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Copper isotopic record in soils and tree rings near a copper smelter, Copperbelt, Zambia

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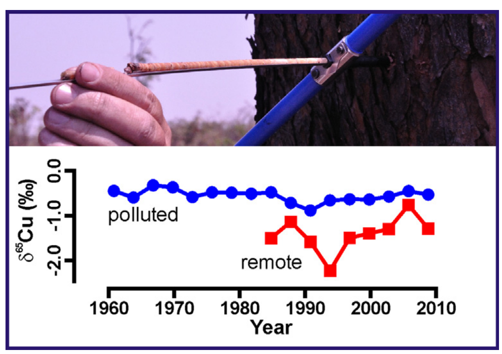
HIGHLIGHTS

- Cu isotopes were measured in smelter affected subtropical soils and pine tree rings.
- Greater Cu isotope fractionation occurs in the polluted soil profile.
- Non-root uptake of Cu recorded by tree rings in the polluted area.
- Cu isotopes are useful tracers for differentiation of aboveground and root uptakes.

GRAPHICAL ABSTRACT



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ABSTRACT

The copper (Cu) content and isotopic composition were studied in soils and in pine tree rings at locations close to and far from the Cu smelter, located at Kitwe, Zambia. The soil in the remote area contained 25–75 mg kg^{-1} Cu, whereas the soil close to the smelter contained 207–44,000 mg kg^{-1} Cu. The δ^{65}Cu at the remote area and close to the smelter varied in the range −0.40 to −0.11‰, and −0.44 to 0.01‰ respectively. The δ^{65}Cu of the surface soil at both profiles (−0.44 to −0.40‰) is similar to the isotopic composition of the concentrates processed in the smelter (−0.75 to −0.45‰), i.e. both locations are affected by Cu ore dust. The increase in the δ^{65}Cu in the direction towards the centre of the profile is caused by the oxidative dissolution of Cu(I) from ore minerals, during which heavier Cu is released. In deeper parts of the profile, there is a slight decrease in δ^{65}Cu because of easier mobilisation of the lighter isotope. The tree rings at the two locations differ in the total contents and isotopic composition. At the less contaminated site, the Cu contents equal 0.4 to 1.1 mg kg^{-1} while, at the polluted site, the Cu contents vary in the range 3 to 47 mg kg^{-1}. Whereas, at the less contaminated location, the tree rings are substantially enriched in lighter Cu (δ^{65}Cu = −0.76 to −2.2‰), at locations close to the smelter the tree rings have an isotopic composition (−0.31 to −0.88‰) similar to that of the contaminated soil or processed ore. The isotopic compositions of the tree rings close to the smelter are affected particularly by interception of dust containing Cu ore. The δ^{13}C in tree rings demonstrate the interconnection of acidification and Cu mobility.

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1. Introduction

Dendrochemical monitoring of environmental changes has a long tradition (e.g. Baes and McLaughlin, 1984; Watmough, 1999) and uses indirect methods, such as the thickness and variability of tree rings, or direct methods of measuring the contents of nutrients and pollutants (e.g. Nabais et al., 1999; Meerts, 2002), or measuring their isotopic composition (McCarroll and Loader, 2004). In a number of cases, direct methods of measuring the content of pollutants document well the temporal changes in contamination and agree with other archives (e.g. Savard et al., 2006; Novák et al., 2010; Zuna et al., 2011), while in some publications the record in the tree rings differ from the other archive material, especially in areas without important local sources (e.g., Bellis et al., 2002; Bindler et al., 2004; Patrick and Farmer, 2006). A record of the pollutants contained in tree rings can be affected by lateral migration of metals in the xylem (Hagemayer and Schafer, 1995; Nabais et al., 1999), or root uptake of pollutants from various parts of the soil profile (Watmough and Hutchinson, 1996; Bellis et al., 2004). In areas with important pollution sources, the tree rings provide a good record of the pollutant contents in the atmosphere (Lageard et al., 2008; Mihaljevič et al., 2008; Mihaljevič et al., 2011, 2015). Non-root uptake of pollutants occurs through interception capture of pollutants by the tree crown and subsequently foliar uptake or diffusion through the bark (Watmough, 1999). In both cases (diffused pollution and point source pollution), the combination of radial and vertical translocation, which may influence elemental distribution in the wood, indicate that the data must be interpreted with caution (Scharnweber et al., 2016). The Copperbelt in Central Africa is a site where both natural and polluted soils with elevated contents of copper (Cu) and cobalt (Co) are present; this is substantially manifested in their contents in plants (Lange et al., 2017) and provides a model environment for studying the biochemistry of these elements.

Copper (Cu) is an important economic commodity and its mining, processing and use, either as a metal (alloys, electrical wires, plumbing, machinery, roofing etc.) or in compounds (fungicide, especially Bordeaux Mixture), substantially affect the environment (Rieuwerts, 2015). Excess Cu affects plant growth and the biodiversity of earthworms, bacteria and fungi, which all affect the C and N cycles in the soil (e.g. Oustriere et al., 2016 and references therein). Simultaneously, it is an essential element that is a component of selected enzymes of microorganisms, plants and animals (e.g. Chen et al., 2015).

Non-traditional isotopes, similar to other isotope applications, constitute a tool as a source and process tracer (Wiederhold, 2015). The $^{65}Cu/^{63}Cu$ isotopic ratio has been found to be a useful tool for differentiating a number of processes that cannot be elucidated by other procedures (e.g. Asael et al., 2007; Bigalke et al., 2010a, 2010b; Liu et al., 2014; Fekiacova et al., 2015). In an exogenic environment, Cu is readily mobilised from primary minerals (chalcopyrite $CuFeS_2$, cuprite Cu_2O) where, if abiotic oxidation of Cu(I) to Cu(II) occurs during dissolution, the resultant solution is enriched in ^{65}Cu (Kimball et al., 2009). On the other hand, incorporation of Cu into secondary minerals in the soil profile leads to enrichment of these minerals in the heavier isotope (Pokrovsky et al., 2008; Bigalke et al., 2011).

The uptake of Cu from soil by plants is not well understood. Copper is bonded in soils especially to organic materials or Fe(III) oxides (Flemming and Trevors, 1989). Iron can be used as a model element for understanding of Cu uptake. Plants have two strategies for Fe uptake (Ryan et al., 2013). The first group of plants employs a strategy consisting in acidification and reduction of Fe and Al oxides in the rhizosphere (dicotyledons and nongraminaceous monocotyledons), while the second group of plants (graminaceous monocotyledons) produce root extrudates reducing and complexing Fe (Ryan et al., 2013). The processes of reduction and complexation of Fe can subsequently affect Cu mobility. For example, enzymes causing reduction of Fe can also reduce Cu(II) and isotopically lighter Cu can be mobilised during this process (Jouvin et al., 2012). Other means of Cu fractionation by plants include preferential uptake and faster diffusion of the lighter isotope and preferential binding of the heavier isotope on the cell walls of the roots (Jouvin et al., 2012).

In dendrochemical investigation of the history of pollution, physiological changes caused by gaseous pollutants can be documented by traditional stable isotopes (Savard, 2010). Tree species exposed to contamination from gaseous pollutants (SO_2, NO_X, O_3 etc.) have an ambiguously elevated $\delta^{13}C$ value in their biomass (e.g. Martin et al., 1988; Freyer, 1979; Savard et al., 2004; Sensula, 2016) and thus the contamination in the past can be demonstrated through effects on assimilation processes.

The objective of this study was to use the isotopic composition of Cu i) to describe alteration of geomaterials in soils and the mobility of Cu in the soil profile, ii) to assess the suitability of Cu isotopes for tracing pollution by Cu, and iii) to distinguish between root and aboveground uptake of Cu by tree biomass.

2. Materials and methods

2.1. Sampling site

The samples were taken in the vicinity of Kitwe, Copperbelt Province, Zambia (Fig. 1). The area is known for its intensive mining and processing of Cu and Co sulfide ores. The area with reserves of ~200 Mt. Cu and >8 Mt. Co, is the largest sediment-hosted stratiform copper–cobalt province (El Desouky et al., 2009). Finely dissimilated sulphides consist mainly of chalcopyrite, malachite, bornite, chalcocite and carrolite (McGowan et al., 2006). Mining in the Copperbelt began in 1920 and culminated in the late 1960s and early 1970s, when production reached 755,000 t of Cu. Production decreased following nationalization in 1982. In 2000, the Zambian government privatized the individual mines. In the first decade of the 21st century, Cu production corresponded to 300,000 t Cu p.a. (Mihaljevič et al., 2011). The Nkana smelter (Fig. 1), which is one of the oldest metallurgy plants in the area, has been in operation since 1931. Initially, the metallurgy plant produced 6000 t of blister copper annually. Production culminated in 1971 (330,000 t of Cu p.a.) and production varied between 100,000 and 125,000 t Cu p.a. between 1993 and 2006 (Vítková et al., 2010). Subsequently, work at the metallurgy plant was terminated in 2009.

Kříbek et al. (2010) described elevated sulphur and metal concentrations in the vicinity of the metallurgy plant in the downwind direction. The soil parameters are statistically clustered in relation to their origin as smelter emissions-specific (S, Co, Cu and Hg), smelter slag-specific (Cr, Zn, Pb and As), bedrock-specific (V, Cr, Ni and Fe) and mine tailings-specific (C_{carb}, Co and Ni) (Kříbek et al., 2010).

The climate in the area corresponds to a humid subtropical climate [Cwa] according to the Köppen climate classification and is characterised by three periods: a rainy period between November and the end of April with tropical storms, followed by a cool dry period from May to the end of August with minimal precipitation, and subsequent hot season lasting from September to November. On an average, approximately 1300 mm of precipitation fall in the Kitwe Region, strong south-easterly winds prevail from March to October and weaker north-westerly winds predominate from November to January (Ettler et al., 2011). Evapotranspiration for the Chambishi catchment (25 km NW from Kitwe) was calculated as 83% (von der Heyden and New, 2003).

2.2. Soils, tree rings and concentrates

Soil samples were taken in August of 2010 at two locations, a “Polluted” site affected by fallout from the metallurgy plant and a “Remote” area, 15 km east of the Nkana smelter, in the direction against the prevailing winds (Kříbek et al., 2010) (Fig. 1, GPS coordinates: 12,8,230,447° S, 28,187,712° E - polluted site; 12,829,287° S, 28,241,288° E - remote site). Soils were sampled in a 0.5 × 1 m (width x length) pit. According to the IUSS Working Group WRB (2014) the studied soils were described as Ferralsols. The soils were dried to