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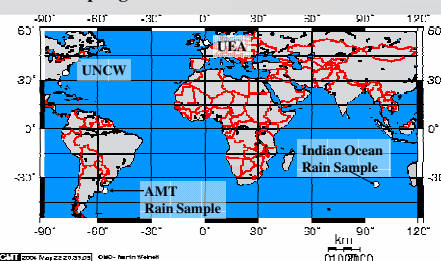
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Rainwater is a major source of metals to the oceans (Duce et al. 1991). The main sources of metals in rains are soils and anthropogenic activities such as high temperature combustion processes. The bioavailability, toxicity and catalytic activity of metals is strongly influenced by their chemical speciation.

Organic material may reach the atmosphere from vegetation including oceanic phytoplankton, combustion or may be derived anthropogenically. Organic compounds in rains and aerosols can include organic acids, amino acids and humic-like substances. Many of these could be potential ligands for metals in the atmosphere.

In order to investigate the extent of copper complexation rain samples were collected at a number of sites and the copper complexation measured using the electrochemical method adsorptive cathodic stripping voltammetry.

Rain Sampling Locations

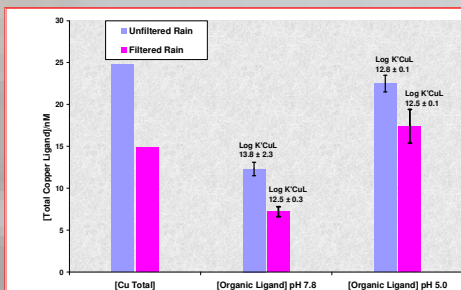


Sample Collection

Rain samples were collected on an event basis using acid cleaned HDPE funnels and bottles (Witt and Jickells, submitted). The UEA rain site was located on the roof of the School of Environmental Sciences building samples in a semi-urban environment. Marine rain samples were collected during an Atlantic Meridional Transect (AMT) aboard RRS James Clark Ross in September/October 2001 and a Southern Indian Ocean Transect at 32 °S in March/April 2002. Samples were collected on the Monkey Island or Crane deck of the ships and samples were only collected when a headwind ensured a lack of contamination from the ship's stack. UNCW samples were collected with automatic wet/dry sensing precipitation collectors in an open area on the UNCW campus, situated approximately 8.5 km from the Atlantic Ocean. Samples collected at UNCW and UEA were stored refrigerated prior to analysis. Marine rain samples were stored frozen and transported back to UEA for subsequent analysis.

Analysis

Copper complexation was measured in rain samples using adsorptive cathodic stripping voltammetry. During work at UEA tropolone was used as the added ligand at a final concentration of 100 μM. At UNCW salicylaldoxime was employed as the ligand. Samples were buffered using HEPES buffer for pH 7.8 and ammonium acetate buffers for lower pH values. Electrochemical measurements were made using a hanging mercury drop electrode.



Dissolved and Particulate Phase Organic Complexation.

Copper complexation was investigated in rain samples collected at UEA, Norwich, before and after filtration through a 0.45 μm nucleopore filter.

The reduction in the copper detected following filtration shows that nearly 40 % of the copper in the rain sample was present in particulate form. The decrease in the total copper present following filtration is also accompanied by a decrease in the organic ligand concentration. There is however, strong organic complexation observed when only the dissolved phase is present, although the conditional stability constants are slightly reduced. This shows that organic complexation is important in both the dissolved and particulate phase for copper ions.

Copper Complexation in Marine and Terrestrial Rain Samples

The complexation of copper in was measured in two marine rain events. The air mass back trajectories associated with these events suggested they were truly marine in origin (Draxel et al). Unfortunately, experimental difficulties and the relatively large volume of rain required (~100 ml) limited the number of titrations which could be carried out. However, these results show the first copper complexation measurements in marine rain.

	Sampling date	[Cu] _{tot} /nM	% CuL	[L]/nM	log K ^{CuL}
UEA Rain	2000/01	10-28	38 - >99.9	10.5-22.5	12.5-12.9
Indian Ocean rain	April 2002	5.6	100	8 ± 0.9	13.6 ± 1.2
AMT Rain	October 2001	24	97	23.3 ± 1.5	12.2 ± 0.1

Similar results are seen for the Indian Ocean and AMT rain samples, with a majority of copper in these rain samples organically complexed. The conditional stability constants indicate the copper is strongly bound to this organic material. The stability constants determined in the oceanic rain samples are similar to those measured under the same conditions in UEA rain. This suggests that organic complexation is an important consideration of copper in rain water not just inland but also in remote oceanic regions far from continental regions.

Humic Material as a Potential Copper Ligand

Humic and fulvic like material has been detected in atmospheric samples and may be a significant proportion of atmospheric organic matter in some regions. To investigate the possibility of humic and fulvic material as complexants in rainwater, two model solutions were prepared containing copper and one of the acids. Humic acid solutions were prepared from solid humic acid (Sigma) and buffered to pH 5. Fulvic acid solutions were prepared from fulvic acid separated from UEA lake water by Lucy Spokes (YEAR) using the methods of Thurman and Malcolm (1981). Concentrations of 1mg/L humic material and 50 nM copper were chosen as these are representative of upper limits of the composition of rainwater (Willey et al 2000, Arimoto et al. 1985). Titrations were carried out on these solutions and the complexation parameters measured were compared to those of rain samples.

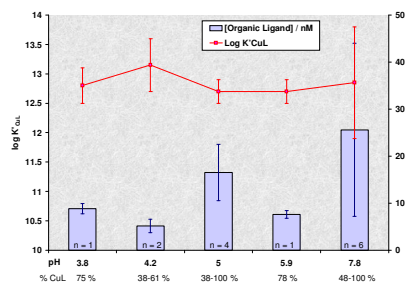
	[Cu] Total/nM	% CuL	[L]/nM	log K ^{CuL}
Humic Acid 1 mg l ⁻¹	50	>99.9	59 ± 1.1	12.9 ± 0.1
Fulvic Acid 1 mg l ⁻¹	50	84	42 ± 2.7	12.8 ± 0.2

The titrations carried out using the fulvic and humic acid model solutions found similar complexation parameters to those measured in the rain samples. The copper in the model solution was found to be predominantly organically complexed in the presence of humic and fulvic acid. These complexes were of a similar strength to those seen in the rain samples titrated under similar conditions. This shows humic and fulvic acids contain organic groups which are capable of forming the strong organic complexes seen in rain waters.

The concentration of organic ligands available to complex with the added copper was around 60 nM in the humic acid and 40 nM in the fulvic acid solution. These are similar concentrations to those observed in the rain samples, the complexes formed in the model solutions were also of a similar strength to those observed in rain water samples. These results are thus also consistent with humic material as a complexing material in rainwater.

Copper Complexation and pH

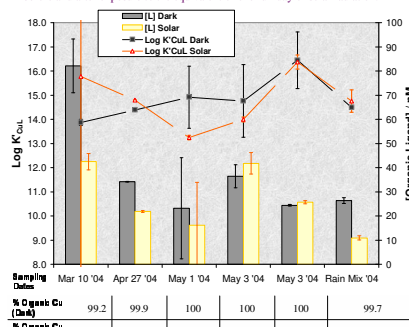
Using UEA rain samples, a range of buffers were used to make copper complexation measurements over a range of pH values likely to be experienced by a rain sample while in the atmosphere and upon its arrival to seawater. In the figure below, "n" indicates the number of titrations carried out at each pH value. A number of UEA rain samples were analysed, and both filtered and unfiltered samples are included.



Strong organic complexation was observed at all of the pH values studied. The strength of organic complexation and the concentration of organic ligands appeared to be independent of the managed pH. These titrations include both filtered and unfiltered rain samples which as discussed above, show some differences in complexation behaviour. Despite these variations it is clear that organic complexation is important for all samples analysed and that Log K^{CuL} falls within a narrow range of values.

Copper Complexation and Photochemistry

In previous work carried out at UNCW an increase in the proportion of Cu(II) was seen in the rain samples collected in the afternoon (Kieber et al.). To probe the relationship between metal speciation and photochemistry experiments have been carried out using a xenon arc light source to simulate solar radiation. Copper complexation was measured in rain samples collected at UNCW both before and after exposure to the equivalent of one full day of solar radiation.



The results of the photochemical experiments carried out at UNCW are presented above with the sampling dates. In most cases the ligand concentration decreases following exposure to solar radiation. However, not all of the ligand is removed and the strength of these ligands remains largely unchanged.

Conclusions

- Copper in rainwater is predominantly present as strongly complexed species.
- Organic complexation is important in both the dissolved and particulate phase.
- Copper complexation in rainwater is not limited to continental regions
- It appears that a significant proportion of the copper arriving in ocean via wet deposition is associated with strong organic complexes and may not be easily available to organisms
- Strong organic copper complexation was observed throughout the pH range likely to be experienced by rain samples in the atmosphere and upon arrival to seawater.
- The results obtained are consistent with humics playing an important role in copper complexation.

Acknowledgements

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