations of Cu, Co, Mg, Ca, Mn, Fe, pH of soils and OM content. In this study, the term free was used to qualify the Cu and Co modeling output mobile fraction, considered as the ionic fraction. Sulfates and carbonates were not considered even if they act as major Cu and Co ligands (Mucchez and Corbella, 2012).

3. Results

3.1. Metal distribution in soils

The results of EF analysis show five different classes (Table 2). The first class considers the elements with minimal enrichment. It includes Ca and Ni. The second class

takes in account elements with moderate enrichment. It includes Mg, Fe, Mn and U. The third class considers elements with significant enrichment. It comprises Cd, Pb and Zn. The fourth class concerns elements with high enrichment. It includes As. Eventually, the fifth class corresponds to elements with extremely high enrichment. It includes Co and Cu. Considering this EF analysis, selected elements of interest are thus Cu, Co, As, Zn, Pb and Cd (i.e., EF ranging from 685.2 to 8.3, respectively; Table 2). These elements are directly related to mineral paragenesis and mining activities in Katanga (Banza et al., 2009; Narendrula et al., 2012; Kaya Muyumba et al., 2015). Furthermore, they are known to be toxic and hazardous at high concentrations (Banza et al., 2009; Cheyns et al., 2014).

The Cu, Co, As, Zn, Pb and Cd concentrations ranged from 11 mg/kg to 126,013 mg/kg, 2 mg/kg to 22,467 mg/kg, 5 mg/kg to 233 mg/kg, 11 mg/kg to 21,886 mg/kg, <1 mg/kg to 1666 mg/kg and <1 mg/kg to 120 mg/kg, respectively. These concentrations relate to the high metallic and metalloid content in the Katanga soils. The positive skewness feature of selected elements illustrates that the majority of samples are located in the lowest intervals of concentrations. As already illustrated in Table 2, large standard deviation, variation coefficient, skewness and kurtosis calculated for each elements imply that these elements have asymmetric distributions with a long tail to the right. This suggests the presence of high extreme values. Asymmetries are also reflected by the numerical test of normality Shapiro-Wilk that gives values of zero for all the selected elements, which indicates that the concentration values are not normally distributed. The first quartile of Cu concentration - essentially in uncontaminated surface soils - is much higher (114 mg/kg) than Cu concentration in the Upper Continental Crust (25 mg/kg; McLennan, 2001). This value can be considered as the geochemical background. Therefore, if this value is compared to guidelines adopted for Cu in Canada, which fluctuate within a wide range from 32 mg/kg to 91 mg/kg depending on the method of determination and the land use (CCME, 2007), it is evident that

the majority of soil samples collected in Katanga exceed these guidelines for Cu. The first quartile of Co concentrations (71 mg/kg) in the same samples is also much higher than concentrations in UCC (17 mg/kg; McLennan, 2001) but in the range or lower than permissible levels for Co in Canada (CCME, 2007; range from 4 mg/kg to 300 mg/kg). In the same way, first quartile of As, Cd, Pb and Zn concentrations may be considered as geochemical background (i.e., 15 mg/kg, 0.5 mg/kg, 12 mg/kg and 32 mg/kg, respectively for As, Cd, Pb and Zn). As for Cu and Co, this As value (i.e., 15 mg/kg) is much greater than UCC value (1.5 mg/kg, McLennan, 2001) and higher than permissible levels for As in Canada (i.e., 12 mg/kg; CCME, 2007). However, for Cd, Pb, and Zn, these background values are smaller than UCC values and permissible levels proposed in Canada. It must be noted that due to naturally high contents of Cu and Co in soils of the Copperbelt the use of Canadian environmental standards for soils (CCME 2007) is purely formal. Natural Cu concentrations span a large range on copper hills (total Cu from 100 mg/kg to values as high as 50,000 mg/kg; Saad et al., 2012; Séleck et al., 2013) and largely exceed those of normal soils (total Cu <100 mg/kg, Faucon et al., 2011). Cobalt concentrations may also be as high as 10,000 mg/kg.

Moreover, according to the calculated statistical parameters, the Katanga soils involve different intervals of concentrations, which are explained by the difference between sampled site types (i.e., metalliferous vs non-metalliferous, and secondary types). The soils from the Katanga Copperbelt, as from the whole Copperbelt of Central Africa, are marked by high natural background levels of metal concentrations (e.g., Key et al., 2004). Similarly, the natural patterns are modified around mining and processing centers (e.g., Mees et al., 2013). Concentrations of selected elements are presented for each site in Table 3. Indeed, concentrations of total Cu (Figure 3a) were higher in samples from naturally metalliferous soils (Kolwezi D, Goma 2 and Fungurume 5, ranging from ~18,000 mg/kg to ~34,000 mg/kg)

compared to disturbed sites (i.e., S1: Kalabi, Etoile, Niamumenda and Ruashi; ~ranging from ~3600 mg/kg to ~18,000 mg/kg), which are in turn higher than S2 (Quartier Gécamines and Vallée Karavia, between ~5000 and ~10,000 mg/kg) and S3 soil types (Kipushi, ~3000 mg/kg) and NM soil type (Baya, Kiswishi and Mikembo, in the range between 15 mg/kg and <70 mg/kg). Closed values between Pr and S1 types can be simply explained by the fact that S1 type is derived from naturally metalliferous type. High concentrations of S2 types are explained by direct pollution around the Lubumbashi smelters, which decreases with the distance (Quartier Gécamines is closer from smelter than Vallée Karavia). Large standard deviation (Figure 3) may be explained by previous studies that have already shown the existence of gradients of copper, from the mineralized rocks outcropping at the top of the hills to the foot slopes on colluviums (i.e., Fungurume hills; Seleck et al. 2013). In the same way, total Co (Figure 3b) is also present in higher concentrations in samples from naturally metalliferous soils (Kolwezi D and Fungurume 5, 6253 mg/kg and 3451 mg/kg; except Goma 2, 715 mg/kg) compared to secondary and non-metalliferous sites (from 5 mg/kg to 840 mg/kg except for Etoile sites, with 2732 mg/kg). Indeed, Etoile site is known for its high Co concentration prior exploitation (Malaisse and Grégoire, 1978; Lange et al., 2014), whereas Goma hills are less enriched in Co (Saad et al., 2012; Lange et al., 2014). Eventually, considering the evolution from naturally metalliferous sites, to S1 and S2 type sites, pH values globally decrease from higher values for Pr type sites (up to 6.6 for Fungurume 5) to intermediate values for S1 type sites (from 5.2 to 5.7, excepted the particular site of Etoile, closer from Pr type sites) and lower values for S2 type sites (from 4.9 to 5.0). S3 type site has highest pH values due to salt efflorescence whereas non-metalliferous sites have naturally acidic pH values (from 4.4 to 5.1). Total organic carbon vary in the range of 2% to 8.6% for all studied sites, except for Vallée Karavia and Ruashi sites that are organic richer (9.4% and 13%, respectively).

3.2. Chemical fractionation of metal in soils

3.2.1 Selective extraction

Faucon et al. (2009) have showed the possibility to predict Co and Cu uptake for metalliferous soils from Katanga, using AA-EDTA (pH = 4.65) extraction. Moreover, the estimation of metal availability using the AA-EDTA extraction method is known to be more suitable for high metal concentration, which is the case for Co and Cu but not for other metals and metalloids (e.g., Zn; Pourret et al., 2015). In this respect, only Cu and Co availability was further estimated using AA-EDTA extraction.

As for total metal concentrations, extractable Cu concentrations (Figure 4a; Table 3) were higher in samples from naturally metalliferous sites and secondary sites compared to S2, S3 and non-metalliferous sites. Indeed, naturally metalliferous soils (Kolwezi D, Goma 2 and Fungurume 5, 8309 mg/kg, 6880 mg/kg and 4581 mg/kg, respectively) show higher concentrations of extractable Cu compared to disturbed sites (i.e., S1: Kalabi, Niamumenda and Ruashi; 5743 mg/kg, 3029 mg/kg, and 1133 mg/kg, respectively). These are themselves higher than S2 (Quartier Gécamines and Vallée Karavia, 1082 mg/kg and 4261 mg/kg, respectively), S3 (Kipushi, 1015 mg/kg) and NM soil type (Baya, Kiswishi and Mikembo, 10 mg/kg, 10 mg/kg and 2 mg/kg). Extractable Cu concentrations for Etoile site are higher than Pr sites and other S1 sites (11,661 mg/kg), mainly because high Cu/Co concentration prior to exploitation. These extractable Cu concentrations correspond to 25% of total Cu concentrations for Pr sites, in 31-33% range for S1 types (except for Etoile 93%), 10- 82% range for S2 types (i.e., Quartier Gécamines and Vallée Karavia, respectively), 37% for S3 type and 15% for NM sites.

Extractable Co concentrations (Figure 4b) are similarly higher in samples from naturally metalliferous soils (Kolwezi D, Goma 2 and Fungurume 5, 422 mg/kg, 53 mg/kg

and 280 mg/kg, respectively) compared to disturbed sites (i.e., S1: Kalabi, Niamumenda and Ruashi; 83 mg/kg, 25 mg/kg, and 57 mg/kg, respectively). These values are themselves higher than in the S2 (Quartier Gécamines and Vallée Karavia, 7 mg/kg and 23 mg/kg, respectively), S3 (Kipushi, 41 mg/kg) and NM soil type (Baya, Kiswishi and Mikembo, 0.3 mg/kg, 6 mg/kg and 0.1 mg/kg). As for Cu, extractable Co concentrations for Etoile site are higher than Pr sites and other S1 sites (387 mg/kg) mainly because high Cu/Co concentration prior to exploitation. These extractable Co concentrations correspond to 7% to 8% of total Co concentrations for Pr sites, in the range between 8% and 20% for S1 types (except for Etoile 93%), between 3% and 27% for S2 types (i.e., Quartier Gécamines and Vallée Karavia, respectively), 23% for S3 type and from 1% to 6% for NM sites. As for total metal concentrations, extractable concentrations for most samples (except NM samples) exceed Canadian guidelines for Cu. Moreover, extractable Co concentrations in the same samples are also in the range or slightly higher than permissible levels for Co (i.e., from 4 mg/kg to 300 mg/kg).

However, the use of AA-EDTA as extractant to predict Co uptake in plants is sometimes described as questionable because of its low ability to explain variations of accumulation in certain studies (Collins and Kinsela, 2010). To address this issue, the metal speciation in soil is studied in order to provides complementary information about the metal concentration bounded to organic matter and Fe- and Mn-oxides (Pourret et al., 2015), and the proportion of free metal (i.e., phytoavailable) remaining in the soils (e.g., Lange et al., 2014).

3.2.2. Speciation modeling

Speciation calculations were performed considering Ca and Mg bind to OM. In such case, Co and Cu species are present as divalent cations or associated with Fe and Mn oxides,

and OM. Considerable variation in the predicted speciation of the metals was observed (Table 3), Co and Cu fractionation for all the 234 samples has shown different behavior between the two metals (Figure 5).

Inorganic Cu concentrations (Figure 5a; Table 3) were higher in samples from naturally metalliferous sites and secondary sites compared to S2 and S3 and non-metalliferous sites. Indeed, the concentration in inorganic Cu (Figure 5a) were higher in samples from Kolwezi D, Goma 2 and Fungurume 5 (17,994 mg/kg, 9705 mg/kg and 7803 mg/kg, respectively) compared to the values obtained for Kalabi, Etoile, Niamumenda and Ruashi (5402 mg/kg, 1755 mg/kg, 565 mg/kg and 28 mg/kg), which are in turn higher compared to Vallée Karavia (192 mg/kg) and Kipushi (2 mg/kg) sites. The inorganic Cu concentrations in Quartier Gécamines are however high (i.e., 3981 mg/kg) for a S2 site. Remaining fractions of Cu are distributed between Fe oxides and OM. Indeed, for naturally metalliferous sites, Cu occurs mostly as inorganic species (between 35% and 53%), then in association with FeOx (from 40% to 43%), and finally together with the OM (from 6% to 21%). This distribution is different for S1 type sites, where Cu mostly occurs being associated with FeOx (in the range from 45% to 91%), with OM (from 16% to 58%), and as inorganic form (from 1% to 29%). S2 type sites speciation is contrasted. Indeed, the Cu speciation in Quartier Gécamines is distributed between inorganic species, FeOx and OM (i.e., 38%, 20%, 27%, respectively), whereas in Vallée Karavia, it is mostly controlled by OM (i.e. 75%). The S3 type site speciation is mostly control by FeOx (89%). Eventually, Cu occurs sorbed to OM in samples for non-metalliferous sites (between 95% and 100%). This distribution is mostly controlled by the OM, which strongly sorb Cu (Tipping, 2002).

Inorganic Co concentrations (Figure 5b; Table 3) were also higher in samples from naturally metalliferous sites and secondary sites compared to S2 and S3 and non-metalliferous sites. Actually, inorganic Co concentrations (Figure 5b) were higher in samples from Kolwezi

D, Goma 2 and Fungurume 5 (5303 mg/kg, 490 mg/kg and 2858 mg/kg, respectively) and from Kalabi and Etoile (704 mg/kg and 1823 mg/kg) compared to Niamumenda and Ruashi (33 mg/kg and 255 mg/kg). The latter are higher than those obtained for Quartier Gécamines, Vallée Karavia and Kipushi (145 mg/kg, 42 mg/kg and 21 mg/kg, respectively). Remaining fractions of Co are distributed between Fe and Mn oxides. Indeed, for naturally metalliferous sites Co occurs mainly as inorganic species (between 69% and 85%), then in association with MnOx (from 6% to 24%). This distribution is quite the same for S1 type sites Kalabi and Etoile, while Co mostly occur associated with MnOx (76% and 34%, respectively) in the Niamumenda and Ruashi sites. For the S2 type sites, Co is fractionated between inorganic species (69% and 49%, respectively) and OM (15% and 32%, respectively). As for Cu, S3 type site speciation of Co is mostly control by FeOx (70%). Eventually, Co is mostly associated with MnOx (between 13% and 80%) in samples for non-metalliferous sites. This distribution is mostly controlled by the MnOx, which strongly sorb Co (Brown and Calas, 2012).

As already highlighted by Faucon et al. (2009) and Lange et al. (2014), Co has its strongest affinity for MnOx, whereas Cu is mostly associated with OM. As performed in Pourret et al. (2015), which consider mobile concentrations as inorganic and organic fractions, such available concentrations will exceed Cu content adopted by Canadian guidelines. In the same way, available Co concentrations are also in the range or slightly higher than permissible levels for Co. However, since the saturation index and the mineral precipitation were not considered here; it could be a limitation of this modeling approach (Pourret et al., 2015). Taking into account that sulfates and carbonates can act as major Cu and Co ligands (e.g., sulfates fo Cu; Faucon et al., 2012a), the inorganic Cu fraction should mostly occur as malachite (Muechez and Corbella, 2012).

3.3. Mineralogy of heavy fraction

X-Ray diffraction allows determining zircon ($ZrSiO_4$), rutile (TiO_2) and quartz (SiO_2) as the most abundant heavy minerals in the soils, which derived from the geological background. Iron oxide and manganese oxide were also determined and identified as a mixture of goethite/hematite and pyrolusite, respectively. The principal primary sulfides are chalcocite for Cu, and carrollite for Co. They were observed in the Kolwezi D, Goma 2, Fungurume 5 and Ruashi samples. They consist of fragments of fresh bedrock containing these primary sulfides. As evidenced by De Putter et al. (2010), Cu is oxidized and mostly present as carbonates (malachite), silicates (chrysocolla), cuprite, and phosphates (pseudo-malachite; $Cu_5(PO_4)_2(OH)_4$) in the oxidized ore. Similar oxidized mineral paragenesis has been observed in the soil samples studied here. Cuprite was furthermore observed in Kolwezi D, Kalabi, and Etoile samples. As detailed by Decrée et al. (2010), Co is also oxidized and mostly present as heterogenite, as observed in the Etoile and Ruashi samples for this study, and spherocobaltite ($CoCO_3$) in Kolwezi D, Etoile and Ruashi samples. Copper sulfates (chalcantite), sulfides (chalcocite) and metallic particles were observed in Quartier Gécamines, Vallée Karavia and Kipushi samples. Indeed, sulfides and metallic particles are probably derived from smelting activities in samples originating from the vicinity of the Lubumbashi smelter. Generally, higher amounts of these anthropogenic particles are detected in grassland areas in the vicinity of smelter (Ettler et al., 2014). Magnesium-sulfate efflorescences with high concentrations of Co were also observed in Kipushi samples, as already evidenced by Mees et al. (2013). These mostly result from a flotation treatment plant. Scanning electron microscope observations were made on these metalliferous soils. They show a very heterogeneous texture, forming aggregates of several hundred micrometers. The particles (size about 100 μm to $<1 \mu m$) of the aggregates are composed by quartz grains,

small Fe/Ti oxides possibly associated with others elements such as Al, Co, Cu, and organic matter. No evidence of argillitization was found, and most of the metals (i.e., Co and Cu) are complexed or sorbed on the aggregate's particules, as sulfides or oxides. Smelting-derived particles (i.e., rounded particles) were observed on samples from the Lubumbashi area (i.e., Vallée Karavia and Quartier Gécamines).

4. Discussion

Mining districts are characterized by soils, in which metals occur naturally at high concentrations. The latter can justify their classification as contaminated sites (Painter et al., 1994). The chemical fractionation of metals in soils also reflects the release of these elements from mining- and smelting-derived particles, and their partitioning into different soil compartments. The dissolution dynamics of metal-bearing particles deposited into soils is highly dependent on their mineralogical composition and soil pH (e.g., Ettler et al, 2014).

4.1. Special feature of natural copper and cobalt habitats

In the present study, the mineralization of naturally metalliferous sites is essentially made up of a copper-cobalt ore, which comprises mainly sulfides, oxides and carbonates (i.e., malachite and heterogenite, respectively for Cu and Co). Sulfides are formed in the more reduced (and deeper) zone of the deposits, while oxides, carbonates, silicates and phosphates mostly form in the shallower part of the weathering profile (De Putter et al., 2010; Decrée et al., 2010). The potential human impact of metal occurrences on these natural soils is rather

limited. Indeed, the distribution of such soils is restricted to largely uninhabited hills setting (e.g., Fungurume V hills; Fig. 2a). Even though gradients of copper concentrations from the mineralized rocks outcropping at the top of the hills to the foot slopes on colluviums have been described (Séleck et al., 2013), Cu and Co should be dominantly present as relatively stable compounds such as malachite and heterogenite (Decrée et al., 2010; De Putter et al., 2010). Stability field for malachite are highlighted on Eh-pH diagram for Cu (Fig. 6a). As evidenced by Garrels (1954), malachite is stable in oxidizing conditions and neutral to alkaline pH and occurs in natural hills. Mining activities will remobilize sulfide from deeper horizon (i.e., chalcocite) and decreased the pH. Around the mining facilities, where NM soils are acidic, Cu will mostly occurred as Cu^{2+} that can be sorbed on the OM. Eh-pH diagram for Co shows that stability field for heterogenite is encountered in oxidizing conditions, and neutral to alkaline fluids (Fig. 6b). Heterogenite may be destabilized in contact with fluids in equilibrium with atmospheric CO_2 (at pH~6), and the metal mobilized as aqueous Co in such way easily explains the high Co concentrations in river water (Atibu et al., 2013). As evidenced by speciation modeling (Fig. 5), total Co and Cu concentration are high in naturally metalliferous sites and even if a small fraction is mobile one may consider that these overall concentrations are still elevated. However as previously stated, since the saturation index and the mineral precipitation were not considered in the present study, mobile Cu and Co fraction should be incorporated in mineral phases (e.g., malachite) as highlighted by Muechez and Corbella (2012). Risks of transfers are thus rather limited. Moreover, in the context of this study, mining activities imply a decreasing pH. This would induce the destabilization of heterogenite, and an enhanced mobility of Co in the environment. A further relevant parameter influencing cobalt behavior is the presence of Mn and/or Mn oxides. Indeed, Co^{2+} may be sorbed onto Mn oxides or co-precipitated with these minerals (Decrée et al., 2015). Since Mn is always present in natural (Katangan) heterogenite, this process has to be taken

into consideration in the mobilization/precipitation of cobalt within the mining environment in Katanga. Apart from these thermodynamic considerations, mineralogical changes resulting from pH and Eh variations are mainly due to destabilization of naturally metalliferous sites.

Vegetation of natural Cu-Co habitats (Figure 2a) could provide ecosystem services in the protection of soil and water. The comparison of plant traits between primary and secondary habitats of different ages highlighted the specific plant traits of primary vegetation habitats (Ilunga wa Ilunga et al., 2015). Plant trait attributes characterizing primary vegetation and not recovered in secondary vegetation were related to perennial species with high lateral spreading capacity, deepest underground system (>30 cm), growth phenology at the end of dry season and xylopodia (i.e. underground tree trunks). These characteristics explain the presence of a permanent and dense vegetation cover in both seasons (dry and rainy seasons) which would induce a stability of the soil, reduction runoff, erosion and metal transfer. Steppic savannah of natural Cu/Co-rich habitat would play a crucial role in the hydrological cycle by reducing runoff and erosion contributing to the service of water supply (Egoh et al., 2011).

4.2. High environmental risks of secondary metalliferous habitats

Secondary metalliferous substrates are known to have an impact on the landscape and the environment of the region where they appear, because of the high concentration of metals and metalloids. These substrates are often covered by a short and sparse vegetation among which appear large superficies of bare soils (Kozlov and Zvereva, 2007). The same situation is reported in the Katanga (Faucon et al., 2011; Saad et al., 2012), where the tropical forest (woodland miombo) is replaced by barren soils and few patches of herbaceous vegetation around the copper-smelter (Prasad, 1989), the recovering of valleys on tailings from

hydrometallurgical plants (Mees et al., 2013) and the natural vegetation is degraded and replaced by heaps of overburden material (Figure 2). As the vegetation cover is low, secondary metalliferous substrates are exposed to wind and water erosion, disseminating metals and metalloids in the environment (Narendrula et al., 2012). It results in high human exposure to metals (especially to Co and U), as demonstrated by Banza et al. (2009) and Elenge et al. (2011). The metal exposure will certainly have short-, mid- and long-term effects on public health in the province (Cheyns et al., 2014). These effects could be worse if the basic environmental regulations are not implemented (Banza et al., 2009).

In addition to the specific geological context in the Katanga Copperbelt, which leads to the abundance of metals in the near-surface horizon and in the soils, the severe effects of the high metal load on human population in this Province also result from the combination of different parameters. Two of them are predominant:

(i) The development of small-scale and artisanal mining in this district is important and definitively constitutes a complex issue, which is driven by economic and social parameters. Actually, unemployment and subsequent poverty leave thousands of people with no other accessible work than artisanal mining. In 2010, an estimation of the total number of diggers (“creuseurs”) for the whole province was as high as 200,000 to 250,000 (Grasser, 2010). This means therefore a lot of men in direct contact with the ore, metal-bearing dust and contaminated water (Mwanamoki et al., 2014). Women and children are also involved because they lived near mine sites and thus are as well exposed to the heavy metals.

(ii) The attraction of job offers induces an important demographic influx and residential proximity close to mines and smelters (Dupin et al., 2013). Banza et al. (2009) have determined that such residential zones are the most important predictor of high metal concentrations in the urine. In addition to these sanitary issues, the mining activities (i.e. modifications of the ore extraction type and related demographic influx near the

exploitation/processing centers) induce changes in land cover, with fragmentation of the landscape, evolution from extensive large to small scale denudation patches, regression of the vegetation cover, and deforestation (Dupin et al., 2013).

Due to dominant south-eastern winds, the metallurgic industry in Lubumbashi has been the source of spatially concentrated atmospheric deposits of non-ferrous metal particles and associated substances in a cone-shaped zone, situated north-west of the original metal processing site (Prasad, 1989; Banza et al., 2002). This has already been observed around other copper smelters (e.g., Kabala and Singh, 2001; Vítková et al., 2011). Indeed, the copper smelter flue dust from Mufulira is composed of chalcantite with trace amounts of various Cu sulfides (Vítková et al., 2011). pH-dependent leaching of chalcantite has revealed that this mineral was most completely dissolved under acidic conditions. In these experiments, the subsequent Cu mobility is controlled by the precipitation of secondary sulfates or the binding to newly formed Fe-oxides (Vítková et al., 2011). Therefore, one can consider that soil pH is the most important parameter influencing metal-solution and soil-surface chemistry. In general, metal and metalloid sorption is smaller at low pH values. Adsorption then increases at intermediate pH from near zero to near complete adsorption over a relatively small pH range (Bradl, 2004). In the present study, the pH values were intermediates and ranged from 4.1 to 7.8 (Table 3). As proposed by Vítková et al. (2011), Cu sulfates were probably almost completely dissolved in the uppermost soil layers and the so-released Cu became sorbed to OM or oxides, as for Vallée Karavia site (Fig. 5).

4.3. Phytoremediation of secondary metalliferous soils

The successful remediation of land affected by mining and ore processing must be based on a perfect knowledge of the original natural ecosystem at metalliferous sites.

Attempts to remediate degraded soils by invasive plants have largely been unsuccessful. Secondary metalliferous soils (Figure 2) can offer unique conditions for plant biodiversity conservation (Faucon et al., 2011). The differences in functional traits between primary and secondary habitats indicate that recent secondary habitats can provide favorable conditions for colonization of plants. It then allows identifying the most appropriate functional plant traits to initiate revegetation of bare soil contaminated by Cu and Co (Ilunga wa Ilunga et al., 2015). These traits can therefore be considered as the main candidates for the revegetation of bare soil created by mining activity to restore degraded landscapes of southeastern mining areas of the Katanga Province (Shutchka et al., 2015). However, the selected traits and species to achieve the post-mining revegetation do not allow the best of restoring an ecosystem and notably their ecosystem services that are often associated to a high plant functional diversity. The transfer of metals by wind erosion would not be reduced by the spontaneous vegetation of secondary habitats as it was comprised primarily of annual species that do not survive during the dry season. Shallow depth of underground system and non-permanent cover plant during the two seasons are not in favor of reducing runoff and wind and water erosion and thus the transfer of metals. A priority for restoration of metal-rich bare soils would be to integrate to these plant communities of secondary habitats, the plant traits of primary habitats such as perennial life-cycle, high underground system, cespitose grasses, growth phenology at the end of dry season and lateral spreading capacity. This approach would create a new functional ecosystem with ecosystem services for the conservation of biodiversity and soil protection.

5. Conclusion

Metal distribution and Co and Cu chemical fractionation in contrasting soils located within individual environmental compartments (soils, mine tailings, smelting waste disposals) from the Katanga were investigated. The Enrichment Factor analysis shows five different

classes in the investigated soils: the minimal enrichment is observed for Ca and Ni. Mg, Fe, Mn and U are moderately enriched. Cd, Pb and Zn are significantly enriched, while Co and Cu are extremely enriched. These elements are directly related to mineral paragenesis and mining activities in Katanga, while the different intervals of concentrations observed for these metals and metalloids can be related to the different sampled site types (i.e., metalliferous vs non-metalliferous, and secondary types). In these soils, total Co and Cu are present in higher concentrations in naturally metalliferous soils compared to secondary and non-metalliferous sites. Similarly, extractable Cu and Co concentrations are most often higher in primary metalliferous soils than in the other ones. In addition to these data, the speciation calculations bring complementary information about metal speciation and the proportion of metals bounded to organic matter, Fe- and Mn-oxides, and the proportion of free metal in the soils. Among others, these calculations have highlighted that inorganic Cu and Co concentrations are higher in samples from naturally metalliferous sites and secondary sites compared to S2 and S3 and non-metalliferous sites.

High metal concentrations in the Katanga Copperbelt soils are derived, for their most important part, from the geological background of which the soils ultimately derived. The abundance of metals and the chemical fractionation of these elements in soils also reflect (i) their release from mining- and smelting-derived particles, and (ii) their partitioning into different soil compartments. The dissolution dynamics of metal-bearing particles deposited into soils is highly dependent on their mineralogical composition and soil pH.

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Table and Figure Captions

Table 1 Location and description of study sites. All sites are in Katanga (Democratic Republic of Congo). Coordinates are in GCS WGS84 (DD).

Table 2 Descriptive statistics, UCC values (McLennan, 2001) and enrichment factors of chemical elements for the whole dataset.

Table 3 Arsenic, Cd, Co, Cu, Pb, Zn, TOC concentrations, and pH values for each site. Copper and Co fractionation for each site: AA-EDTA and speciation modeling using WHAM 6. Concentrations are given in mg/kg. Inorg = ionic form, –MnOx = bound to manganese oxides, –FeOx = bound to iron oxides, –OM = bound to organic matter.

Figure 1 Geological sketch map of the Katanga Copperbelt (modified from Cailteux et al., 2005) and sampling point locations.

Figure 2 Photographs from (a) natural copper hill (i.e., undisturbed by mining activities from Fungurume region (photograph available on <http://copperflora.org/>) (b) mine deposits from quarry (i.e., naturally metalliferous soils disturbed and reworked by mining activities) Niamumenda (photograph taken by Bastien Lange) (c) bare soils contaminated by metalliferous fallout from copper smelter Vallée Karavia (photograph taken by Michel-Pierre Faucon) and (d) tailings from hydrometallurgical process Kipushi (photograph taken by Gilles Colinet).

Figure 3 (a) Cu and (b) Co concentrations for each site. There are no significant differences between sites with the same letter (results of one-way ANOVA followed by post-hoc multiple comparison, Tukey HSD test). Error bars = standard deviation.

Figure 4 (a) Cu and (b) Co AA-EDTA extractable concentrations for each site. There are no significant differences between sites with the same letter (results of one-way ANOVA followed by post-hoc multiple comparison, Tukey HSD test). Error bars = standard deviation.

Figure 5 Fraction of (a) Cu and (b) Co concentrations for each site, as modeled using WHAM 6.0. There are no significant differences between sites with the same letter (results of one-way ANOVA followed by post-hoc multiple comparison, Tukey HSD test). Inorg = ionic form, –MnOx = bound to manganese oxides, –FeOx = bound to iron oxides, –OM = bound to organic matter. Error bars = standard deviation.

Figure 6 Eh–pH stability diagrams at 25°C for (a) Cu minerals and dissolved species of Cu and (b) Co minerals and dissolved species of Co. Fluids are typical of groundwater with $[\text{Cu}^{2+}] = 10^{-4}$ mol/L, or $[\text{Co}^{2+}] = 10^{-4}$ mol/L, $P_{\text{CO}_2} = 10^{-2}$ and 200 mg/L SO_4^{2-} (after De Putter et al., 2010; Decrée et al., In Press) .