Copper complexation in wet precipitation: Impact of different ligand sources

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HIGHLIGHTS

- Cu complexation in wet precipitation was examined by DPASV.
- Cu ligands ranged between 0.07 and 1.9 μM.
- Logk_{app} were determined in the range 6.5–9.6.
- Among ligands, sources of terrestrial origin appear to be of particular importance.
- Vegetation and anthropogenic emissions seem to have a prominent impact.

ARTICLE INFO

ABSTRACT

Cu complexation in wet precipitation samples was measured by the method of differential pulse anodic stripping voltammetry (DPASV), which presumed the existence of 1:1 Cu ion–ligand complexes. The wet precipitation samples were collected throughout the rainy period (September 2011–May 2012) from four sampling stations of central and southern Greece, two of which were located in urban coastal areas of its mainland (Athens, $n = 24$; Elefsina, $n = 11$) and the other two on the island of Crete (Heraklio, $n = 26$; Ligortynos, $n = 12$), comprising different features concerning population density, urban/rural/industrial character and influence from the sea. Total Cu (TCu), total organic and inorganic carbon (TOC, IC), pH, conductivity, several inorganic macro-constituents (Cl^-, Br^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}), n-alkanes and polycyclic aromatic hydrocarbons (PAHs) were determined for better characterization of the predominant sources and influences.

Significant complexation of Cu ions was determined in almost all wet precipitation samples examined, with the apparent complexing capacity of Cu ions in unfiltered samples ranging between 0.07 and 1.9 μM and apparent stability constants (logK_{app}) in the range 6.5–9.6, which corresponds to values comparable to those deriving from a limited number of studies having a common 'detection window'. The percentage in the mass of TOC complexed with copper was up to 4%.

Among ligands, sources of terrestrial origin appear to be of particular importance. In terrestrial sources, vegetation and anthropogenic emissions seem to have a prominent impact.

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1. Introduction

Cu in the atmosphere derives from both natural and anthropogenic sources contributing emissions of similar magnitude (Nriagu and Pacyna, 1988). The global flux of Cu removed from the atmosphere via wet deposition is 150×10^6 kg yr^{-1} (Kieber et al., 2004). This corresponds to complete removal of the estimated Cu input into the troposphere and indicates that essentially all Cu released into the global atmosphere is removed by rain (Witt et al., 2007a).

Cu complexation plays an important role in affecting photochemical reactions in the atmosphere, with large differences in photoreactivity between weakly and strongly bound Cu (Witt et al., 2007b). It is possible that metal-organic complexation, which

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enhances the uptake of gaseous organic compounds and the solubility of metals in atmospheric water, is responsible for the relatively high abundance (25%) and unusual stability of Cu(I) in rainwater (Kieber et al., 2004). Cu speciation is also involved in many important atmospheric redox reactions (Sedlak and Hoigné, 1993). This has a direct impact on the chemistry of atmospheric waters since it is the free hydrated Cu ion which controls the catalytic capabilities for reactions such as SO_2 oxidation (Witt et al., 2007b).

Humic like substances (HULIS) have been identified in the atmosphere as a dissolved organic carbon (DOC) component in aerosol, rain and fog water samples (Gelencser et al., 2000; Krivácsy et al., 2000). Their content in polycarboxylic acids, which effectively complex metals such as Cu, classify them among the most prominent ligands in atmospheric precipitations (Okochi and Brimblecombe, 2002). Likens and Galloway (1983) have reported that dissolved macromolecular organic compounds (>1000 Da) accounted for 35–43% of total organic carbon in precipitation. 10% and more of the organic carbon in aerosol collected in German urban and rural areas, has been reported to be attributed to humic-like compounds (Harves et al., 1998). Krivácsy et al. (2000) indicate that these may participate in cloud condensation.

Inorganic metal speciation in precipitation is a strong function of both precipitation source and its pH (Zhang et al., 2001). In rainwater at pH 7.7 more than 99.9% of Cu (II) is organically complexed (Spokes et al., 1996). Cheng et al. (1994) have investigated chemical speciation of some trace metals in rainwater using DPASV and ion-exchange method under atmospheric pH conditions. They have indicated that half of Zn, Pb and Cd in the soluble fraction were present as metal aqua ions and/or small inorganic complexes, whereas half of Cu in the soluble fraction was present as larger complexes of organic ligands. Cu in the soluble fraction was mainly present in the molecular weight range of 1000 to 5000 Da, which includes both fulvic and humic acids.

Organic material contained in atmospheric water and fog droplets consists, in a high percentage, of polyols, polyethers, aliphatic mono- and dicarboxylic acids and unsaturated polyacidic compounds (probably fulvic/humic acids) (Saxena and Hildemann, 1996; Pun et al., 2000). Aldehydes, esters, organic nitrates, aliphatic nitro-compounds, amines and amino acids do not appear as major contributors to water-soluble organic compounds (WSOC) (Decesari et al., 2001; Okochi and Brimblecombe, 2002).

The attribution of specific organic ligands in precipitation to a particular source still remains very difficult, since natural dissolved organic matter in the atmosphere comprises a complex mixture of organic compounds of varying composition, molecular weight, chemical and natural features (Perdue and Ritchie, 2003), which are affected by diverse processes and factors such as microbial activity, temperature and photooxidation (Bourbonniere et al., 1997). Despite efforts to investigate the role of organic complexation in controlling trace metal speciation in rainwater and its potential to modify metal solubility in precipitation (Maring and Duce, 1989; Zhuang and Duce, 1993; Plavšić et al., 2008) information on this significant issue still remains very limited.

The goal of this study is therefore to contribute to the investigation of Cu complexation in wet precipitation, based on rainwater samples collected from four sampling sites of the central and southern part of Greece, throughout the rainy period of 2011–2012, comprising different features of population density, urban/rural/industrial activities and vicinity from the sea. For further evaluation of the results, determination of total Cu (TCu), total organic carbon (TOC), inorganic carbon (IC), ions (Cl⁻, Br⁻, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}), n-alkanes and polycyclic aromatic hydrocarbons (PAHs) were also carried out.

2. Materials and methods

2.1. Sampling stations

Two of the sampling sites (Athens and Elefsina) are located in the Greek mainland at an altitude of 130 and 5 m, respectively, from the sea surface and two at Crete, which is the largest Greek island located at the southern part of the country (Heraklio and Ligortynos; altitude of 50 and 380 m, respectively) (Fig. S1; supplemental material).

Within the metropolitan area of Athens, the capital of Greece, where approximately 5 million inhabitants reside and which is characterized by heavy traffic, the rainwater samples were collected at the locations of 'Nea Ionia', a suburb of the city at a distance of 7 km north its centre. Elefsina is one of the mostly industrialized areas of the country where oil refineries, iron and steel mills, cement factories etc. operate. Heraklio, with 170,000 inhabitants, is the fourth largest in population Greek city and the largest one on the island of Crete. Ligortynos is a small remote Cretan village of approximately 500 inhabitants, without any industrial activity, where agriculture (olive and vinery cultivation) is the predominant occupation of its inhabitants. The selected sampling sites are located at different distances from the sea, at some tens of meters in the case of Elefsina and at approximately 2 km in Heraklio, 10 km in Athens and 12 km in Ligortynos. Regarding Athens, Elefsina and Ligortynos the closest coastline is found southwards of the sampling sites, whereas in the case of Heraklio northwards.

2.2. Sampling

Samplings were performed between September 2011 and May 2012, a period which actually includes the greatest number of wet precipitation incidents in the eastern Mediterranean. During summer rain events in Greece are limited, possessing the features of rapid storms, being rather rare at the southern areas of the country including the island of Crete. The time series of samples from Athens and Heraklio are complete (24 and 26 wet precipitation samples, respectively), while from Elefsina and Ligortynos fewer samples (11 and 12, respectively) were obtained. In all the areas studied sampling stations were located at a height of almost 5 m from the ground surface. Wet precipitation samplers, consisting of 2 L volume quartz containers and of 25 cm diameter glass funnels, were in all cases placed at the sampling sites in the beginning of each rain event and withdrawn on its termination, in order to avoid collection of dry deposition.

During their transportation, samples were maintained refrigerated. In the laboratory, part of the sample was directly used for Cu complexing capacity measurements. Simultaneously, another part of the sample (from the same stock solution) was placed in a polyethylene container (previously soaked with HNO_3 4 M for 1 week and finally rinsed with Milli-Q water 18.2 MΩ cm; Millipore, Bedford, MA, USA) and appropriately acidified for avoiding any interaction with the container's walls. Samples for TOC, n-alkanes and PAHs measurements were kept in glass containers, whereas those for the rest of the parameters were kept in polyethylene containers. Subsamples for TOC measurement were kept frozen, whereas those used for ions measurement were filtered through 0.45 μm acid-washed cellulose acetate membrane filters. pH, conductivity, L_T and TOC measurements were made within 48 h from collection of the samples and the rest of determinations were done within one week. All glass equipment used was prewashed with chrome-sulfuric acid, rinsed several times with Milli-Q water and precombusted for 1 h at 550 °C. All sample manipulations were carried out inside a clean room supplied with HEPA filtered air.