Chemosphere 167 (2017) 28–35

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Organic complexation of copper in throughfall and open field bulk deposition: Influence of the tree canopy of Mediterranean forest ecosystems

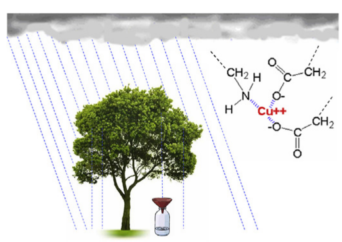
Sotirios Karavoltsos [a,*], Fotios Fotiadis [a], Panagiotis Michopoulos [b], Aikaterini Sakellari [a], Marta Plavšić [c], Athanassios Bourletsikas [b], Kostas Kaoukis [b], Nikolaos S. Thomaidis [d], Manos Dassenakis [a], Michael Scoullos [a]

[a] *National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Environmental Chemistry, Panepistimiopolis, 157 84, Athens, Greece*
[b] *H.A.O. DEMETER, Institute of Mediterranean Forest Ecosystems, Terma Alkmanos, 115 28 Athens, Greece*
[c] *Ruđer Bošković Institute, Center for Marine and Environmental Research, P.O. Box 180, 10002 Zagreb, Croatia*
[d] *National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Analytical Chemistry, Panepistimiopolis, 157 84, Athens, Greece*

H I G H L I G H T S

- Cu complexation in forest throughfall was studied for the first time by DPASV.
- Samples were collected from two different Mediterranean forest ecosystems.
- In throughfall (TF) and bulk deposition (BD) copper was fully complexed.
- Cu ligands concentrations were determined 3–4 fold higher in TF than in BD.
- HULIS seem to be the most widespread type of ligands in both type of precipitations.

G R A P H I C A L A B S T R A C T



A R T I C L E I N F O

Article history:
Received 21 April 2016
Received in revised form
16 September 2016
Accepted 26 September 2016

Handling Editor: Martine Leermakers

Keywords:
Throughfall
Bulk deposition
Copper complexing capacity
Apparent stability constant
Canopy

A B S T R A C T

The complexing capacity for Cu ions (L_T) and the apparent stability constant values ($\log K_{app}$) were measured in throughfall (TF) and open field bulk deposition (BD), at two Mediterranean forest ecosystems of western Greece. L_T was measured for the first time in the TF of natural forests.

Concentrations of L_T were three-to-four-fold higher in TF (mean ± st.dev: 2014 ± 769 nM for Varetada and 1565 ± 595 nM for Karpenissi) compared to those in BD (531 ± 517 nM and 468 ± 321 nM, respectively). In all TF and BD samples, L_T concentrations were significantly higher than the corresponding total Cu concentrations, indicating that Cu was fully complexed. The L_T/TOC ratios in TF were found comparable between the two study sites (235 ± 149 nM mg^{-1} C for Varetada and 256 ± 233 nM mg^{-1} C for Karpenissi) and with those of BD (226 ± 257 and 163 ± 163 nM mg^{-1} C, respectively). The determined mean $\log K_{app}$ values were almost identical in TF (6.8 ± 0.7 at Varetada; 6.8 ± 0.6 at Karpenissi) and BD (6.5 ± 0.6 at Varetada; 6.8 ± 0.3 at Karpenissi), pointing to the fact that regardless of the enrichment of TF in ligands ($L_{T(TF)} > L_{T(BD)}$) the type of binding sites remain the same.

* Corresponding author.
E-mail address: skarav@chem.uoa.gr (S. Karavoltsos).

http://dx.doi.org/10.1016/j.chemosphere.2016.09.131

The logK_{app} values which were obtained herewith are similar to those obtained for humic-like substances (HULIS), indicating them as the most widespread type of ligands in BD and TF.

1. Introduction

The atmosphere constitutes one of the major routes through which metal ions can be conveyed to long distances and impact remote ecosystems (Shotyk et al., 1996). Trace metals can be deposited by dry fallout and scavenged by fog, cloud and rain droplets, by occult and wet deposition (Avila and Rodrigo, 2004).

Numerous studies on the atmospheric deposition of trace metals at terrestrial ecosystems have been conducted since the 1970s (Heinrichs and Mayer, 1977; Smith and Siccama, 1981; Itoh et al., 2006). The organic matter composition of atmospheric deposition has also been studied (Likens et al., 1983; Saxena and Hildemann, 1996; Latif et al., 2005; Santos et al., 2012), while in the last two decades several studies have dealt with the role of organic complexation in controlling trace metal speciation in rainwater and aerosols (Chester et al., 1993; Cheng et al., 1994; Spokes et al., 1996; Okochi and Brimblecombe, 2002; Witt et al., 2007a, b; Plavšić et al., 2008; Karavoltsos et al., 2013).

Organic complexation of Cu is recognized to be a significant determinant of its chemical and biological reactivity (Moffett and Dupont, 2007). Since free hydrated Cu is especially chemically active, participating in several reactions, the degree of its organic complexation is of particular interest (Weschler et al., 1986). Multiple relevant sources of Cu organic complexants in precipitation potentially exist. Okochi and Brimblecombe (2002) found that humic-like substances represent the most significant ligands in the atmosphere, with several polycarboxylic acids and hydroxyl forms also being responsible for trace metal complexation. The tendency of natural humic substances to form stable complexes with Cu has been well demonstrated in natural waters (Shank et al., 2004; Yang and van den Berg, 2009; Whitby and van den Berg, 2015), as well as in atmospheric precipitation, in which Orlovic-Leko et al. (2009) have detected the presence of substances similar to humic acids. Spokes et al. (1996) found that Cu in many semi-urban rainwater samples was largely present in an organically complexed form, since inorganic ligands are too weak to provide the strong complexes which could be measured. Karavoltsos et al. (2013) demonstrated that ligand sources of terrestrial origin appear to be of particular importance to Cu complexation, with vegetation and anthropogenic emissions having a potentially prominent impact.

For the consideration of vegetation as a potential source of organic ligands for Cu in precipitation, the study of forest ecosystems is of particular significance due to the large interacting surface area of the forest canopy with the atmosphere. Throughfall (TF), which constitutes the water flux collected under the forest canopy, results from all processes including accumulation of dry deposition, direct assimilation or release of elements (leaching) and/or removal of dry deposition (wash off) occurring in the phyllosphere (Moreno et al., 2001). According to Hongve (1999) leaf litter is an important source of natural DOC, with litter percolates containing significant fractions of colored and highly refractory hydrophobic acids (humic substances) and a variable fraction of biodegradable compounds. Differences have also been recorded in the levels of DOC between open field bulk deposition (BD) and TF, with the highest concentrations detected in the latter (Solinger et al., 2001; Liu and Sheu, 2003). Humic-like phenolics such as tannins, as well as various carboxylic acids, are contained in TF and leaf extracts (Qualls and Haines, 1991; Kraus et al., 2003) and may strongly correlate with metals (Scalbert et al., 1999). Organic matter in soil solution constitutes a very important factor controlling metal mobility (Hou et al., 2005). Qualls and Haines (1991) have estimated a DOC percentage equal to 30% in the soil solution of an A-horizon, deriving from throughfall DOC. Organic matter in TF is therefore expected to influence the behavior of metals in the soil. Despite the fact that Cu environmental pathways, together with its availability and transport or immobilization in ecosystems are linked to its speciation, the Cu complexing capacity (L_T) of TF in natural forests has been rarely studied so far. A single study of L_T in TF is only available, which was however realized in artificial groves of four tree species, located at the area of an institute in Japan, characterized as suburban (Hou et al., 2005).

The objective of the present study was the determination for the first time of the complexing capacity for Cu ions in TF of natural forest ecosystems. In order to study the canopy influence on atmospheric inputs, a comparison of TF and BD was performed. Samples were collected at two temperate climate Greek forest ecosystems with different vegetation types. For the physicochemical characterization of the samples, pH, conductivity, the concentrations of total copper (TCu), total organic and inorganic carbon (TOC, IC), as well as the concentrations of major ions were determined. The environmental impact of metal complexation is also discussed.

2. Materials and methods

2.1. Sampling stations

The study was conducted at two different Mediterranean forest ecosystems of the mainland of Greece (Fig. S1; supplemental material). The first sampling area is located at Varetada near the small town of Amfilohia in western Greece. It is a hilly region with a relatively small slope (38°50′46″ N; 21°18′18″ E). The sampling plot has an altitude of 360 m, its area is 0.27 ha and the annual mean rainfall 1184 mm (average value of years 1996–2013). The vegetation of the area consists of close, broad-leaved, evergreen trees of 10–15 m height. The number of trees which were included in the sampling plot was 296. The vegetation consists of trees (*Quercus ilex, Arbutus unedo, Quercus coccifera, Quercus frainetto, Cercis siliquastrum*) and shrubs (*Rhamnus alaternus, Erica arborea, Fraxinus ornus, Asparagus maritimus*) of 40–60 years of age.

The second sampling plot is located at an altitude of 1170 m at the foothills of the Tymfristos mountain in Evrytania prefecture, close to Karpenissi, a small town of central continental Greece (38°52′28″ N; 21°51′57″ E). The area covered is also 0.27 ha and the annual rainfall 1616 mm (average value of years 1997–2013). The forest area is covered mainly by fir trees (*Abies borisii regis*) of 20–25 m height and other forest species such as *Ilex aquifolium, Sambucus nigra, Rubus fructicosus, Rubus caesius, Fragaria vesca*. In the sampling plot the total number of fir trees was 95, of approximately 100 years of age.

2.2. Sampling

For both of the studied sites, open field bulk deposition (BD) and