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Atmospheric Deposition: A Potential Source of Trace Metal Organic Complexing Ligands to the Marine Environment*

Malcolm Nimmo,[a,#] *Gary R. Fones,*[b] *and Roy Chester*[c]

[a]*Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, Devon UK*

[b]*Department of Environmental and Biological Sciences, University of Lancaster, Lancaster, Lancashire UK*

[c]*Oceanography Laboratories, Department of Earth Sciences, University of Liverpool, Bedford Street North, Liverpool, L69 3BX, UK*

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The present study confirms the existence of rainwater and seawater soluble metal (Cu, Pb, Cd, Ni and Co) complexing organic ligands associated with end-member aerosol populations. The end member aerosols being representative of a European urban aerosol population (LUAP – Liverpool Urban Aerosol Population), and an aerosol population representative of crustal dominated material (Mesh Saharan dust, collected off the west African coast). The investigations carried out by ACSV (adsorptive cathodic stripping voltammetry) clearly indicated that these end-members were a source of organic complexing ligands for all the considered metals. For LUAP Cu 26%, Pb 55%, Cd 36%, Ni 26% and Co 27% of the total seawater soluble fraction was $\text{ACSV}_{\text{non-labile}}$ (*i.e.* that fraction of the dissolved metal which is released after UV irradiation) compared to the corresponding values for Saharan dust (Cu 59%, Pb 23%, Cd 56%, Ni 66%, Co 23%). From these studies it was apparent that the dissolution for all metals and their respective fractions in both seawater and artificial rainwater was a rapid process with

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[#] Author to whom corresponence should be addressed.

no further release after *ca.* 30 minutes. The studies displayed for a number of the metals re-adsorption of $\mathrm{ACSV}_{\text{non-labile}}$ metal to the aerosol particulate surface (Co and Pb – Saharan / seawater; Co and Cd – LUAP / seawater) implying that different geochemical pathways are taken by different metal speciation fractions leading to potential differences in their marine residence times.
Conditional formation stability constants and complexing capacities for Ni were determined for seawater after being equilibrated with both end member aerosols. Log K'_{NiL} detected were 18.3 ± 0.3 and 19.26 ± 0.4 for LUAP and Saharan dust respectively. The equivalent complexing capacities were 1.0 ± 0.1 nmol mg^{-1} and 0.038 ± 0.005 nmol mg^{-1} respectively.

INTRODUCTION

Previous studies have highlighted the occurrence of organically complexed dissolved trace metals in natural waters (open ocean, coastal, estuarine and freshwaters). The major focus of the detection of operationally defined metal species has been in seawater. Nimmo *et al.*[1] using a simple analytical speciation scheme determined significant metal–organic complexation (31–41% for Ni, 98–99% for Cu, 0–18% for Fe) in a series of Liverpool Bay seawater samples. The practical speciation scheme employed consisted of adsorptive cathodic stripping voltammetric (ACSV) analyses of the dissolved metals before and after UV irradiation of the seawater sample. Using a similar scheme van den Berg *et al.*[2] have additionally determined appreciable quantities of dissolved metal–organic interactions in Mediterranean seawater for Al and Cr. Organic complexation of Co in seawater has also been quantified (Zhang *et al.*).[3] Cu has been shown to be organically complexed in seawater (Gerringa *et al.*,[4] Campos and van den Berg[5]) with strong and weak Culigand conditional stability constants being measured in marine waters (log $K'_{\mathrm{CuL}} = 15.6$ – Donat and van den Berg;[6] log $K'_{\mathrm{CuL}} = 6.6$ – Robinson and Brown[7]).

An understanding of the chemical speciation of dissolved trace metals is essential if we are to understand metal aquatic biogeochemical cycles. Marine biogeochemical processes which are influenced by changes in trace metal speciation are (i) biological uptake, (ii) biotoxicity, (iii) adsorption / desorption, (iv) precipitation / dissolution.

The source of the organic ligands complexing with the dissolved trace metals in marine systems has previously been assumed to originate from terrestrial run off, *in situ* biological production and regeneration in the water column or from the sediments. However, recent studies (summarised in Table I) have clearly illustrated the presence of dissolved organic metal complexing ligands in rainwaters (Ni and Co – Nimmo and Chester,[8] Ni, Co, Cu, Pb and Cd – Nimmo and Fones,[9] Cu, Zn, Pb – Cheng *et al.*,[10] Cu –

TABLE I

Recent studies indicating the presence of trace metal organic complexing ligands in rainwater

Elements	Analytical technique	Sampling location	$\frac{\text{\% non-labile}}{\text{total dissolved}}$	Reference
Ni, Co	ACSV (DMG)	NW Med.	Ni: 25, Co: 44	Ref. 8
Ni, Co, Cu, Cd, Pb	ACSV (DMG & Oxime)	Irish Sea	Ni: 28, Co: 33, Cu: 26, Cd: 33, Pb: 27	Ref. 9
Cu, Pb, Zn	ASV	Canada	Zn: 24, Cu: 36, Pb: 49	Ref. 34
Ni	ASCV (DMG)	Irish Sea	log K_{NiL} = 18–19.5; $\mathrm{CC_{Ni}}$* = 2–10 nM	Ref. 9
Cu	ACSV (Tropolone)	Rural East England	log K_{CuL} = 11–14; $\mathrm{CC_{Cu}}$* = 10.2–25 nM	Ref. 11

*$\mathrm{CC_{Cu}}$ = copper complexing capacity.
*$\mathrm{CC_{Ni}}$ = nickel complexing capacity.

Spokes *et al.*[11]), indicating that atmospheric wet deposition might be a significant additional source or recycling process to freshwater and marine environments. Nimmo and Chester[8] investigated the dissolved organic complexation of Ni and Co in a series of north-western Mediterranean rainwater samples. Dissolved Ni and Co were measured, using ACSV, before ($\mathrm{ACSV_{labile}}$) and after UV irradiation ($\mathrm{ACSV_{total}}$) of the samples to evaluate the organic complexation. The extent of organic complexation varied markedly from sample to sample with an observed range of complexation (expressed as a percentage of the total dissolved trace metals) for Ni of 0–79% and 0–82% for Co. The overall average % organic complexation was found to be 25% and 44% for Ni and Co respectively. A similar approach was taken for detection of the pool of organic metal (Cu, Pb, Cd, Ni and Co) complexing ligands in Irish Sea rainwaters (Nimmo and Fones[9]). Complexing ligands for all the considered metals were detectable. An overall % of the $\mathrm{ACSV_{non\text{-}labile}}$ dissolved metal of the total dissolved metal fraction were found to be 32 for Cu, 38 for Cd, 33 for Pb, 35 for Ni, 38 for Co.

Cheng *et al.*[10] recently evaluated the dissolved speciation of Cu, Pb, Cd, and Zn in rainwaters using a scheme combining physical characterisation by size fractionation and chemical characterisation by dissociation kinetics with final detection by DPASV (differential pulse anodic stripping voltammetry). They reported that for Zn, 76% of the total dissolved fraction present in the rainwater was $\mathrm{ASV_{labile}}$ and 64% of the total dissolved Cu and 51% of the total dissolved Pb was present as the $\mathrm{ASV_{labile}}$ fraction, contributing further evidence to the existence of metal organic complexes in rainwaters. It is therefore apparent that in rainwaters metal organic complexing ligands exist and represent a potential pool not previously considered, of complexing ligands to the marine coastal and open ocean zones, which may modify surface marine trace metal biogeochemical processes.

The source and environmental availability of these ligands have so far not been studied. The presented work discusses contrasting sources *i.e.* aerosol populations derived from two end member populations one from an urban environment and the second representing a crustal source (Saharan dust collected off the coast of North Africa) as possible atmospheric sources. Evaluation was achieved by carrying out laboratory simulations involving the mixing of aerosol end members in seawater/artificial rainwater followed by $ACSV_{labile}$ and $ACSV_{total}$ determinations. The kinetics of solubilisation of the metal complexing material were also monitored during simulations to aid in the prediction of the immediate environmental impact of such deposition.

The laboratory simulations carried out on LUAP were then compared with detected metal organic complexation observed in rainwater samples and from seawater/rainwater solubility investigations with high volume collected aerosol samples from a rural/coastal sampling site in NW England.

EXPERIMENTAL

Source of Aerosol End Members

Two end member aerosol populations were used in the current study. The urban aerosol material used was LUAP, (Liverpool Urban Aerosol Particulate). This has also been used in other studies (*e.g.* Ref. 12) as being representative of a typical urban environment. The LUAP was retrieved from the high volume ventilation filtration system located at the University of Liverpool campus. As Liverpool is situated on the north western coast of England, dominated by westerly winds passing over the Irish Sea, the aerosol population is classed as a marine dominated urban aerosol.

The crustal end member aerosol was collected using a nylon mesh off the west coast of Africa (transect 04°13'N 28°55'W to 06°56'N 28°07'W). The chemical characteristics of the collected dust was indicative of Saharan dust which is transported on the north east trade winds across the Atlantic, leading to Saharan dust pulses.[13]

Methodology

Each of the aerosol end member populations underwent timed rainwater and seawater solubility studies. These experiments were carried out in a Class 100 clean laminar flow cabinet. The procedure was as follows; one litre of pressure filtered (acid washed 0.45 μm, Sartorious cellulose acetate membrane filter) and MnO_2 cleaned (overnight with 4 x 10^{-4} M; see Ref. 14) UV irradiated (2 hours under a 500 W Hg discharge lamp) seawater was placed into an acid washed 1 litre Teflon bottle. Teflon containers were used to minimise the potential of adsorption of solubilised trace metals, organic complexing ligands and metal – organic complexes. Approximately 10 mg or 50 mg of the urban dust (100 mg Saharan dust) was weighed out accurately, added to the seawater / rainwater. At pre-determined time intervals (*i.e.* 1, 2, 5, 10, 15, 30, 60, 180, 300 minutes and 24 hours), aliquots were withdrawn and immediately filtered through a 0.45 μm cellulose acetate membrane filter into a 125 ml clean HDPE (high density polyethylene) storage bottle. The filter units had previously been acid washed and rinsed thoroughly with Milli-Q water to minimise contamination. The time for each filtration was about 20 seconds. The 100 ml aliquot was then divided into two. One half was acidified with 1:1 »Aristar« HCl whilst the other 50 ml was untreated. Untreated samples were then analysed by ACSV for Cu, Cd, Pb, Ni and Co, before UV irradiation yielding the $\text{ACSV}_{\text{labile}}$ whereas the acidified samples were analysed after UV irradiation yielding the total dissolved metal concentrations. $\text{ACSV}_{\text{non-labile}}$ fractions may then be calculated ($\text{ACSV}_{\text{non-labile}} = \text{ACSV}_{\text{total}} - \text{ACSV}_{\text{labile}}$).

The solubility of the trace metals associated with LUAP in rainwater at pH = 4.3 was undertaken as described above using 10 mg of the dust in artificial rainwater. Artificial rain water was prepared in Milli- Q water following the recipe of Statham and Chester,[15] and had a composition; (a) cations (μM): Na^+ (5), K^+ (2), Ca^{2+} (5), Mg^{2+} (2), NH_4^+ (20), H^+ (23), and (b) anions (μM): Cl^- (9), NO_3^- (35) and SO_4^{2-} (10). The pH was adjusted to 4.3 by the dropwise addition of quartz-distilled HNO_3. A pH of 4.3 was chosen to be representative of urban rainfall.

The chosen analytical technique ACSV enabled the dissolved species of Ni, Co, Cu, Pb and Cd to be determined by direct analysis in the equilibrated seawater and artificial rainwater. The analytical procedure for the determination of dissolved Ni and Co was based on a method originally designed by Pihlar *et al.*[16] For a determination, 15 cm^3 of the equilibrated seawater or artificial rainwater was pipetted into a polarographic cell. To this was added 150 μl of 1.0 mol dm^{-3} boric acid (»Analar« boric acid, Merck) solution to give a sample pH of 8.4. Thirty μl of 0.1 mol dm^{-3} dimethylglyoxime (»Analar« DMG, Merck) stock solution was pipetted into the polarographic cell to give a solution concentration of 2×10^{-4} mol dm^{-3}. The solution was then purged with nitrogen for five minutes to remove dissolved oxygen. An initial stripping scan (using a Metrohm Polarecord 506 polarograph) was carried out by collecting any formed metal complex on a hanging mercury drop electrode (HMDE – Metrohm 663 VA) at –0.6 V (*vs.* Ag/AgCl) for one minute. After a ten second quiescent period a differential pulse cathodic scan was applied at the HMDE (scan rate 15 mV/s and pulse height 40 mV). Reduction of the Ni and Co adsorbed at the HMDE occurred at –0.89 V and –1.02 V (*vs.* Ag/AgCl) respectively. The current response was then calibrated by two internal standard additions, generally 8 nM for Ni and 4 nM for Co (Spectrosol, Merck).

Similarly the technique employed to determine Cu, Pb and Cd in the equilibrated seawater and artificial rainwater was developed from that of van den Berg.[17] For a determination of dissolved Cu, Pb and Cd, 15 cm^3 of the sample was pipetted into a clean polarograph cell, to which was added 150 μl of 1.0 mol dm^{-3} HEPES (»Analar«, Merck) stock solution yielding a pH of 7.8. To the buffered solution, 30 μl of 4×10^{-3} mol dm^{-3} stock solution of oxine (»Analar«, Merck) was added to yield a solution concentration of 8×10^{-6} mol dm^{-3}. For dissolved Cu analyses, a one minute collection period was maintained at –1.4 V on the HMDE. After a 10 second quiescent period, the potential was adjusted to –0.2 V followed by a 20 second wait period, to allow for the metal to diffuse out of the mercury drop and form an adsorbed film of complexes. A differential pulse cathodic scan was then applied at the HMDE (5 mV/s scan rate and 40 mV pulse potential) and Cu reduction potential was observed at –0.34 V. For the determination of Pb and Cd it was found that the sensitivity was considerably less than that for Cu and that the large Cu reduction peak masked the Pb reduction peak. This interference was minimised by commencing the reduction scan at –0.4 V. The collection time was altered depending on the metal concentration, usually one to three minute collection periods were employed. Reagents used in ACSV analysis were cleaned prior to used after 24 hour equilibration with a 1 x 10^{-4} M MnO_2 suspension. All reagent metal blanks were below the analytical detection limits. The acceptable accuracy for the applied ACSV technique used in this study has been previously stated elsewhere.[18]

Experiments were also performed to determine the potential loss or addition *via* adsorption to the reaction vessel walls or *via* contamination of trace metals in seawater/artificial rainwater. To assess adsorptive losses seawater/rainwater solutions were spiked with Ni 20 nM, Co 2 nM, Cu 35 nM, Pb 30 nM and Cd 3 nM. This solution was then placed into a 1 litre Teflon bottle. Aliquots were drawn off (after 24 hours equilibration) and treated as described above and then analysed for $ACSV_{labile}$ and $ACSV_{total}$ dissolved trace metals. Adsorption of all considered trace metals during the experimental time period was negligible. This experiment also illustrates that there were no sources of metal organic complexing ligands either from the reaction vessel or during the filtration stage as there was no difference between the measured $ACSV_{labile}$ and $ACSV_{total}$ (and hence $ACSV_{non\text{-}labile}$) dissolved metal fractions.

The experimental blanks were determined from $ACSV_{labile}$ and $ACSV_{total}$ analyses of trace metal »free« seawater and artificial rainwater which had been equilibrated in Teflon bottles for 24 hours. No observed changes in the seawater or rainwater trace metals concentrations were detected, therefore, the contribution of contaminant trace metal fractions were minimal.

Comparative seawater and rainwater solubility studies on selected high volume collected aerosol samples from the Irish Sea were carried out. Samples were collected using an »in-house« high volume collector and Whatman 41 filters were used as the collection material. The sampling site was located at Hazelrigg, 4 kilometres from Morecombe Bay, NW England. Details of the sampling equipment and sampling protocols may be found in Ref. 14. During a rainwater or seawater solubility study a portion of the collected sample (third) was placed into a 1 L Teflon bottle and 250 ml seawater or artificial rainwater, prepared as described above, was added whilst being shaken and allowed to equilibrate for 1 hour. Then the seawater / rainwater was filtered and analysed, as above, for $ACSV_{labile}$ and $ACSV_{total}$. The effects of potential contamination of the different metal fractions for the Whatman 41 was investigated by placing a blank filter in clean seawater, equilibrated for 1 hour. Following filtration the dissolved metal $ACSV_{labile}$ and $ACSV_{total}$ fractions were determined. Contamination for all metals was not detected (< limits of detection). Additionally the potential adsorption of metal fractions onto the filter material during equilibration was evaluated with a metal spiked seawater sample. No significant differences were detected for all metals before and after equilibration between both the $ACSV_{labile}$ and $ACSV_{total}$ metal fractions, indicating negligible adsorption of metal fractions and $ACSV_{non\text{-}labile}$ metal fraction contamination of the rainwater or seawater from the filter material.

THE OPERATIONALITY OF ACSV ANALYSIS

A measure of the extent of organic complexation may be established by taking the difference between $\text{ACSV}_{\text{labile}}$ and $\text{ACSV}_{\text{total}}$ dissolved metal concentrations, yielding the $\text{ACSV}_{\text{non-labile}}$ metal fraction.

The value of the $\text{ACSV}_{\text{labile}}$ metal fraction is dependent upon the competition for metal complexation between the solubilised organic and inorganic complexing ligands in the seawater or artificial rainwater and the added ligand used in ACSV analyses (*i.e.* DMG or oxine). The competition is set by the comparable α-coefficients for the natural and added complexing ligands. The lability of metals measured by ACSV in the presence of organic material may be defined from theory. The distribution of dissolved metals amongst the various ligand groupings is determined by the concentration of the added (AL) and natural ligands (L) and by the respective stability constants of the metal complexes formed. Hence the $\text{ACSV}_{\text{labile}}$ metal may be defined as:

$$[\mathrm{M}_{\text{labile}}] = [\mathrm{M}^{n+}]\,(\alpha_{\mathrm{m}'} + \alpha_{\mathrm{MAL}}) \tag{1}$$

where $\alpha_{\mathrm{m}'}$ is the inorganic complexation α-coefficient[19] and α_{MAL} is that for the metal complexation with the added ligand. (The $\mathrm{M}_{\text{labile}}$ may also include metal that is present as weak organic complexes, which have α-coefficients $< \alpha_{\mathrm{MAL}}$). The $\alpha_{\mathrm{m}'}$ value may be calculated from:

$$\alpha_{\mathrm{m}'} = 1 + \Sigma\beta_{\mathrm{ML}i}\,[\mathrm{L}]^i$$

$\beta_{\mathrm{ML}i}$ being the inorganic stepwise conditional constants adapted from Turner *et al.*[20] (adjusted for seawater/rainwater ionic strength). L are the inorganic ligand concentrations.

α_{MAL} is calculated from:

$$\alpha_{\mathrm{MAL}} = (\beta'_{\mathrm{M(AL)}i} C_{\mathrm{AL}i}) \tag{2}$$

$\beta'_{\mathrm{M(AL)}i}$ is the conditional stability constant for the complex of metal M with i added ligands AL, and C_{ALi} are the added ligands concentrations. Published stability constants (Cu, Cd and Pb – Martell and Smith,[21] Ni – van den Berg and Nimmo,[22] Co – Zhang *et al.*[3]) were corrected for side reactions with the major cations and anions and the analytical pH (8.4 for Ni and Co; 7.8 for Cu, Pb and Cd).

The total metal concentrations, C_{M} is given by:

$$C_{\mathrm{M}} = [\mathrm{M}^{n+}]\,(\alpha_{\mathrm{M}'} + \alpha_{\mathrm{MAL}} + \alpha_{\mathrm{ML}}) \tag{3}$$

α_{ML} is the coefficient for the natural complexation , with an effective single ligand, L,

$$\alpha_{ML} = K'_{ML}C_L \tag{4}$$

where K'_{ML} is the effective conditional stability constant of the natural complex and C_L is the effective ligand concentration. Metal ions present in the rainwaters may be complexed by different types of natural ligands. The group of detected ligands determines α_{ML}. Weak ligands, *i.e.* those that have $\alpha_{ML} < \alpha_{MAL}$ would dissociate in the presence of the added ligands and would therefore be measured in the $ACSV_{labile}$ fraction whereas strong natural metal complexes having a $\alpha_{ML} < \alpha_{MAL}$ would form $ACSV_{non\text{-}labile}$ complexes which are detected only after UV irradiation. Table II presents the calculated α_{MAL} for the applied analytical conditions with the equivalent $\alpha_{m'}$ for both the artificial rainwater and the seawater.

All $\alpha_{m'}$ values were greater in seawater compared to rainwater owing to the major inorganic species present in seawater. The applied α_{MAL} at each analytical pH in rainwater were greater than the equivalent $\alpha_{m'}$. Therefore any metal inorganic complexes will dissociate with the addition of the ACSV ligand and be measured in the $ACSV_{labile}$ fraction. There was also very little difference associated between α_{MAL} for Co and Ni in both seawater and rainwater allowing direct data comparisons to be made between the two media, the α_{MAL} being much greater than corresponding $\alpha_{m'}$. However there was a large differences between α_{MAL} for oxine in seawater compared to rainwater (*i.e.* α_{MAL} seawater < α_{MAL} rainwater) owing to the strong competition of Mg/Ca complexation for oxine. As Table II illustrates for Pb the $\alpha_{m'}$ seawater is similar to the α_{MAL} seawater whereas for Cd, α_{MAL} seawater is calculated to be lower than the equivalent $\alpha_{m'}$. This is clearly in error owing to the ability of Cd to be detectable in seawater by ACSV. This discrepancy for

TABLE II

Calculated Ni, Co, Cu, Pb, and Cd $\alpha_{m'}$ and α_{MAL} in seawater and artificial rainwater at the applied analytical pH

	$\alpha_{m'}$				α_{MAL}			
	Rainwater		Seawater		Rainwater		Seawater	
	pH = 7.8	pH = 8.4	pH = 7.8	pH = 8.4	pH = 7.8	pH = 8.4	pH = 7.8	pH = 8.4
Ni	–	0.01	–	0.20	–	10.12	–	9.82
Co	–	0.02	–	0.25	–	5.61	–	5.45
Cu	0.27	–	0.65	–	9.07	–	6.73	–
Pb	0.32	–	1.24	–	2.15	–	1.08	–
Cd	0.01	–	1.05	–	1.13	–	0.05	–

Cd may be explained by inaccuracies in the published complex stability constants for the first order complex Cd-oxine complex and/or (ii) greater importance of the Cd-oxine higher order complex for which there are no published data. Clearly therefore there is a need to re-evaluate the complex formation constants of Cd and Pb with oxine.

With the addition to the measurement of $\mathrm{ACSV}_{\text{non-labile}}$, Ni complexing capacity titrations were carried out on equilibrated seawater with both the Saharan dust and the LUAP end-members. The theory and practical protocols relating to these determinations maybe found in Ref. 22.

RESULTS AND DISCUSSION

End-member aerosol trace metal seawater/rainwater solubilities (after 24 hours equilibration) and corresponding $\mathrm{EF}_{\mathrm{crust}}$ (crustal enrichment factors) are presented on Table III. The evaluation of $\mathrm{EF}_{\mathrm{crust}}$ has been widely utilised to attribute the predominant sources of the aerosol associated trace metals in sample populations (see for example Refs. 23 and 24).

The elemental crustal enrichment factor for the soluble metals in the end-member aerosol were calculated from:

$$\mathrm{EF}_{\mathrm{crust}} = \frac{([\mathrm{E}]/[\mathrm{Al}])_{\mathrm{aerosol}}}{([\mathrm{E}]/[\mathrm{Al}])_{\mathrm{crust}}} \tag{5}$$

Where

[E] = Aerosol elemental concentration after total acid digestion (*i.e.* concentrated HF / $\mathrm{HNO_3}$ – see Ref. 14 for further analytical details)

[Al] = Aerosol aluminium concentration after total acid digestion

$([\mathrm{E}]/[\mathrm{Al}])_{\mathrm{crust}}$ = Elemental crustal ratio (taken from Ref. 25).

Calculated $\mathrm{EF}_{\mathrm{crust}} > 10$ would indicate enrichment indicating an non-crustal aerosol source. $\mathrm{EF}_{\mathrm{crust}}$ values 10 would be indicative of an aerosol elemental crustal source. It is apparent therefore, (Table III) that the LUAP has a strong anthropic chemical signature with high trace metal solubilities and very high $\mathrm{EF}_{\mathrm{crust}}$ values (*e.g.* $\mathrm{EF}_{\mathrm{crust}}$ Pb = 1282; Cd = 1865). The Saharan dust illustrated contrasting behaviour with low $\mathrm{EF}_{\mathrm{crust}}$ (< 10 for all metals) with correspondingly low seawater solubilities (< 10% for all metal except Cd). These general findings are consistent with the literatur.[12,13,26] Trace metals associated with anthropically influenced aerosols have a greater association with the »exchangeable« (potentially environmentally mobile) solid phase as determined from sequential leach analyses,[26] whereas Saharan dust trace metals are incorporated in the more residual crustal lattice solid phase.

TABLE III

End-member (LUAP and Saharan dust) aerosol trace metal EF_{crust} and seawater and artificial rainwater solubilities

	LUAP EF_{crust}	LUAP / SW % Soluble	LUAP / RW % Soluble	Saharan EF_{crust}	Saharan / SW % Soluble
Ni	28	23	30		7.2
Co	17	37	23	1.0	4.7
Cu	68	49	57	0.82	9.3
Pb	1282	88	26	3.9	2.3
Cd	1865	61	58	1.5	18.6

The release of total dissolved trace metal fractions into seawater and artificial rainwaters for both aerosol end-members was found to be an extremely rapid process. The results from the kinetic experiments are plotted and presented in Figures 1 (LUAP/artificial rainwater), 2 (Saharan dust/seawater), 3 (LUAP/seawater). The figures present the $ACSV_{non\text{-}labile}$, $ACSV_{labile}$ and total dissolved fractions. All total dissolved metal fractions rapidly attained equilibrium (within 30 minutes) both in the seawater and artificial rainwater and for contrasting end member aerosol populations. The present observations are in agreement with Williams *et al.*[27] who showed that for PFA in aqueous suspension, Fe, Mn, Cu, and Zn exhibited a fast initial leach rate (first few minutes) followed by a slower rate of dissolution over the following six hours. A similar observation was reported by Statham and Chester[15] for Mn from marine eolian particles in artificial rainwaters. Recently, Hamilton-Taylor *et al.*[28] have found for Pb, Zn and Cu that the dissolution kinetics of rural aerosol in a range of natural freshwaters was rapid (again minutes) and after 30 minutes there was little or no further dissolution.

No difference was detectable in the solubilities for different total dissolved metal fractions with different concentrations of LUAP in seawater (10 and 50 mg l^{-1}), implying little influence on the dissolution of trace metals with changing particle/solution ratio. A comparable ascertain was made by Williams *et al.*[27] for PFA equilibrated in aqueous solution.

$ACSV_{non\text{-}labile}$ fractions were detectable for all trace metals in both rainwater and seawater simulations using LUAP and Saharan dust, verifying the potential source of aerosol material for metal organic ligands to the marine environment.

The kinetics of solubilisation behaviour of the $ACSV_{non\text{-}labile}$ are also illustrated on Figures 1–3. As with the total metal fractions rapid rates of dissolution were exhibited with no changes occurring after 30 minutes. Generally the $ACSV_{non\text{-}labile}$ metal fraction behaved in a similar manner to the

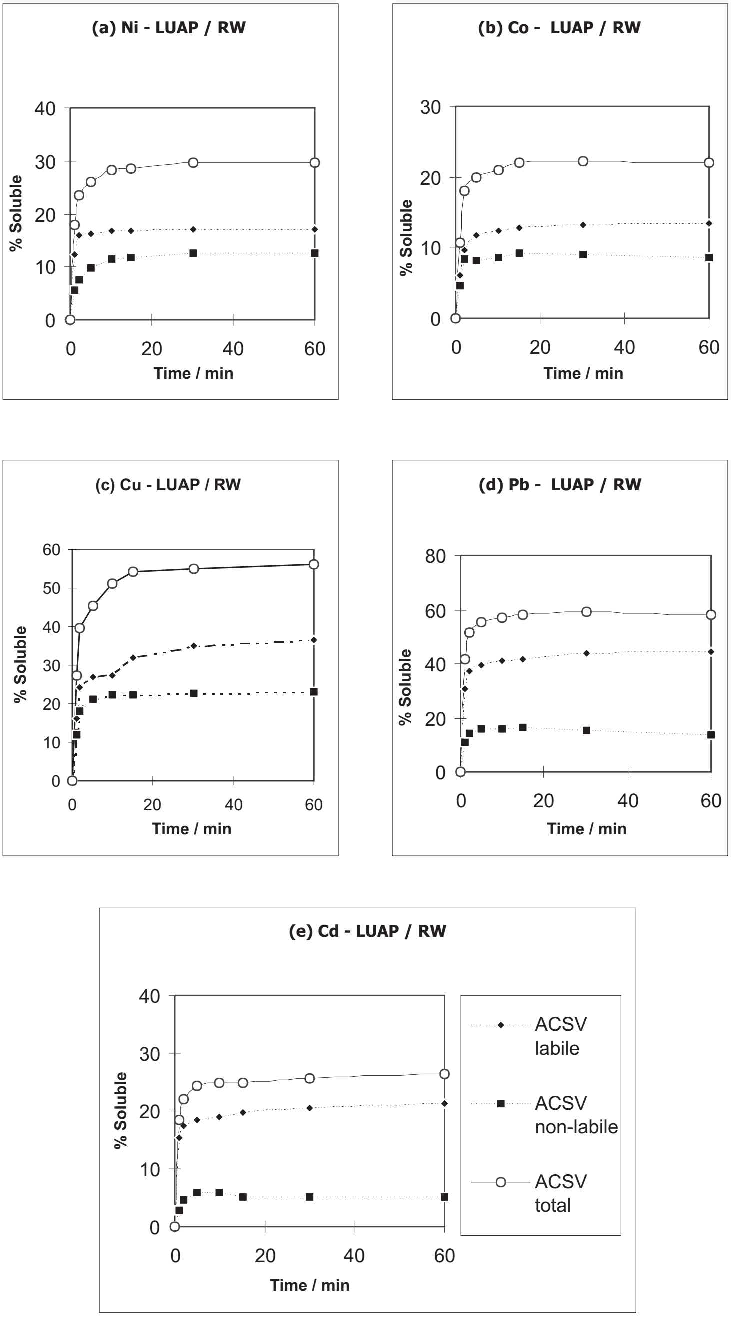

Figure 1. Release of trace metal fractions ($ACSV_{non\text{-}labile}$, $ACSV_{labile}$ and total) from LUAP (10 mg l^{-1}) into artificial rainwater (expressed as % soluble of total aerosol trace metal). (a) Ni, (b) Co, (c) Cu, (d) Pb, (e) Cd.

$ACSV_{total.}$ However for a number of metals this was not always the case. The $ACSV_{non\text{-}labile}$ fractions for Co and Cd associated with LUAP equilibrated in seawater indicated adsorptive behaviour immediately following solubilisation. A similar observation was detected for the $ACSV_{non\text{-}labile}$ fractions of Co and Pb associated with the Saharan dust equilibrated in seawater. These results would suggest that different metal fractions ($ACSV_{non\text{-}labile}$ and $ACSV_{labile}$) may have different reactivities, with the $ACSV_{non\text{-}labile}$ fraction undergoing preferential adsorption. This clearly has implications on their marine biogeochemical cycling and the influence on these processes of dissolved organic complexing ligands. Changes in their biogeochemical cycles will occur leading to differences in individual metal species oceanic residence times.

Comparison of the % $ACSV_{non\text{-}labile}$ / $ACSV_{total}$ (this gives a simple indication of the relative organic complexation of the dissolved trace metals) for LUAP associated Ni and Co at equilibrium indicates greater values in rainwater than seawater (Table IV), indicating relatively greater aerosol solubilities of organic complexing ligands compared to Ni and Co solubilities in rainwater. The relative increase in metal complexing ligand fractions for Ni and Co may have derived from the enhanced solubility of basic organic aerosol associated compounds, possible N containing compounds. Heterocyclic N compounds derived from aerosols have recently been detected,[29] and these compounds have been found to have significantly elevated solubilities in aqueous solution below pH = 6.[30] Complexation of Ni and Co by N containing organic compounds form very stable complexes with high complex formation stability constants. Clearly further investigations are required to evaluate the chemical associations of the soluble complexing ligands. An increase of the % $ACSV_{non\text{-}labile}$ / $ACSV_{total}$ for Cu, Pb and Cd was detected in seawater compared with rainwater (for LUAP – Table IV). Such differences may be attributed to either (i) greater solubility of acidic organic compounds

TABLE IV

% $ACSV_{non\text{-}labile}$ / $ACSV_{total}$ Ni, Co, Cu, Pb and Cd fractions (after 24 hours equilibration) soluble in seawater and artificial rainwater from LUAP and Saharan dust

Metal	Seawater		Rainwater
	Saharan (100 mg l^{-1})	LUAP (10 mg l^{-1})	LUAP (10 mg l^{-1})
Ni	66	26	43
Co	23	27	39
Cu	59	53	35
Cd	56	36	19
Pb	23	55	24

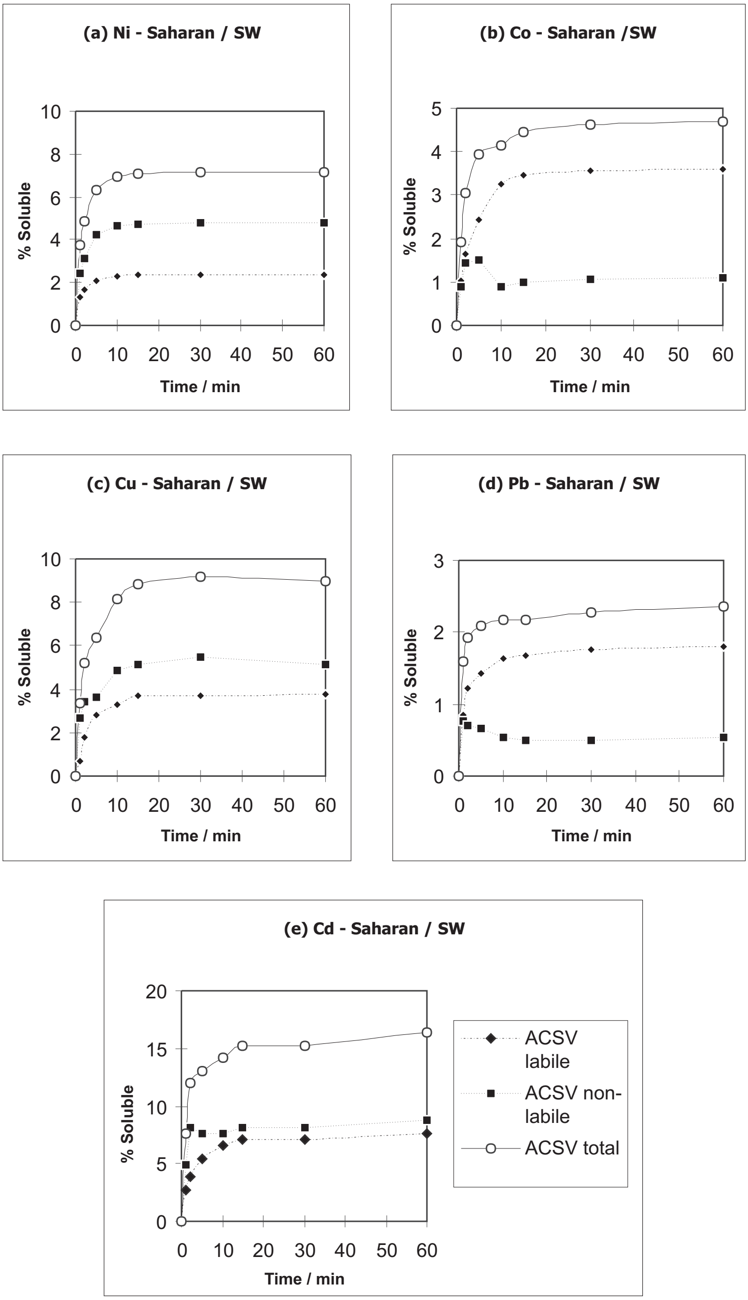

Figure 2. Release of trace metal fractions ($\mathrm{ACSV}_{\text{non-labile}}$, $\mathrm{ACSV}_{\text{labile}}$ and total) from Saharan dust (100 mg l^{-1}) into seawater (expressed as % soluble of total aerosol trace metal). (a) Ni, (b) Co, (c) Cu, (d) Pb, (e) Cd.

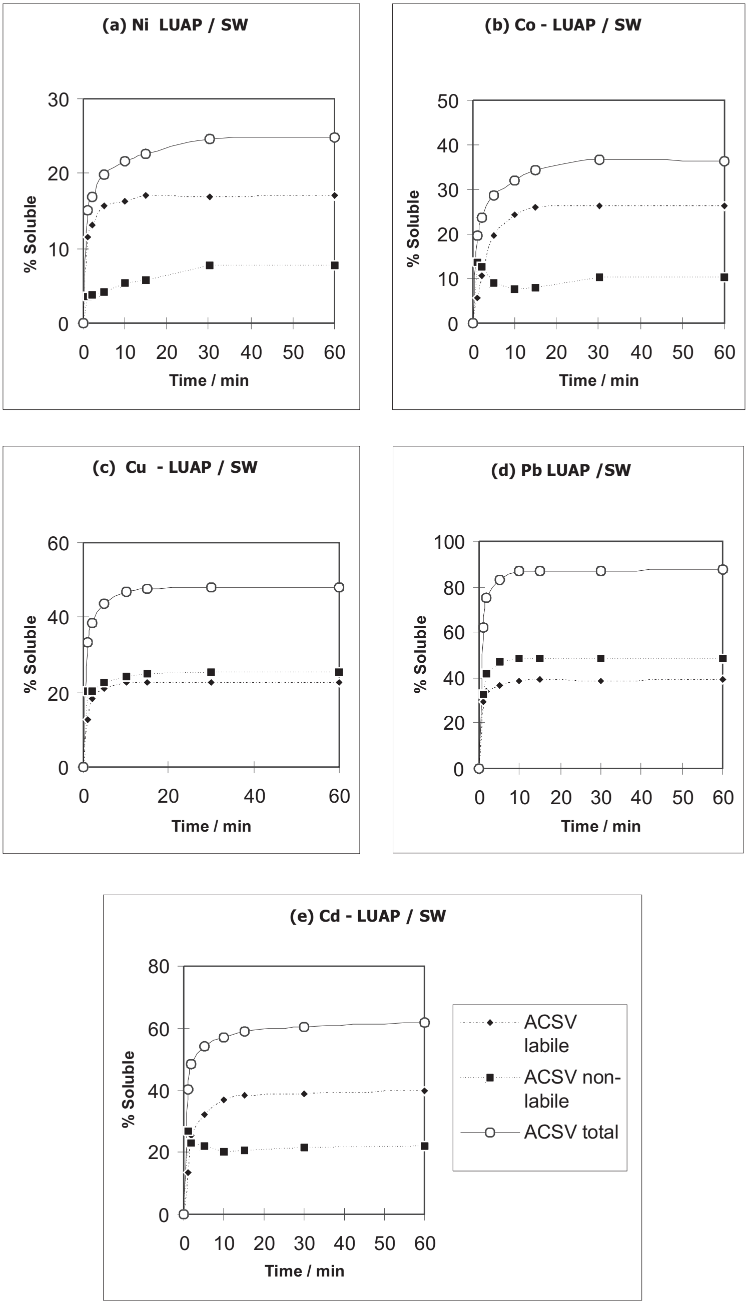

Figure 3. Release of trace metal fractions ($ACSV_{non\text{-}labile}$, $ACSV_{labile}$ and total) from LUAP (10 mg l^{-1}) into seawater (expressed as % soluble of total aerosol trace metal). (a) Ni, (b) Co, (c) Cu, (d) Pb, (e) Cd.

complexing specifically with Cu, Pb and Cd possibly S containing organic compounds or (ii) the comparatively lower metal α-coefficients in seawater with the ACSV added organic ligand leading to the detection of a wider range of organic metal complexes as the ACSV $_{\text{non-labile}}$ fraction.

Crustal end members seawater solubilised trace metals generally had either similar (Co) or greater relative organic complexation (Ni, Cu, Cd) except for Pb than the equivalent equilibrated LUAP (Table IV). The source of complexing ligands from crustal material such as desert dust is quite surprising as such material has a low organic content. Another possible source, on the Saharan dust, of the soluble organic complexing compounds might be the injection into the aerosol population of seasalts which would have organic coatings derived from the sea surface microlayer. Organic complexing ligands have been found in the seawater for Ni and Cu,[1] Co,[3] and Pb[31] although little evidence has been observed for Cd. To further investigate the source of the metal complexing ligands, precursor crustal material should be considered in future experiments.

To characterise the aerosol seawater soluble metal complexing ligands, equilibrated samples of seawater with the LUAP and Saharan dust were determined for Ni complexing capacities and the conditional stability constant for complex formation. This was carried out as explained previously by van den Berg and Nimmo.[22] Very high conditional stability constants were detected ($\log k'_{\text{NiL}} = 18.3 \pm 0.3$ and 19.26 ± 0.4 for LUAP and Saharan dust respectively). Such stable organic complexes for Ni have been previously observed in seawater with $\log k_{\text{NiL}}$ ranging from 17.3 – 18.7.[22] The end member aerosols had a Ni complexing capacity equivalent to 1.0 ± 0.1 nmol mg^{-1} (LUAP) and 0.038 ± 0.005 nmol mg^{-1} (Saharan dust).

To complement the model solubility studies, seawater and rainwater solubility investigations were carried out on a series of selected coastal high volume collected aerosol samples (North west coast of England, $n = 8$; samples were chosen to represent all wind systems influencing the sampling site). The results of these studies are presented on Table V. In addition the elemental EF_{crust} are presented on Table V and are compared with the end member LUAP. Considering the EF_{crust} (for all elements $\text{EF}_{\text{crust LUAP}} > \text{EF}_{\text{crust Irish Sea}}$) it is clearly apparent, as expected, that the »Irish Sea« aerosols are lower in anthropic character than the LUAP aerosol population.

The presence of metal complexing ligands were detected for all the considered metals. However contrary to the LUAP no differences between all the relative metal and complexing ligand solubilities between seawater and rainwater was observed, these being contrary to those observations for LUAP with particular reference to Ni and Co. The contrasting behaviour for the two aerosol populations may be accounted by the following (i) lower anthropic chemical character of the Irish sea aerosol (as shown by comparatively lower EF_{crust} compared to those of LUAP), or (ii) anthropic derived metal complexing organic ligands may have been modified during transport

TABLE V

Soluble % $ACSV_{non\text{-}labile}$ / $ACSV_{total}$ Ni, Co, Cu, Pb and Cd from Irish Sea aerosol samples (n = 8) equilibrated in seawater / artificial rainwater, coastal NW England rainwaters

	Irish Sea aerosol		Irish Sea rainwater	Irish Sea aerosol
	seawater	rainwater	(rainfall wt. mean)	EF_{crust}
Ni	23 ± 9	33 ± 10	35	14
Co	22 ± 7	28 ± 9	33	1.8
Cu	33 ± 10	28 ± 10	32	14
Cd	24 ± 8	22 ± 7	25	428
Pb	35 ± 15	31 ± 8	34	290

from the urban source by photochemical, and/or wetting and drying cycles.[11,32] Wetting and drying cycles lead to the uptake of H_2SO_4 and HNO_3 yielding low pH and high ionic strengths within the aerosol hydration layer possibly rendering a fraction of the soluble organic material unavailable for metal complexation at the analytical pH. Table V additionally compares the % $ACSV_{non\text{-}labile}$ / $ACSV_{total}$ metal fractions for a series of rainwaters collected at a comparable sampling location and period as the »Irish Sea« aerosol collection. There are no practical differences detectable between the aerosol rainwater solubility simulations and the collected rainwaters (for all the considered metals), which would indicate that the model simulation studies mimic the natural process of the dissolution in rainwater of aerosol associated complexing ligands.

CONCLUSIONS

Laboratory simulation studies were performed with LUAP and Saharan dust in seawater and artificial rainwater (LUAP). Kinetic studies clearly illustrated rapid desorption with equilibrium being reached within 30 minutes for all the considered metals (Ni, Co, Cu, Cd and Pb) and their different speciation fractions ($ACSV_{non\text{-}labile}$, $ACSV_{labile}$, $ACSV_{total}$). Rapid dissolution of aerosol associated trace metals is consistent with the literature (*e.g.* Refs. 15, 27, 28).

All metals released in seawater and artificial rainwater for both aerosol end members were organically complexed to some degree, represented by the % $ACSV_{non\text{-}labile}$ / $ACSV_{total}$ with enhanced relative solubilities of Ni and Co complexing ligands from LUAP in rainwater compared to seawater. The origin possibly basic, N containing species being possible candidates.

The % $ACSV_{non\text{-}labile}$ fractions soluble in seawater from high volume collected aerosol samples from the Irish Sea were also detected. No difference were apparent for the % $\mathrm{ACSV}_{\text{non-labile}}$ / $\mathrm{ACSV}_{\text{total}}$ in seawater and rainwater for Ni and Co (and Cu, Pb and Cd) which was contrary to the observations using LUAP. Such contrasting behaviour (compared to LUAP) may be explained by (i) the »Irish Sea« aerosol population being a »dilution« of the anthropic end member aerosol with natural aerosol compounds leading a lower relative contribution of soluble metal organic complexing ligands or (ii) by atmospheric processes (photochemical; aerosol wetting/drying cycles) during urban aerosol transport, from source to the »Irish sea« aerosol sampling location, modifying the soluble complexing organic material.

The behaviour of the $\mathrm{ACSV}_{\text{non-labile}}$ post deposition with time for LUAP associated Co and Cd in seawater and Co and Pb associated with Saharan dust in seawater clearly indicated rapid re-adsorption possibly following organic complexation. It is therefore apparent that organic complexation of dissolved trace metals by aerosol derived complexing ligands potentially will influence the biogeochemistries of trace metals in surface marine waters.

Characterisation of the aerosol soluble ligands in seawater for Ni was carried out by complexing capacity titrations. Conditional stability constant of $\log K'_{\mathrm{NiL}} = 18.3 \pm 0.3$ – Saharan dust; 19.26 ± 0.4 – LUAP were calculated, with corresponding complexing capacities of 1.0 ± 0.1 nmol mg^{-1} (LUAP) and 0.038 ± 0.005 nmol mg^{-1}.

Clearly the present study offers the first direct evidence of soluble metal complexing ligands associated with aerosol material, which compliments previous studies which have detected complexing organic ligands in rainwaters collected from the NW England,[9] NW Mediterranean[8] and SE England.[11] However still very little is known about the chemical composition of the soluble organic complexing ligands. Future studies should be focused to evaluate the factors controlling (pH, ionic strength, aerosol source) the solubility of metal complexing organic material and to attempt to chemically identify the major soluble organic components. Included in these studies should be the evaluation of an expanded suite of trace metal complexing capacities and metal complex formation conditional stability constants (other than Ni).

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SAŽETAK

Atmosfersko taloženje: potencijalni izvor liganada za kompleksiranje kovina u tragovima u morskom okolišu

Malcolm Nimmo, Gary R. Fones i Roy Chester

U kišnici i morskoj vodi nađeni su topljivi organski ligandi koji kompleksiraju kovine (Cu, Pb, Cd, Ni i Co), i koji su u vezi s krajnjim članovima aerosolnih populacija. Krajnji su članovi reprezentativni za populaciju urbanih aerosola u Europi (LUAP – Liverpool Urban Aerosol Population), te za populaciju aerosola koji sadrže litosferski materijal (sitna saharska prašina, prikupljena u blizini obale zapadne Afrike). Istraživanja su obavljena pomoću ACSV (adsorpcijska voltammetrija katodnog otapanja) i pokazuju da spomenuti krajnji članovi predstavljaju izvor organskih liganada za sve ispitivane kovine. U slučaju frakcije LUAP topljive u morskoj vodi dio nazočnih kovina koja se oslobađa nakon UV ozračivanja (Cu: 26%, Pb: 55%, Cd: 36%, Ni: 26% i Co: 27%) nađen je tehnikom ACSV nelabilnom. Za usporedbu, vrijednosti dobivene za saharsku prašinu iznose Cu: 59%, Pb: 23%, Cd: 56%, Ni: 66% i Co: 23%. Ova su ispitivanja pokazala da je proces otapanja u morskoj vodi i kišnici svih kovina i njihovih frakcija vrlo brz, te da nema daljnjeg oslobadjanja nakon *ca.* 30 minuta. Kod nekoliko kovina dolazi do readsorpcije ACSV-nelabilne kovine na površinu čestice aerosola (Co i Pb – saharska prašina/morska voda; Co i Cd – LUAP/morska voda), što upućuje na to da pojedine frakcije ispitivanih kovina podliježu različitim geokemijskim reakcijskim putovima što dovodi do potencijalnih razlika njihovih vremena zadržavanja u moru.

Uvjetne konstante stabilnosti i kapacitet kompleksiranja za Ni u morskoj vodi određene su nakon uravnotežavanja s obje krajnje aerosolne vrste. Utvrđene vrijednosti log K'_{NiL} iznose 18,3 ± 0,3 i 19,26 ± 0,4 za LUAP odnosno za saharsku prašinu. Ekvivalentni kapaciteti kompleksiranja su 1,0 ± 0,1 nmol mg^{-1} i 0,038 ± 0,005 nmol mg^{-1}.