

## Lead and copper speciation in remote mountain lakes

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### Abstract

We determined the chemical speciation of lead and copper in remote mountain and high-latitude lakes at different times of the year, providing background data for regions in Europe least affected by anthropogenic effects. The lakes are characterized by low ionic strength, clear waters, and oligotrophic conditions; are fed predominantly by atmospheric precipitation; and are ice-covered during a large part of the year. Lead- and copper-complexing ligands were determined by cathodic stripping voltammetry with ligand competition using Calcein blue and salicylaldoxime, respectively. Water column averages of the dissolved lead concentrations ranged from 0.2 to 0.9 nmol L<sup>-1</sup>, with generally lowest levels during the prolonged winter ice cover, whereas dissolved copper concentrations, varying from 1 to 1.7 (±0.1) nmol L<sup>-1</sup>, showed no significant seasonal variations. The lead speciation was controlled by complexation with ligands at concentrations mostly below 2 nmol L<sup>-1</sup>, with values for the stability constant (log K<sub>PbL</sub>') of 12.5–13.7; calculated ionic lead concentrations (–log[Pb<sup>2+</sup>] values) were 11.9–14.5. Copper complexation was controlled by ligands at concentrations of 12–21 nmol L<sup>-1</sup>, with values for log K<sub>CuL</sub>' of 13.5–14.0 and –log[Cu<sup>2+</sup>] values of 14.4–15.1. The concentration of the copper-binding ligands, but not those for lead, varied seasonally, with about 50% higher concentrations during open water conditions compared to periods of ice cover. The data were consistent with the presence of only one class of ligands for copper and lead. The stability constant of the ligands is similar to that of fulvic acid; however, evidence regarding the actual nature of the ligands is still lacking. The lake data show that (1) competition between calcium and lead causes a reduction in the stability constant of approximately one log-unit for each order of magnitude of Ca<sup>2+</sup>, and (2) lead scavenging in the lakes is moderated by complexation.

Copper and to a lesser extent lead are known to occur complexed with organic matter in the ocean (Hanson et al. 1988; Capodaglio et al. 1990) and in lacustrine systems (Xue and Sigg 1993; Achterberg et al. 1997; Taillefert et al. 2000). These studies indicate the importance of complexation with organic ligands for elements such as lead and copper. Although both copper and lead are involved in biological processes, only copper is an essential micronutrient that can be either biolimiting or toxic to aquatic organisms depending on concentration and chemical speciation (Brand et al. 1986; Morel et al. 1991).

Most studies of the distribution of trace metals or trace metal speciation in freshwater have focused on lowland or eutrophic lakes or both, often with an emphasis on the redox-

driven cycling of elements at oxic–anoxic boundaries (Balistrieri et al. 1992a, 1994, 1995; Achterberg et al. 1997; Xue et al. 1997; Xue and Sunda 1997; Xue and Sigg 1999; Taillefert et al. 2000), whereas comparatively few studies have been carried out on relatively pristine lakes (e.g., Nojiri 1985; Aldrich et al. 2001; Skjelkvale et al. 2001). Preliminary data on a mountain lake suggest that lead is fully complexed by organic matter (Fischer and van den Berg 2001) and copper similarly complexed in an alpine lake (Averyt et al. 2004).

In this study we report on the dissolved organic speciation of lead and copper in remote alpine and subarctic lakes located across Europe. The lakes selected for this study are located at high altitude or high latitude (subarctic) lakes, situated above the tree line, without an inlet stream or with only a minor or seasonal inlet stream. The lakes are unusual in that they receive all inputs either directly from atmospheric precipitation or indirectly via runoff from the catchment. Because of their remoteness they are not affected by local anthropogenic inputs and the catchments are relatively undisturbed. Rainfall composition influences the chemistry of these lakes significantly, as the catchments tend to be small, with poorly developed soil layers or no soil at all and igneous rocks as the predominant bedrock, resulting in very little weathering (Catalan and Camarero 1992). Other characteristics of these lakes are generally a low primary productivity and low levels of organic matter, low nutrient concentrations, and, for the mountain lakes, a rather high solar radiation, making them quite fragile with little buffering against changes in for instance pH or metal ion concentrations.

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### Acknowledgments

Lluís Camarero and Marc Ventura assisted with sample collection at Lake Redo and provided data for temperature, pH, and O<sub>2</sub>. Hans-Joerg Thies and Ulrike Nickus did the same for Lake GKS. Leif Lien collected samples at Ovre Neadalsvatn. Evžen Stucklík was the site operator at Ladove and further assistance with sampling and lake data was given by Ota Strunecký, Martin Blazo, Linda Nedbalova, and Jan Turek. Bjoern Rosseland and Gunnar Raddum assisted with sampling of Lake Ferguson. Atte Korhola was the site operator for the Finnish lakes and further assistance with sampling and lake chemistry was given by Sanna Sorvari, Milla Rautio, Laura Forsström, and Raino-Lars Albert.

This research was financially supported by the EMERGE project of the EU (EVK1-CT-1999-00032).

## Sampling and analytical methods

**Study sites**—The water columns of five lakes were studied in detail, along with the surface waters of a further 19 lakes that were sampled just once. All lakes were oligotrophic or ultraoligotrophic, located above the local tree line and were not subject to local sources of contamination. The catchments were relatively undisturbed and covered by poorly developed soils or bare rocks. Basic morphological parameters are summarized in Table 1.

**Sampling**—Lake Redo was studied most frequently (four times), Ladove was sampled twice, and the other lakes were sampled once. Samples were taken from the water column in the deepest part of each lake, in winter through a hole in the ice and in summer using a rubber or aluminum boat. The samples were collected either via a length of silicone tubing attached to a battery-powered peristaltic pump and lowered to the appropriate depth (Redo, Gossenkoellesee [GKS], Ladove Pleso, Lake Ferguson) or using a Niskin bottle (Redo 1998 for depths greater than 10 m and all of Ovre Neadalsvatn). During 1997 and 1998 the samples from GKS and Redo were filtered in-line through 0.45- $\mu\text{m}$  pore size filters (Millipore) into 500-ml low-density polyethylene (LDPE) bottles. Pump-collected samples were pressure-filtered in-line, whereas Niskin bottle-collected samples were suction-filtered within an hour of sampling (Lake Redo), or 2 d later (Ovre Neadalsvatn). During 2000/2001 water samples were filtered in-line with a 0.2- $\mu\text{m}$  pore size Sartorius filtration cartridge fitted to the outflow of the pumped water, except when samples had been bottle collected (samples deeper than 10 m and some of the Finnish lakes, as indicated in the results).

The Finnish lakes were sampled in the middle of each lake at 1 m depth, either using a peristaltic pump with silicone tubing and in-line cartridge filtration (0.2  $\mu\text{m}$ ), or with a Limnos water sampler followed by 0.45- $\mu\text{m}$  filtration later in the laboratory.

At each depth one unfiltered and two filtered samples were taken for the analysis of dissolved metal concentrations (operationally defined as metals that pass through the respective filters) and metal speciation studies, respectively. The unfiltered samples were used here as a check on possible sample contamination during the filtration step and to obtain total acid-soluble metal concentrations (not reported here). Samples for metal determinations were acidified to pH 2.2 with purified HCl and stored at room temperature. Samples for speciation studies (0.2- or 0.45- $\mu\text{m}$  filtered) were frozen as soon as possible and stored at  $-20^{\circ}\text{C}$  until analysis.

LDPE sample bottles were cleaned by soaking in hot detergent (24 h) followed by soaking in 5 mol L<sup>-1</sup> nitric acid and 1 mol L<sup>-1</sup> purified hydrochloric acid (1 week each), and stored filled with Milli-Q (MQ) water acidified to pH 2.2 with purified hydrochloric acid.

**Analytical methods**—Instrumentation and reagents: Trace metal concentrations and speciation were determined by voltammetry using a Metrohm VA 663 electrode stand connected via an IME-663 module to a computer-controlled potentiostat ( $\mu$ -Autolab, PSTAT 10 or PGSTAT 10, Eco

Chemie). Dissolved lead was measured by anodic stripping voltammetry (ASV) with either a rotating, mercury-film, glassy carbon disk electrode, or a hanging mercury drop electrode (HMDE). Dissolved copper and the speciation of lead and copper were determined by cathodic stripping voltammetry (CSV) using the HMDE as the working electrode. The reference electrode was double junction Ag/AgCl, 3 mol L<sup>-1</sup> KCl, and the counterelectrode was a glassy carbon rod.

Water was purified by reverse osmosis (Milli-RO, Millipore) followed by ion exchange, giving MQ water. Hydrochloric acid and ammonia were purified by sub-boiling distillation using a quartz condenser. Standard metal solutions were prepared by appropriate dilution of atomic-absorption standard solutions (Spectrosol, BDH) acidified to pH 2 with HCl. A stock solution of 0.01 mol L<sup>-1</sup> salicylaldoxime (SA) (BDH) was prepared in 0.1 mol L<sup>-1</sup> HCl. The SA was recrystallized by addition of MQ water to a concentrated solution in methanol acidified with HCl. The pH buffer containing 1 mol L<sup>-1</sup> HEPES (*N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid, Aristar grade) and 0.55 mol L<sup>-1</sup> NaOH was cleaned using Chelex resin. Preparation of all other reagents was as before (Fischer and van den Berg 1999, 2001).

The concentration of fulvic acid was determined by fluorimetry: 389-nm excitation, 468-nm emission detection, 10-nm slit width, with calibration against aqueous solutions of Suwannee River fulvic acid reference material (IR101F-1, International Humic Substances Society) on a Perkin Elmer SL5 luminescence spectrometer.

**Determination of metal concentrations:** All samples were ultraviolet (UV)-digested (45 min, using either a 125- or a 600-W high-pressure mercury vapor lamp, in polytrifluorochloroethylene capped acid-cleaned silica tubes) to decompose organic substances prior to voltammetric metal analysis.

Lead in the 1997/1998 samples was determined by square-wave (SW) ASV using a rotating, glassy carbon disk electrode (RDE), in situ plated with mercury in the presence of thiocyanate (Fischer and van den Berg 1999). The Ladove samples from September 2000 were analyzed by 10 Hz SWASV using an HMDE, preceded by 5-min deposition at  $-0.9$  V. In all other samples lead was determined by 50 Hz SWASV using an RDE with a preplated mercury film: The electrode was conditioned daily in a 0.01 mol L<sup>-1</sup> ammonium acetate (NH<sub>4</sub>Ac) buffer solution by cycling the potential 50 times between  $-0.8$  and  $+0.8$  V. The mercury film was preplated from a buffered (0.01 mol L<sup>-1</sup> NH<sub>4</sub>Ac) solution containing 30  $\mu\text{mol L}^{-1}$  Hg after a 10-min purge with nitrogen, 10-min deposition at  $-0.4$  V, followed by a scan from  $-0.3$  to 0.0 V. Samples were partly neutralized with purified ammonia and buffered with NH<sub>4</sub>Ac (final concentration 0.01 mol L<sup>-1</sup>) at a pH of 4–4.5, and mercury was added to a final concentration of 3  $\mu\text{mol L}^{-1}$ , followed by a 5-min purge with nitrogen gas. The conditioning potential was  $-0.1$  V, the deposition potential  $-1.5$  V, conditioning time 20 s, deposition time 10 min, equilibration time 10 s, and the scan was from  $-0.9$  to  $-0.25$  V. ASV scans obtained by the latter method are shown in Fig. 1.

Copper was determined by CSV in the presence of 30

Table 1. Basic morphological parameters of the sampling sites; data from the EMERGE database, (The MOLAR Water Chemistry Group 1999), (Thies et al. 2002), J. Turek (pers. comm.), and N. J. Anderson (pers. comm.). Sampling dates: GKS, Jul 97; Redo, Feb 98, Nov 00, May and Sep 01; Ovre Neadalsvatn, Mar 98; Ladvoe, Sep 00 and Jul 01; Ferguson, Aug 01; Finnish Lakes, Sep 01.

Lake	Location	Latitude N	Longitude E	Lake altitude m a.s.l.	Catchment area km <sup>2</sup>	Lake area km <sup>2</sup>	Max. depth m	Mean depth m	Lake volume × 10 <sup>6</sup> m <sup>3</sup>	Water residence time d
Lake Redo	Pyrennes, Spain	42.64	0.78	2,235	1.53	0.241	73	32	7.75	1,217–1,404
Gossenköllesee	Alps, Austria	47.23	11.01	2,413	0.59	0.016	9.9	4.6	0.076	52
Ovre Neadalsvatn	Norway	62.78	8.98	728	16.00	0.500	18	3.9	1.95	24
Ladove Pleso	Tatras Slovakia	49.18	20.16	2,057	0.13	0.017	18	6.7	0.114	180
Lake Ferguson	Greenland	66.97	-50.67		75	7.5	86	50	375	
Mallajärvi	Lapland, Finland	69.09	20.66	776	1.18	0.165	13			
Saanajärvi	Lapland, Finland	69.04	20.88	679	5.25	0.701	24			
Masehjärvi	Lapland, Finland	69.04	20.98	680	1.58	0.167	10			
613	Lapland, Finland	68.93	21.03	613	3.96	0.153	5			
1,009	Lapland, Finland	69.17	21.05	1,009	0.97	0.099	12			
Stuorramohki	Lapland, Finland	69.24	21.07	1,024	0.96	0.186	27			
Salmijärvi	Lapland, Finland	69.05	21.18	712	7.18	0.848	11			
Vuobmegasvairi	Lapland, Finland	69.27	21.19	900	0.38	0.012	3.5			
Kohpejärvi	Lapland, Finland	69.06	21.22	774	2.20	0.206	3.5			
Ridni	Lapland, Finland	69.27	21.36	987	1.66	0.133	14			
Toskaljärvi	Lapland, Finland	69.19	21.45	704	13.38	0.999	22			
Somaslompolo	Lapland, Finland	69.26	21.51	760	1.63	0.162	10			
Kaskašjärvi	Lapland, Finland	68.82	21.64	764	4.43	0.313	2			
Juovvatsohkak	Lapland, Finland	68.84	21.67	776	1.05	0.182	2			
Porevarri	Lapland, Finland	69.24	21.68	794	1.66	0.111	5.5			
Muoddajärvi	Lapland, Finland	69.19	21.68	705	8.98	0.231	10			
Harrejärvi	Lapland, Finland	69.16	21.75	660	12.71	0.279	2			
Aatsajokisaivo	Lapland, Finland	68.74	21.88	615	1.51	0.017	5			
Tarjijungajjärvi	Lapland, Finland	68.70	21.98	656	0.83	0.168	2			

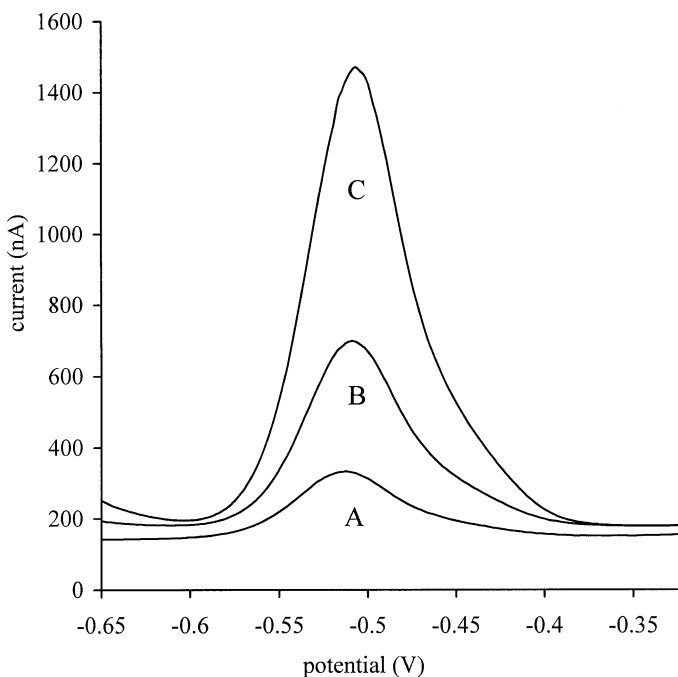


Fig. 1. Anodic stripping voltammograms for a Redo lake water sample with a preplated Hg film, pH 4.5, 5-min deposition at  $-1.5$  V: (A) original scan of the sample containing  $0.26 \text{ nmol L}^{-1}$  Pb; (B) after addition of  $0.5 \text{ nmol L}^{-1}$  Pb; (C) after addition of  $1.5 \text{ nmol L}^{-1}$  Pb.

$\mu\text{mol L}^{-1}$  SA (Campos and van den Berg 1994) and HEPES to buffer the pH at 7.8: deposition potential  $-1.1$  V, deposition time 30 s, 10 s conditioning at  $-0.1$  V, and scans by SWCSV (10 Hz) from 0 to  $-0.65$  V.

**Complexing ligand titrations:** The samples were thawed overnight at  $4^\circ\text{C}$ , and carefully swirled to ensure dissolution of any particulates that might have formed by the freezing process. Complexing ligand titrations were carried out in 28-ml polystyrene tubes (Bibby, Sterilin) that were cleaned by soaking in  $1 \text{ mol L}^{-1}$  HCl, and then conditioned twice with titrations prior to first use to minimize metal ion adsorption onto the walls.

**Lead speciation**—Lead-complexing ligands were determined by CSV in the presence of Calcein blue (CB) (8-[*N,N*-bis{carboxymethyl}aminomethyl]-4-methylumbelliferone) (Fischer and van den Berg 2001). The CB concentration was  $500 \text{ nmol L}^{-1}$  and the pH was adjusted to 7 with TES (*N*-tris[hydroxymethyl]methyl-2-aminoethanosulfonic acid) buffer ( $0.01 \text{ mol L}^{-1}$  final concentration). The equilibration was overnight and the concentration range was usually between 0 and  $10 \text{ nmol L}^{-1}$  of added Pb but had to be adjusted for some lakes to a narrower or wider range. The concentration of PbCB in equilibrium with the natural ligand(s) was determined by differential-pulse CSV: adsorption potential  $-0.15$  V, adsorption time 90–120 s, pulse frequency  $10 \text{ s}^{-1}$ , pulse height 25 mV, step height 5 mV.

The stability constant of lead with CB was calibrated against ethylenediaminetetraacetic acid (EDTA) in UV-di-

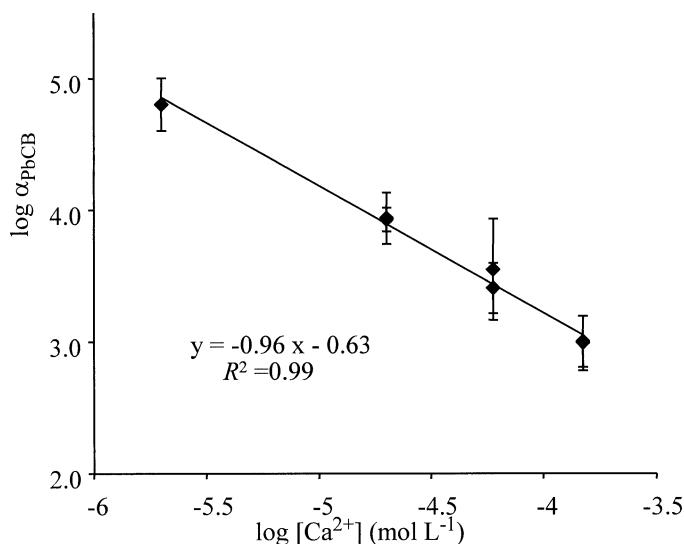


Fig. 2. Variation of  $\log \alpha_{\text{PbCB}}$  as a function of calcium concentrations (log scale). The straight line represents the linear regression through the data.

gested MQ water at a range of calcium concentrations ( $2$ – $150 \mu\text{mol L}^{-1}$ ) similar to the range encountered in the sampled lakes. Therefore, EDTA additions were made to MQ water with added calcium, containing  $500 \text{ nmol L}^{-1}$  CB,  $0.01 \text{ mol L}^{-1}$  TES, and  $10 \text{ nmol L}^{-1}$  Pb, and equilibrated overnight before the labile lead concentration was determined. The ratio  $X$ , of the reduction current in the presence of EDTA over that in the absence of EDTA was used to calculate values for  $\alpha_{\text{PbCB}}$  (van den Berg 1985):

$$\alpha_{\text{PbCB}} = [(\alpha'_{\text{Pb}} + \alpha_{\text{PbEDTA}})X - \alpha'_{\text{Pb}}]/(1 - X) \quad (1)$$

where  $\alpha_{\text{Pb}}$  is the  $\alpha$  coefficient for inorganic complexation of lead and  $\alpha_{\text{PbEDTA}}$  is the  $\alpha$  coefficient of the EDTA complex of lead that was calculated using an ion-pairing model for different calcium concentrations (van den Berg pers. comm.). It can be seen in Fig. 2 that the values for  $\alpha_{\text{PbCB}}$  decreased with increasing calcium concentrations. The resulting linear equation:

$$\log \alpha_{\text{PbCB}} = (-0.96 \pm 0.05)\log[\text{Ca}^{2+}] - (0.63 \pm 0.20)$$

was used to calculate  $\alpha_{\text{PbCB}}$  values for each lake according to its calcium concentration (here and elsewhere “ $\pm$ ” indicates the standard deviation). As the EDTA calibrations were performed at the same CB concentrations as used in the titrations ( $500 \text{ nmol L}^{-1}$ ), the resultant  $\alpha_{\text{PbCB}}$  did not require recalculation for different CB concentrations. The data for lake GKS (Fischer and van den Berg 2001) were recalculated here using the same  $\alpha_{\text{PbCB}}$  values as those used for this study to maintain consistency.

Conditional stability constants were calculated by linearization of the titration data (Ruzic 1982; van den Berg 1982) using the following equation (Fischer and van den Berg 2001):

$$\frac{[\text{Pb}^{2+}]}{[\text{PbL}]} = \frac{[\text{Pb}^{2+}]}{[\text{C}_L]} + \frac{1}{K'_{\text{PbL}}[\text{C}_L]} \quad (2)$$

where  $K'_{\text{PbL}}$  is the conditional stability constant for complexation of lead with natural ligands (L):

$$K'_{\text{PbL}} = \frac{[\text{PbL}]}{[\text{Pb}^{2+}][\text{L}']}$$

where  $[\text{L}']$  is the concentration of L not complexed by lead,  $[\text{PbL}]$  the concentration of lead complexed with L, and  $[\text{Pb}^{2+}]$  the free ionic concentration of lead.  $C_L$ , the total ligand concentration, is defined as the sum of  $[\text{PbL}]$  and  $[\text{L}']$ . A plot of  $[\text{Pb}^{2+}]/[\text{PbL}]$  as a function of  $[\text{Pb}^{2+}]$  is linear in the presence of a single, dominant ligand (Ruzic 1982; van den Berg 1982), with a slope equal to  $C_L$  and a y-axis intercept equal to  $(K'_{\text{PbL}}C_L)^{-1}$ . Linearity of the plots for these titrations, which went well beyond the ligand concentration, suggested that the lead complexation was dominated by a single complexing ligand for the detection window investigated. The sensitivity was estimated from the linear part of the titration curve where L had been saturated with lead.

**Copper speciation**—Copper-complexing ligands were determined by CSV using ligand competition against SA (Campos and van den Berg 1994). A 100-ml sample aliquot was transferred to a Teflon bottle to which HEPES buffer (0.01 mol L<sup>-1</sup>, pH 7.8) and SA (5 μmol L<sup>-1</sup>) were added. Ten-milliliter aliquots were pipetted into 10 polystyrene tubes with previously added copper to give a concentration range of 0 to 80 nmol L<sup>-1</sup> copper. Aliquots were allowed to equilibrate overnight with the reagents at room temperature. The concentration of copper bound by SA was determined by CSV using an adsorption potential of -0.1 V and a deposition time of 60 s.

The sensitivity was calculated from the high end of the titration data and was corrected for its underestimation because of incomplete formation of CuL using an iterative procedure similar to that used before (Turoczy and Sherwood 1997). A first estimate of the sensitivity was obtained from the last few points (3–4) of the titration. This estimate was used to calculate first estimates for labile and organically complexed copper for the metal additions. The data were then linearized using an equation as for lead; plots of  $[\text{Cu}^{2+}]/[\text{CuL}]$  as a function of  $[\text{Cu}^{2+}]$  were straight for all samples tested, suggesting that the organic copper complexation was dominated by a single type of ligand. Therefore, a one-ligand model was used. The initial estimates for  $C_L$  and  $K'$  were then used to recalculate  $[\text{CuL}]$  and  $[\text{Cu}_{\text{labile}}]$  and correct the sensitivity in an iterative manner. This method takes into account the systematic error that would otherwise occur because of incomplete saturation of the ligands in that part of the titration used to calculate the sensitivity. The corrected values for S were 5–20% greater than the initial value.

The value of  $\alpha_{\text{CuSA}}$  was calibrated against EDTA analogously to the method described above for lead, by addition of EDTA to the lake water samples.

## Results and discussion

**General water column conditions**—Background information on the water chemistry of the sampled lakes is summarized in Table 2. Most of the lakes had a low ionic

strength with conductivities typically  $\leq 20 \mu\text{S cm}^{-1}$ , and a low alkalinity, usually below  $100 \mu\text{mol L}^{-1}$ . Some of the Finnish lakes and Lake Ferguson in Greenland had greater alkalinities, up to  $532 \mu\text{mol L}^{-1}$ , because of more alkaline bedrock. The concentrations of calcium and magnesium roughly covaried with the alkalinity, indicating that carbonate from bedrock or glacial moraines was the main source of the alkalinity. Lowest as well as highest concentrations occurred in the subarctic/arctic lakes (i.e., Finland, Norway, and Greenland). Calcium constituted the major cation in the alpine lakes, which is important for metal speciation considerations, whereas for about half of the subarctic lakes sodium was the major cation because of the proximity to the sea.

The dominant anions in these lakes were bicarbonate and sulfate. The majority of the lakes had circumneutral pH values, 6.2–7.6, with the exception of three Finnish lakes, which had lower pH values of 5.6–5.8. Because of relatively low productivities in these lakes (leading to very transparent waters) and poorly developed soils and vegetation in the catchments, dissolved organic carbon (DOC) values tended to be low, especially in the high mountain lakes, ranging from 0.3 to 2.3 mg L<sup>-1</sup>. Nitrate values were very low in the subarctic lakes in Norway and Finland ( $\leq 1 \mu\text{mol L}^{-1}$ ), whereas higher values were found in Redo, GKS, and Ladove (11–17 μmol L<sup>-1</sup>) as well as in Lake Ferguson (19 μmol L<sup>-1</sup>). This is consistent with the available atmospheric nitrate deposition data: Nitrate concentrations in rainwater were 4 μmol L<sup>-1</sup> at a station close to Ovre Neadalsvatn, 11 μmol L<sup>-1</sup> at Redo, 13 μmol L<sup>-1</sup> at GKS, and 18 μmol L<sup>-1</sup> at a site near Lake Ladove (MOLAR Water Chemistry Group 1999).

Depth profiles of temperature, pH, and dissolved oxygen at the time of sampling are shown, where available, in Fig. 3. As a general pattern, the lakes were ice-covered every winter for 6 months or more, from around November/December until the spring thaw in June/July. Most of the lakes were dimictic and during the early summer the lakes would at first tend to mix and then restratify for a short period until the autumn overturn. During the open-water season, the lakes were fully oxygenated except for waters close to the sediments in deep lakes where a minor degree of oxygen depletion occurred in the deepest part of the hypolimnion, near the sediments. The depletion was more pronounced during the long period of ice cover because of the gradual breakdown of organic matter.

The pH profiles were relatively constant with depth. Average water column values can vary considerably, however; e.g., in September 2000 the pH of Ladove was about 7.3, whereas the following July it was only 6.1, caused by melt water draining into the lake, which tends to cause a temporary decline in pH, alkalinity, calcium, and major ion concentrations. The transparency of mountain lakes is known to be very high, leading to deep penetration of UV light, which is thought to be a cause for DOC breakdown to the bottom of the shallower lakes (Sommaruga and Psenner 1997).

**Filtration effects**—Initially (1997–1998) water samples were filtered in-line through 0.45-μm membrane filters, whereas subsequent samples were filtered where feasible using a cartridge with a 0.2-μm cutoff and an internal 0.45-μm prefilter. This change was made as filtration through the

Table 2. Overview of the chemical composition of the sampled lakes. Fulvic acid concentrations were determined by fluorimetry; conductivity, alkalinity, pH, Ca, Mg DOC and NO<sub>3</sub> data are from the EMERGE database of the project lakes and from B. O. Rosseland (pers. comm.), not necessarily sampled in the same year or season as this study, which explains apparent discrepancies between DOC and fulvic acid concentrations for some lakes.

Lake	Conductivity μS cm <sup>-1</sup>	Alkalinity μmol L <sup>-1</sup>	pH	Ca μmol L <sup>-1</sup>	Mg μmol L <sup>-1</sup>	DOC mg C L <sup>-1</sup>	NO <sub>3</sub> μmol L <sup>-1</sup>	Fulvic Acid mg L <sup>-1</sup>
Lake Redo	12	45	6.7	33	1	0.4	11	0.2
Gossenköllesee	20	100	6.9	71	4	0.4	13	0.1
Ovre Neadalsvatn	6	17	6.2	17	4	0.7*	0	0.7
Ladove Pleso	14	65	6.6	44	1	0.3	17	0.2
Lake Ferguson	71	532	7.1	168	117	4.6*	19	3.3
Finland:								
Mallajärvi	9	45	6.7	17	8	0.7	0	0.6
Saanajärvi	40	156	7.2	85	29	1.9	1	7.8
Masehjavri	18	102	7.0	37	16	2.3	0	3.2
613	19	98	6.9	47	12	1.8	0	12.4
1,009	5	5	5.8	5	<4	0.3	1	0.1
Stuorramohki	13	19	6.3	22	8	0.3	0	0.2
Salmijärvi	13	74	6.8	32	8	1.5	0	1.1
Vuobmegasvarri	19	96	6.8	45	16	1.0	0	1.9
Kohpejavri	19	150	6.8	55	12	1.5	0	1.5
Ridni	8	33	6.5	15	4	1.8	1	0.2
Toskaljärvi	46	345	7.6	112	95	0.7	0	0.7
Somaslompolo	32	145	7.2	75	45	0.3	0	0.5
Kaskasjärvi	9	39	6.5	15	8	1.4	0	2.6
Juovvatsohkak	5	4	5.6	35	8	1.2	0	1.3
Porevarri	41	186	7.3	95	66	1.0	0	1.6
Muoddajavri	38	181	7.3	82	58	1.1	0	1.3
Harrejavri	47	400	7.6	125	62	1.5	0	3.1
Aatsajokisaivo	16	117	6.9	30	21	2.0	0	4.3
Tarjjunjargajavri	5	4	5.6	7	8	2.2	0	3.9

membrane filters was much slower, requiring sometimes several filter changes, and was more prone to contamination because of the handling difficulties. This variation in the use of a 0.2-μm cartridge and 0.45-μm membrane filters affects only the lead data, as all samples used for copper had been cartridge filtered. It is likely that the lead concentration in cartridge-filtered samples is reduced because of more lead being removed by the smaller pore size of the cartridge filters. Our measurements (not shown) indicated a drop of 10–20% (47 samples) in the dissolved lead concentration between 0.45- and 0.1-μm membrane filters. The difference between the 0.45-μm membrane and 0.2-μm cartridge must be less and the 10–20% effect can be used as an upper limit. This <10–20% effect is much less than the differences seen between lakes. We considered this effect on the data set as unimportant as it does not affect the basic findings and conclusions. We have no evidence for a difference in the lead-complexing ligand concentrations caused by 0.2- or 0.45-μm filtration.

*Concentration and distribution of dissolved lead and copper*—Vertical profiles of dissolved lead and copper concentrations are shown in Figs. 4 and 5, whereas dissolved lead concentrations in the Finnish lakes are summarized in Table 3, together with average water column concentrations for all other lakes.

*Lead*: Average dissolved lead concentrations in the water column ranged from  $0.23 \pm 0.02$  nmol L<sup>-1</sup> (Redo, November 2000) to  $0.89 \pm 0.19$  nmol L<sup>-1</sup> (GKS), whereas the Finnish lakes surface waters showed a range from 0.28 nmol L<sup>-1</sup> (Stuorramohki) to 0.73 nmol L<sup>-1</sup> (Tarjjunjargajavri). Atmospheric inputs were clearly the cause for enhanced surface water levels of Redo in May (due to the inflow of melt water), September, and November, whereas the winter (February) data showed nearly constant lead concentrations in the water column due to the lack of inputs. The lead concentration in Ovre Neadalsvatn was similarly low and constant under ice cover (March 1998). The influence of the spring melt on the lead concentration was noticeable also at Ladove (as in Redo) where average dissolved Pb concentrations increased from  $0.32 \pm 0.16$  nmol L<sup>-1</sup> in September 2000 to  $0.88 \pm 0.22$  nmol L<sup>-1</sup> the following July when snow and ice in the catchment were melting. Higher average dissolved lead concentrations in GKS and Ladove could be related to shorter water residence times (compared to Redo) or higher atmospheric inputs (or both) compared to Ovre Neadalsvatn in northwest Norway and Lake Ferguson in Greenland, which are both much further away from European continental lead sources than GKS in Austria and Ladove in Slovakia.

Lead concentrations in the majority of the Finnish lakes were  $\sim 0.3$ – $0.4$  nmol L<sup>-1</sup>, which is not as low as expected

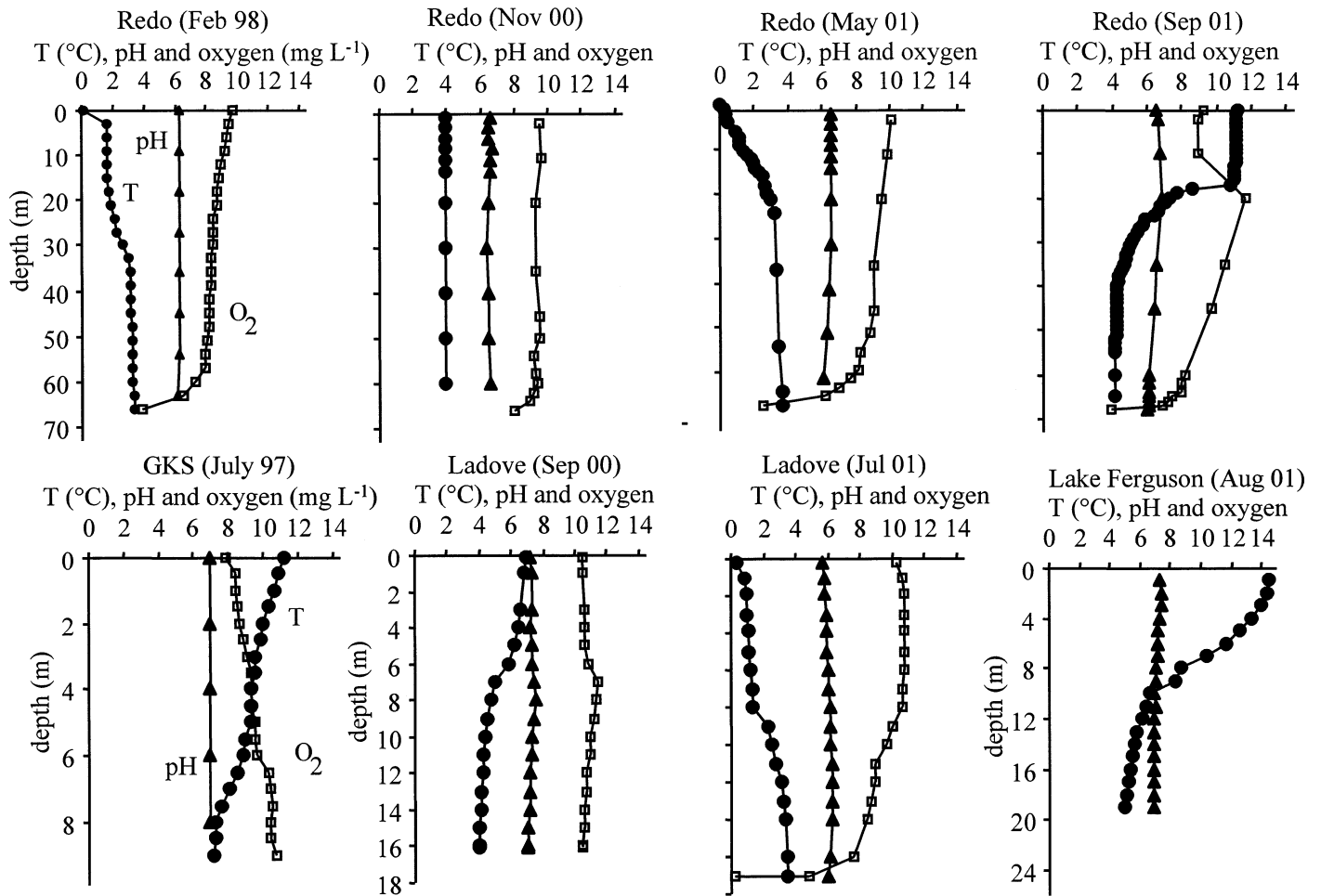


Fig. 3. Depth profiles of temperature, pH, and oxygen for Lake Redo, Gossenkoellesee (GKS), Ladove, and Lake Ferguson at the time of sampling.

given that this region in northwest Finland is considered to be one of the cleanest in Europe (Rühling 1992). On the other hand, in some of the smaller and shallower lakes the lead concentration may have been close to that of the atmospheric water input because of a relatively short residence time of the water. The lead concentrations in these lakes are lower than in some of the more central European lakes, and they are at the low end of a survey of  $\sim 150$  Finnish head-water lakes, which had a range of  $<0.14$  to  $9.6 \text{ nmol L}^{-1}$  lead in the surface waters with a median value of  $1.6 \text{ nmol L}^{-1}$  (Tarvainen et al. 1997). Lead concentrations in less remote lakes tend to be greater. For instance, seasonal surface water concentrations in Lochnagar, a Scottish mountain lake in relative proximity to industrial areas of Edinburgh, varied from  $2.5$  to  $5.7 \text{ nmol L}^{-1}$  (mean  $4.0 \text{ nmol L}^{-1}$ ) (Yang et al. 2002). Hall Lake dissolved lead concentrations ranged from  $0.01$  up to  $4.9 \text{ nmol L}^{-1}$  at the sulfide maximum (Balistrieri et al. 1994). Lower lead concentrations have been found too, such as  $0.24 \text{ nmol L}^{-1}$  in Lake Mashu, a deep oligotrophic lake in Japan (Nojiri et al. 1985),  $0.01$ – $0.39 \text{ nmol L}^{-1}$  Pb in Lake Sammamish (Balistrieri et al. 1995), and lead concentrations of  $0.02$ – $0.05 \text{ nmol L}^{-1}$  in the Great Lakes (Superior, Erie, and Ontario) (Nriagu et al. 1996), which are close to

open ocean concentrations, e.g.,  $0.050$ – $0.100 \text{ nmol L}^{-1}$  lead in the Northwest Atlantic (Wu and Boyle 1997). Clearly the lake water residence time is an important factor determining the residual concentration of a scavenged element like lead.

**Copper:** Average dissolved copper concentrations in the water columns of Redo and Ladove ranged from  $1.0$  to  $1.7 \pm 0.1 \text{ nmol L}^{-1}$ . The copper concentration was constant in the water columns of these two lakes. The lack of increased levels at the surface suggests that atmospheric inputs of copper were minor or that they were balanced by inputs from runoff and lake mixing. There were no significant seasonal variations, implying a balance between inputs and removal of copper from the water column on which the long period of ice cover had no apparent effect. Relatively constant copper concentrations in the water column are a common feature also in other lakes (Nriagu et al. 1996), significant changes only occurring at oxic–anoxic boundaries (Balistrieri et al. 1992b, 1994), whereas in our study the water columns of the lakes remained fully oxic. This constancy is in contrast to the decrease in the lead concentration due to scavenging when the lakes were ice-covered, suggesting that the copper concentration was stabilized and less

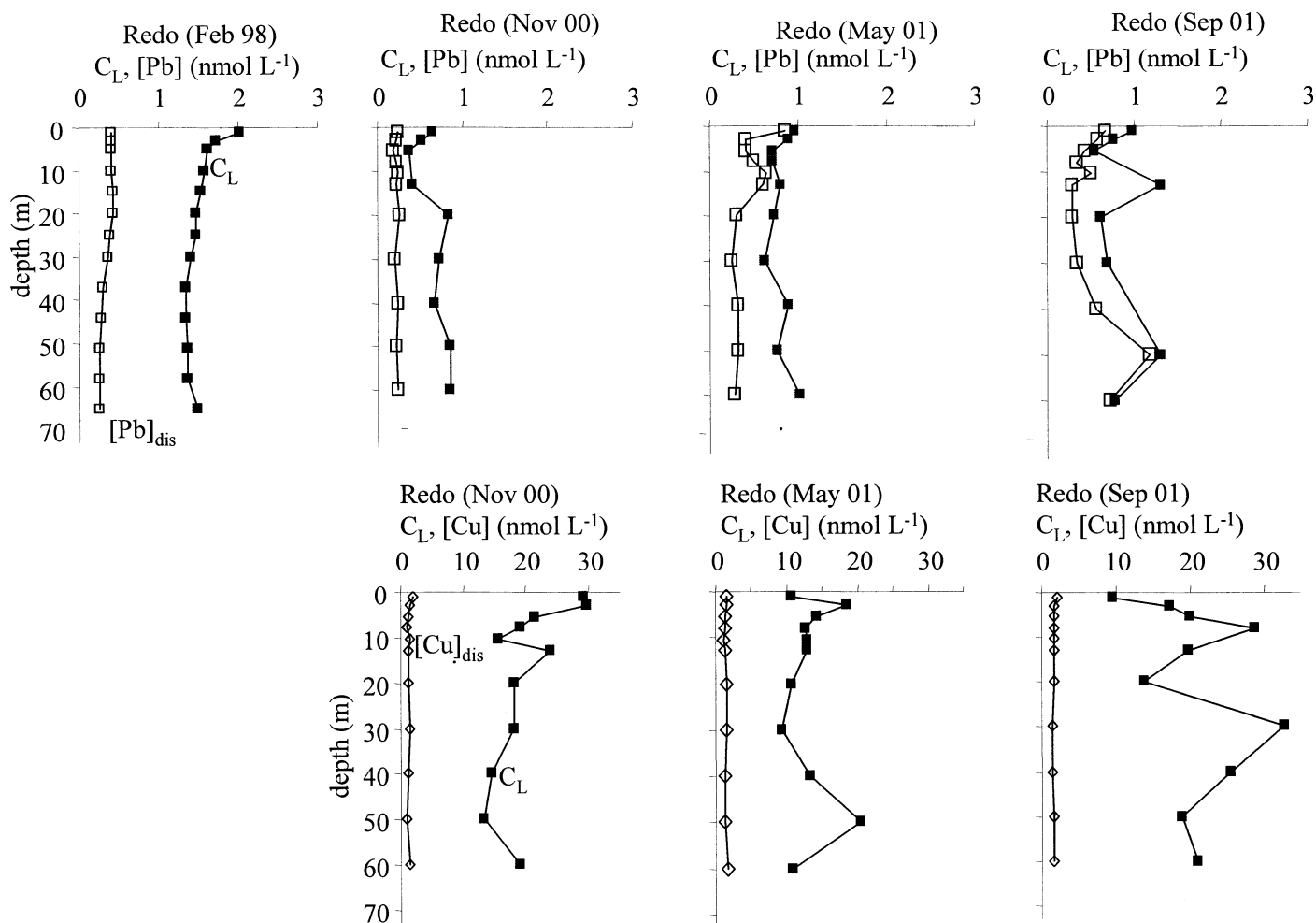


Fig. 4. Depth profiles of dissolved Pb and Pb-complexing ligand and dissolved Cu and Cu-complexing ligand concentrations for Lake Redo.

affected by adsorptive removal. This is supported by the fact that filtered and unfiltered copper concentrations were almost the same, so very little copper was bound to particulates (data not shown).

The copper concentrations found throughout the water columns of these lakes are low compared to some other freshwaters. Dissolved copper in Hall Lake ranged from 0.57  $\text{nmol L}^{-1}$  in anoxic bottom waters up to 18  $\text{nmol L}^{-1}$  in oxic surface waters (Balistreri et al. 1994), and in Lake Sammamish from 1.8  $\text{nmol L}^{-1}$  in anoxic bottom waters to 8.8  $\text{nmol L}^{-1}$  at the surface (Balistreri et al. 1992b). Median copper concentrations were 4.7  $\text{nmol L}^{-1}$  (range 1.0–36  $\text{nmol L}^{-1}$ ) in Finnish headwater lakes (Tarvainen et al. 1997); 6.5–13  $\text{nmol L}^{-1}$  in Esthwaite Water (a lowland lake) (Achterberg et al. 1997); 2.4 to 32  $\text{nmol L}^{-1}$  (mean 11.8  $\text{nmol L}^{-1}$ ) in surface waters of Lochnagar, a Scottish mountain lake (Yang et al. 2002); 12  $\text{nmol L}^{-1}$ , 14  $\text{nmol L}^{-1}$ , and 13  $\text{nmol L}^{-1}$  in Lake Superior, Lake Erie and Lake Ontario, respectively (Nriagu et al. 1996); and 1.1  $\text{nmol L}^{-1}$  in Lake Mashu (Nojiri et al. 1985).

**Lead- and copper-complexing ligands:** The distribution of lead- and copper-complexing ligands in the water columns

of the lakes is plotted in Figs. 4 and 5. Table 3 gives the data for the Finnish lakes and average water column concentrations, calculated free metal ion concentrations, and conditional stability constants. Example titrations for lead and copper and the corresponding linearization plots are shown in Figs. 6 and 7, respectively.

**Lead-complexing ligands:** Lead was found to be fully complexed by organic complexing ligands with the concentration of the complexing ligands always in excess of the lead concentration. The increase in response for lead upon saturation of the ligands was marked (Fig. 6A), indicating that the organic complexation was much stronger than the inorganic complexation of lead. The linearized plots of the titrations were straight, indicating that a single ligand dominated the speciation. Lead-complexing ligand concentrations were lower than the copper-complexing ligand concentrations (see below), and were in most cases less than 2  $\text{nmol L}^{-1}$ , especially in the mountain lakes. Concentrations were greater in some subarctic lakes: Ovre Neadalsvatn ( $5.0 \pm 1.0 \text{ nmol L}^{-1}$ ), Saanajärvi (4.8  $\text{nmol L}^{-1}$ ), lake 613 (4.3  $\text{nmol L}^{-1}$ ), Kaskasjärvi (11.3  $\text{nmol L}^{-1}$ ), Porevarri (3.8  $\text{nmol L}^{-1}$ ), and Harrejävri (11.8  $\text{nmol L}^{-1}$ ). Although above the tree line,



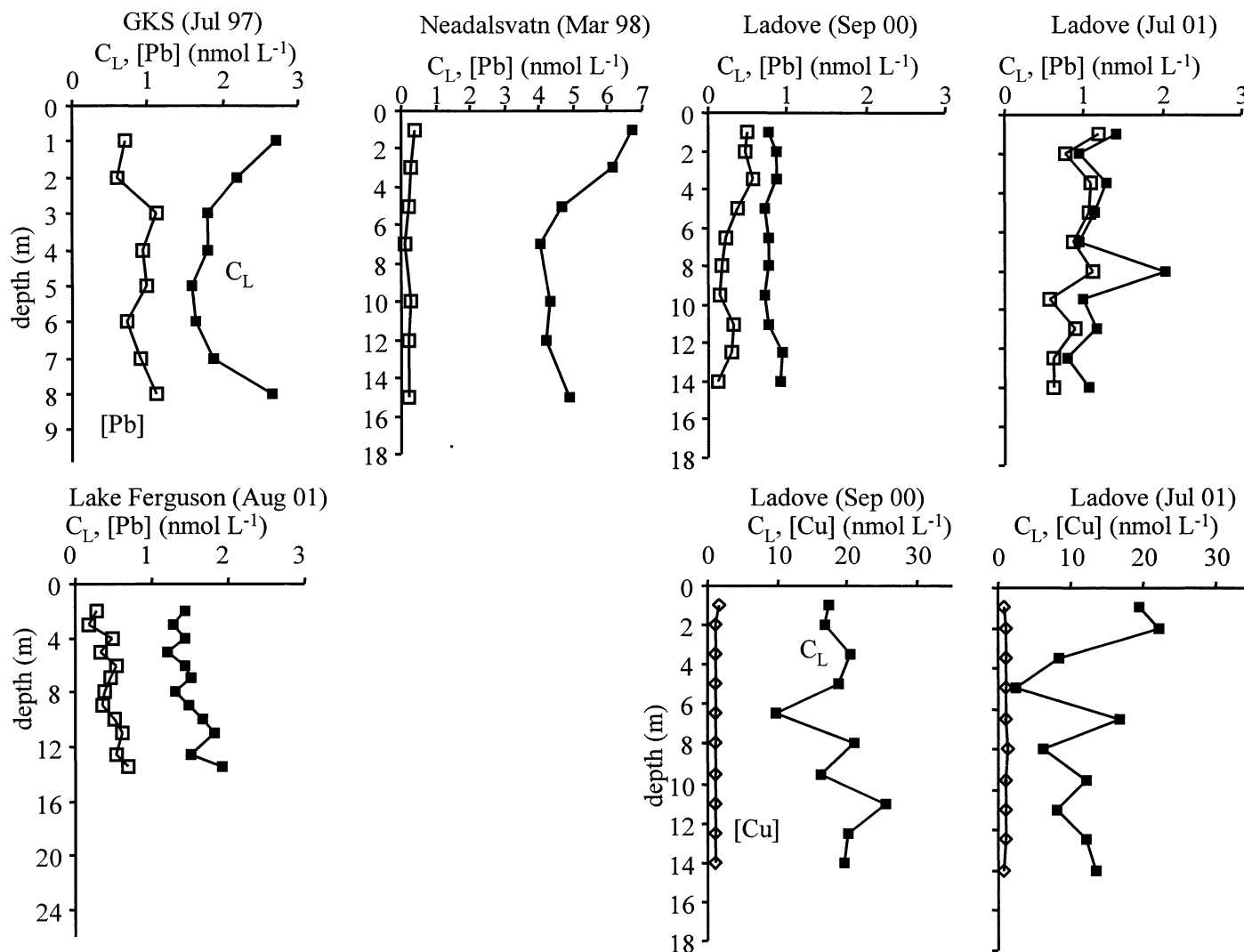


Fig. 5. Depth profiles of dissolved Pb and Pb-complexing ligands for GKS, Ovre Neadalsvatn (note the different scale), Ladove, and Ferguson as well as depth profiles of dissolved Cu and Cu-complexing ligand concentrations for Ladove.

these lakes were at lower altitude than the mountain lakes (GKS, Redo, and Ladove). It is possible that relatively continuous soil cover and vegetation in the catchment of the subarctic lakes had caused increased levels of humic materials, which may have contributed to the ligands. Furthermore, the Finnish lakes were more shallow, e.g., Kaskasjärvi and Harrejavri had a maximum depth of just 2 m, so the 1-m 'surface' samples were just 1 m above the sediments; another difference was that there was much less precipitation in Lapland ( $\sim 400 \text{ mm yr}^{-1}$  compared to  $>1,200 \text{ mm yr}^{-1}$  in the mountains and at Neadalsvatn).

The average stability constant ( $\log K'_{\text{PbL}}$ ) in the water columns of the lakes was between  $12.5 \pm 0.2$  and  $13.7 \pm 0.5$ , and  $13.5 \pm 0.7$  in the Finnish lakes. The calculated degree of organic complexation of lead,  $\alpha_{\text{PbL}}$ , was  $\sim 10^3$ , much greater than that for the very weak inorganic complexation of lead ( $\alpha_{\text{Pb}} = 2$ ). As a result, the free ionic lead concentrations were lowered by the organic complexation to  $-\log[\text{Pb}^{2+}]$  values of  $11.9 \pm 0.5$  to  $14.5 \pm 0.2$  (water column averages) and of 11.9 to 15.4 ( $13.3 \pm 0.9$ ) for the Finnish lakes.

The range of detected complex stabilities is large (Table 3), especially in the Finnish lakes, suggesting the presence of different complexing ligands or sites in the different lakes, or competition by cations other than lead,  $\text{Ca}^{2+}$  for instance.

The lead-complexing ligand concentrations in the water columns of GKS and Ovre Neadalsvatn, and in Redo February 1998 and September 2001, were greater in the surface and bottom waters than at intermediate depths, whereas systematic variations were absent in the other profiles. Surface water increases could be from atmospheric input or runoff, whereas bottom water increases could have a benthic source. Such inputs would only be apparent when they are associated with a temporary stratification of the lake.

Stronger lead complexation has previously been linked with increasing DOC concentrations in Paul Lake (Taillefert et al. 2000). A DOC profile was only available for GKS (not shown) and insufficient data are available to compare trends. There were no systematic seasonal variations in the ligand concentrations in the lakes. In Redo, highest lead-complexing capacities ( $1.5 \pm 0.2 \text{ nmol L}^{-1}$ ) occurred during the win-

Table 3. Dissolved lead and copper concentrations, complexing ligand concentrations ( $C_L$ ),  $-\log[\text{Pb}^{2+}]$ ,  $-\log[\text{Cu}^{2+}]$ , and stability constants for the Finnish lakes and as water column averages and standard deviations, for the other lakes.

Lake	Date	Pb			Cu				
		Pb (nmol L <sup>-1</sup> )	$C_L$ (nmol L <sup>-1</sup> )	$-\log[\text{Pb}^{2+}]$	log $K'_{\text{PbL}}$	Cu (nmol L <sup>-1</sup> )	$C_L$ (nmol L <sup>-1</sup> )	$-\log[\text{Cu}^{2+}]$	log $K'_{\text{CuL}}$
Redo	Feb 98	0.35 ± 0.07	1.5 ± 0.2	13.3 ± 0.1	12.7 ± 0.1	1.4 ± 0.3	20.2 ± 5.4	15.1 ± 0.2	14.0 ± 0.2
	Nov 00*	0.23 ± 0.02	0.7 ± 0.2	12.8 ± 0.2	12.6 ± 0.3	1.4 ± 0.2	13.3 ± 3.4	14.8 ± 0.2	13.9 ± 0.2
	May 01*	0.45 ± 0.19	0.8 ± 0.1	12.7 ± 0.4	12.8 ± 0.3	1.7 ± 0.2	20.8 ± 6.9	14.8 ± 0.2	13.8 ± 0.3
	Sep 01*	0.54 ± 0.26	0.9 ± 0.3	12.3 ± 0.5	12.7 ± 0.5				
	Jul 97†	0.89 ± 0.19	2.0 ± 0.4	13.4 ± 0.1	13.3 ± 0.3				
GKS	Mar 98	0.25 ± 0.09	5.0 ± 0.1	14.5 ± 0.2	13.2 ± 0.1				
	Sep 00*	0.32 ± 0.16	0.8 ± 0.1	12.9 ± 0.3	12.7 ± 0.2	1.2 ± 0.2	18.5 ± 4.1	15.0 ± 0.2	13.8 ± 0.2
Ladove Pleso	Jul 01*	0.88 ± 0.23	1.2 ± 0.4	11.9 ± 0.5	12.5 ± 0.2	1.0 ± 0.1	12.2 ± 6.1	14.4 ± 0.3	13.5 ± 0.5
	Aug 01	0.45 ± 0.15	1.5 ± 0.2	13.2 ± 0.5	13.7 ± 0.5				
Finland:									
Mallajärvi	Sep 01*	0.33	0.5	13.5	13.2				
Saanajärvi	Sep 01*	0.31	4.8	12.0	13.2				
Masehjärvi	Sep 01*	0.38	1.1	14.3	14.6				
613	Sep 01*	0.37	4.3	12.7	13.6				
1,009	Sep 01*	0.38	1.1	13.3	13.6				
Stuorramohki	Sep 01*	0.28	0.6	13.7	13.8				
Salmijärvi	Sep 01*	0.39	0.6	13.4	13.2				
Vuobmegasvarri	Sep 01*	0.52	0.7	13.3	12.9				
Kohpejärvi	Sep 01*	0.38	0.6	13.8	13.5				
Ridni	Sep 01	0.31	1.2	14.3	14.2				
Toskajärvi	Sep 01	0.42	1.1	13.2	13.0				
Somaslompolo	Sep 01	0.31	1.6	13.5	12.6				
Kaskasjärvi	Sep 01	0.41	11.3	12.2	13.6				
Juovvatsokhak	Sep 01	0.46	0.9	12.9	12.9				
Porevarri	Sep 01	0.46	3.8	11.9	13.0				
Muoddajarvi	Sep 01	0.35	1.9	13.6	13.0				
Harrejavi	Sep 01	0.42	11.8	11.9	12.8				
Aatsajokisaivo	Sep 01	0.49	1.5	13.7	14.0				
Tajjunjargajarvi	Sep 01	0.73	1.6	15.4	15.5				

\* These samples were filtered using a 0.2 μm cartridge; the other samples using a 0.45 μm membrane filter.

† Data from Fischer and van den Berg 2001.

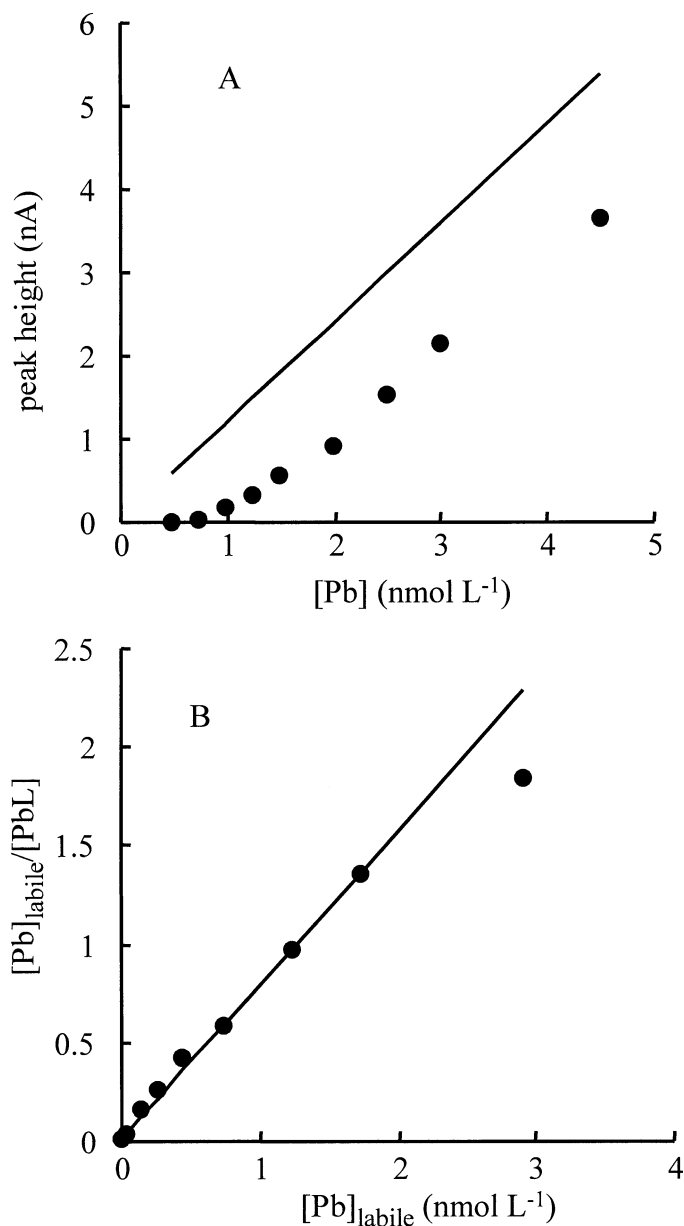


Fig. 6. Pb-complexing ligand titration of a sample from Lake Ferguson (120-s deposition at  $-0.15$  V,  $0.5 \mu\text{mol L}^{-1}$  CB,  $0.01 \text{ mol L}^{-1}$  TES,  $0.49 \text{ nmol L}^{-1}$  total dissolved Pb): (A) peak current as a function of total dissolved Pb; (B) linearization of the data.

ter (February 1998), whereas the other samplings, including May 2001 at the end of ice cover, yielded average  $[C_L]$  ranging from  $0.7 \pm 0.2 \text{ nmol L}^{-1}$  to  $0.9 \pm 0.3 \text{ nmol L}^{-1}$ . At Ladove the average lead-complexing capacity was higher in July 2001 ( $1.2 \pm 0.4 \text{ nmol L}^{-1}$ ) than in September 2000 ( $0.8 \pm 0.1 \text{ nmol L}^{-1}$ ).

The complex stability of the lead species in these mountain and subarctic lakes (Table 3) is high compared to other waters (Table 4). Competition by major cations (predominantly calcium) is a factor of  $10^3$  greater in seawater, which may well explain the difference with those waters. Lower complex stability was obtained by ASV for lead species in Paul Lake (Taillefert et al. 2000): It will be interesting to

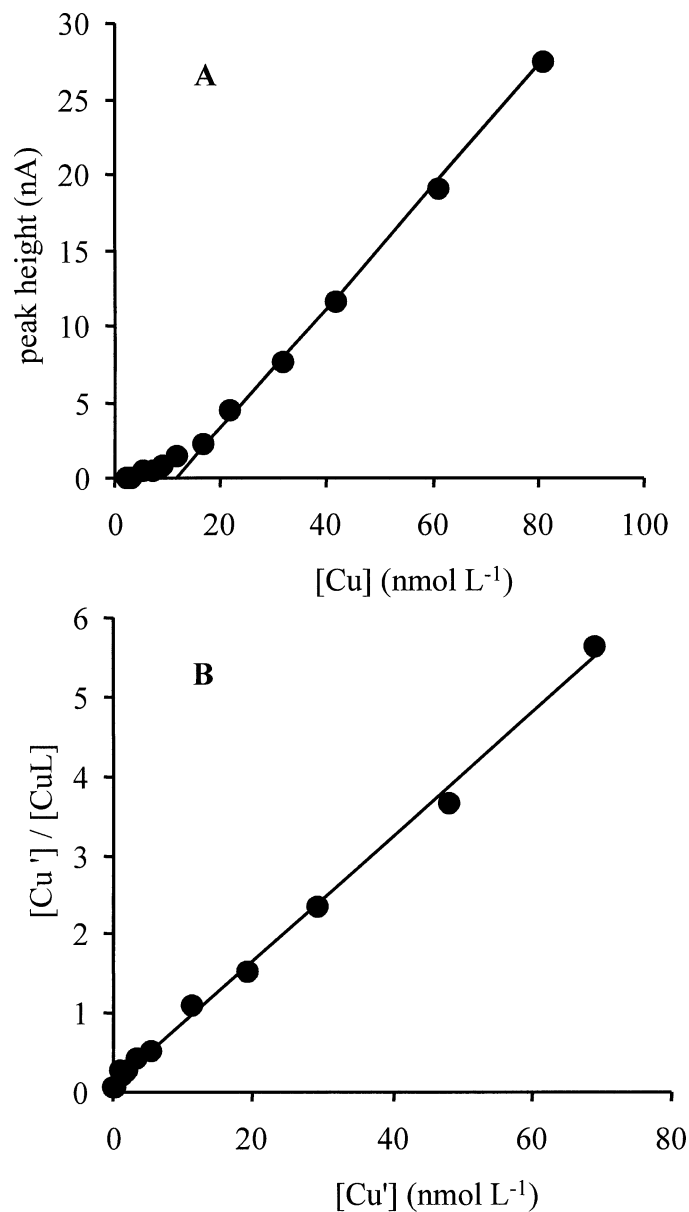


Fig. 7. Results of a copper titration of a sample from Lake Redo (60-s deposition at  $-0.1$  V,  $5 \mu\text{mol L}^{-1}$  SA,  $0.01 \text{ mol L}^{-1}$  HEPES,  $1.1 \text{ nmol L}^{-1}$  total dissolved Cu): (A) peak height as a function of total copper; (B) linearization of the data.

investigate whether the difference is due to the use of a different technique with a different detection window.

The  $K'_{\text{PbL}}$  values are several orders of magnitude higher than those for fulvic acid (Buffle et al. 1977); however, this does not rule out humic and fulvic substances as the source of these ligands as it is known that large polyelectrolytic ligands may well contain a large number of weak as well as a small number of much stronger complexation sites that only become apparent when determined at the low metal and ligand concentrations in the lakes.

The ionic lead concentrations in the study lakes are mostly lower than in seawater (Table 4) in spite of its lower lead concentration due to the high complex stability in the lakes.

Table 4. Comparison of dissolved lead concentrations,  $-\log[\text{Pb}^{2+}]$ , lead-complexing ligand concentrations, and conditional stability constants from the literature.

Site	Method	Natural pH Analytical pH	Pb (nmol L <sup>-1</sup> )	$-\log[\text{Pb}^{2+}]$	CL <sub>x</sub> (nmol L <sup>-1</sup> )	log K <sub>g</sub>	Reference
NE Pacific	DPASV	— 8.1	0.017–0.049	12.0–13.0	(1) 0.22–0.56	(1) 9.4–10.0	Capodaglio et al. 1990
Terra Nova Bay (Ross Sea)	DPASV	—	0.025–0.114	—	(1) 0.25–0.91	(1) 9.3–9.9	Scarponi et al. 1995
South San Francisco Bay	DPASV	7.9	0.12–0.20	12.5	(1) 0.89 ± 0.35 (2) 12.8 ± 1.9	(1) 10.5 (2) 8.6	Kozelka et al. 1997
Narragansett Bay	DPASV	7.8–7.9	0.13–0.32	11.9–12.4	(1) 0.6–1.0 (2) 5.1–8.2	(1) 9.9–10.2 (2) 8.6–8.8	Kozelka and Bruland 1998
Paul Lake*	DPASV	—	~0.2–3.7	—	(1) 9.2 ± 4	(1) 9.4 ± 0.8	Taillefert et al. 2000
Fulvic acid	ISE	6.3 ± 0.2 5.0	—	—	—	4.1	Buffe et al. 1977

\* Below oxic–anoxic transition.

The  $\text{Pb}^{2+}$  levels were lowest in the subarctic lakes because of greater stability of the PbL complexes: Average values for  $-\log[\text{Pb}^{2+}]$  were  $14.2 \pm 0.2$  for Ovre Neadalsvatn,  $13.2 \pm 0.5$  for Lake Ferguson, and  $>13.5$  for half of the Finnish lakes.

Copper-complexing ligands: *Complex stability*: Plots of the titration data according to Eq. 2 were straight, indicating that the speciation of copper was dominated by one class of ligand; this ligand was present in large excess to the dissolved copper concentrations and at higher concentration than the lead binding ligand. Average water column concentrations for  $[\text{C}_L]$  at Redo and Ladove ranged from  $12.2 \pm 6.1$  to  $20.8 \pm 6.9$  nmol L<sup>-1</sup>. The stability of the copper complexes was similar at Redo and Ladove, with average water column values for  $\log K'_{\text{CuL}}$  of  $13.8 \pm 0.3$  to  $14.0 \pm 0.2$  for Redo, and  $13.5 \pm 0.5$  to  $13.8 \pm 0.2$  for Ladove. Ionic copper concentrations ( $-\log[\text{Cu}^{2+}]$  values) were  $14.4 \pm 0.3$  to  $15.1 \pm 0.2$ .

The average value for the conditional stability constant for copper ( $\log K'_{\text{CuL}}$  13.5–14.0) in these low-conductivity lakes is about a log-unit less than that (15.8) in New Zealand alpine lakes (Averyt et al. 2004) at the same analytical pH (pH 7.8) but there is overlap in the data ranges. Although the same voltammetric method was used, a higher detection window ( $20 \mu\text{mol L}^{-1}$  SA) was used in that work compared to the  $5 \mu\text{mol L}^{-1}$  SA used here, so it is possible that stronger ligands were detected if these were present. On the other hand, there is a large discrepancy between the calibrated complex stability of the CuSA complexes ( $\alpha_{\text{CuSA}}$ ) that alone could explain the difference in the calculated values for  $K'_{\text{CuL}}$ : The constants from Campos and van den Berg (1994) corrected to the ionic strength of the lakes (by using a salinity of 0.1) give a value for  $\log \alpha_{\text{CuSA}}$  of  $10^{6.9}$  for  $20 \mu\text{mol L}^{-1}$  SA, whereas a value of  $10^{8.5}$  was used for the New Zealand lakes study (Averyt et al. 2004). Averyt et al. (2004) recalibrated the constants for the CuSA species using a potentiometric method that could be based on activities rather than concentrations depending on the calibration method but the method was not discussed in detail. They subsequently used a value of 200 for  $\alpha_{\text{Cu}}$  (inorganic complexation of copper) to correct the constants to the  $\text{Cu}^{2+}$  scale. According to our speciation model  $\alpha_{\text{Cu}}$  should be between 2 and 3 for low-ionic-strength mountain lakes: Inorganic copper speciation is mostly controlled by carbonate ions, and the carbonate concentration in these lakes tends to be very low (alkalinity between 4 and  $400 \mu\text{Eq L}^{-1}$ ) and our measurements were at pH 7.8, explaining the low value for  $\alpha_{\text{Cu}}$ , much lower than the value of 200 (Averyt et al. 2004) used for the recalibration of  $\alpha_{\text{CuSA}}$ . It is possible that the high  $\alpha_{\text{Cu}}$  value includes an activity coefficient but this is not indicated and the details of the method are apparently being published elsewhere (Averyt et al. 2004). The complex stability of CuSA and  $\text{CuSA}_2$  used in our work had been calibrated (Campos and van den Berg 1994) against EDTA using the same CSV method as used for the measurements of the samples, and is therefore independent of the value selected for  $\alpha_{\text{Cu}}$  and does not require correction using an activity coefficient.

It will be necessary to further evaluate the calibration of the CuSA complex stability in the future to come to an

agreement regarding the stability of the copper species in these and other lakes.

**Copper ligand distribution:** The depth profiles of copper-complexing ligands in Redo in November 2000 and May 2001 were concave (the ligand concentrations were higher at the surface and near the sediments), whereas the remaining profiles showed no systematic variation with depth. The higher surface and deepwater concentrations tended to mirror the same pattern seen for the lead-complexing ligands, albeit at a 10× greater concentration of the copper-complexing ligands. The average ligand concentrations for Redo and Ladove were higher during the open water season (Ladove  $18.5 \pm 4.1$  nmol L<sup>-1</sup>, Redo  $20.2 \pm 5.4$  and  $20.8 \pm 6.7$  nmol L<sup>-1</sup>) than at the end of winter (Ladove  $12.2 \pm 6.1$  nmol L<sup>-1</sup>, Redo  $13.4 \pm 3.4$  nmol L<sup>-1</sup>), whereas dissolved copper concentrations showed little variation. Similar to the ligand concentrations, the DOC concentrations in the water column of Redo were also lower during the winter, and lowest at the end of ice cover (Camarero et al. 1999), increasing again as a result of algal activity during the summer. High concentrations of complexing ligands were probably caused by algal material in Esthwaite Water (Achterberg et al. 1997), where the high ligand concentrations coincided with a phytoplankton bloom. A study of Lake Greifen has also provided evidence for biological production of copper-complexing ligands (Xue and Sigg 1993). However, the mountain lakes studied here have very low ionic strength as well as low nutrient concentrations, and productivity is low. It is possible that the ligands in these lakes are from humic and fulvic materials, and not directly produced by algae.

These log  $K'_{CuL}$  values and ligand concentrations are similar to the L<sub>1</sub> class of copper-complexing ligands found in other lakes (Table 5) despite the almost one order of magnitude higher dissolved copper concentrations and eutrophic nature of some of those lakes (e.g., Lakes Greifen and Sempach). So the lower productivity of Redo and Ladove and potentially lower rates of release of organic ligands by phytoplankton and other microorganisms is not reflected in lower steady-state concentrations of copper-complexing ligands of the L<sub>1</sub> class.

The combination of high log  $K'_{CuL}$  values and large excess of ligands gives rise to low cupric ion concentrations in the lakes studied here.  $-\log[Cu^{2+}]$  values for lake Redo were 14.4–15.6 ( $14.9 \pm 0.5$ ) and for Ladove 13.7–15.3 ( $14.7 \pm 0.4$ ). This strong degree of complexation may well be a cause for the lack of seasonal variation in copper concentrations, as it would tend to keep the copper in solution.

**Possible systematic method-related errors:** To maintain consistency of the data our measurements were at constant concentration of added competing ligands (SA or CB) and at constant pH. In spite of this, the detection windows still varied between the lakes because of differences in major ion concentrations (see below). It is in principle possible that different ligands are detected (if present) if the detection window is greatly shifted (van den Berg and Donat 1992). The data treatment of the titrations with lead and copper indicated that only one ligand type dominated in each sample. This is confirmed by the relative constancy of the com-

Table 5. Comparison of dissolved copper concentrations,  $-\log[Cu^{2+}]$ , copper-complexing ligand concentrations, and conditional stability constants from the literature.

Site	Method	Natural pH		Cu (nmol L <sup>-1</sup> )	$-\log[Cu^{2+}]$	C <sub>L</sub> (nmol L <sup>-1</sup> )	log K <sub>s</sub>	Reference
		Analytical	pH					
Esthwaite Water	CSV of Cu-tropolone complexes	~6.7–9.9	—	2.8–13.2	10.9–14.1	(1) 6.8–29.4	(1) 11.1–14.4	Achterberg et al. 1997
Lake Lucerne	CSV of Cu-catechol, -oxine, &-tropolone complexes, and Cu-ISE	7.8	—	9.44	14.41	(1) 18.5–19.0	(1) 14.3	Xue and Sunda 1997
		—	7.8	—	—	(2) 100–110	(2) 10.8–11.0	
Lake Greifen	CSV of Cu-catechol, -oxine, &-tropolone complexes, and Cu-ISE	—	—	12.6–23	15.16–15.19	(3) 6.0	(3) 8.6	Xue and Sunda 1997
		—	8.0	—	—	(1) 25.6–56.9	(1) 14.6–15.8	
Lake Sempach	CSV of Cu-catechol, -oxine, &-tropolone complexes, and Cu-ISE	—	—	13.5	15.11	(2) 110–350	(2) 12.5–13.2	Xue and Sunda 1997
		—	7.9	—	—	(3) 10.0	(3) 8.6	
Humic acid	Ion-exchange	6.0	—	—	—	(2) 100	(2) 12.6	Taga et al. 1991
		—	6.0	—	—	(1) 6.2–7.0	(1) 6.2–7.0	
Humic acid	ASV	6.0	—	—	—	(2) 4.9–5.6	(2) 4.9–5.6	Fukushima et al. 1992
Humic acid	CSV of Cu-catechol complexes	—	—	—	—	(1) 30.0	(1) 12.5	Xue and Sigg 1999
Fulvic acid	ISE	7.8	—	—	—	(2) 200	(2) 10.3	Buffie et al. 1977
		—	8.0	—	—	—	8.42	
Fulvic acid	CSV of Cu-catechol complexes	—	—	—	—	(1) 27.3	(1) 14.1	Xue and Sigg 1999
		—	8.0	—	—	(2) 250	(2) 11.7	

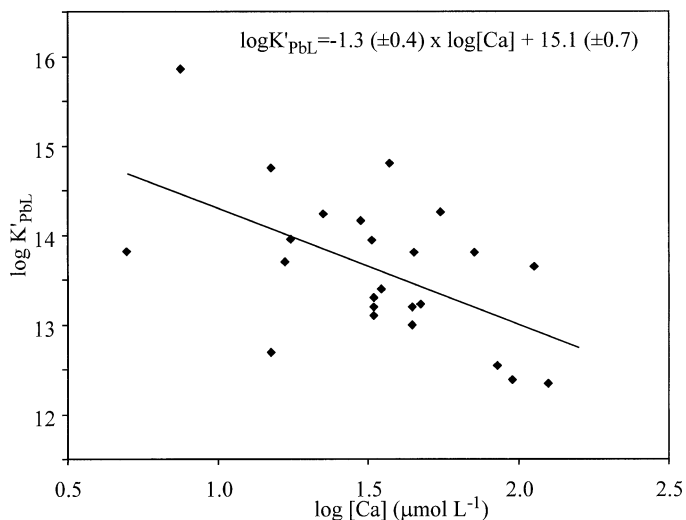


Fig. 8. Stability of the lead complexes ( $\log K'_{\text{PbL}}$ ) as a function of the calcium concentration ( $\log[\text{Ca}^{2+}]$ ) in the lakes.

plex stability within individual lakes when several depths were studied. It is therefore likely that this study at least found the most important ligands in these lakes; however, it is possible that much weaker metal binding ligands (or other complexing sites on the same ligands) have not been detected.

It has been suggested that ligands could be present in the type of buffers used for this study (Mash et al. 2003). The possibility of errors due to such ligands in the pH buffers was eliminated by titration with copper of  $0.01 \text{ mol L}^{-1}$  HEPES buffer in UV-digested freshwater and with lead of  $0.01 \text{ mol L}^{-1}$  TES buffer in UV-digested MQ water. Both titrations were straight, indicating that ligands were not present in the buffer solutions at significant levels. Any contribution of ligands from the pH buffers to the apparent ligand concentration in these lake waters was therefore below the limit of detection.

Effects of major cation competition on metal complexation: It is known that the pH tends to affect the stability of copper complexes with ligands in lakes (van den Berg and Kramer 1979; Averyt et al. 2004); pH effects on fulvic acids have been known of for a long time (e.g., Gamble 1970), and  $\text{Ca}^{2+}$  is known to compete with lead for fulvic acid binding (Pinheiro et al. 1999). The major ions likely to affect metal complexation in the study lakes are  $\text{H}^+$  and  $\text{Ca}^{2+}$ . Our measurements were at constant pH to simplify the measurements and to facilitate comparison, but the lake data have a reasonable spread of calcium concentrations, which makes it possible to investigate the effect of calcium on the complex stability for lead (the copper speciation was determined in only two lakes, so there is insufficient spread of calcium concentrations). A plot of  $\log K'_{\text{PbL}}$  as a function of  $\log[\text{Ca}^{2+}]$  (Fig. 8) shows that  $\log K'_{\text{PbL}}$  decreases at a rate of 1.3 units per order of magnitude of  $[\text{Ca}^{2+}]$  (in  $\mu\text{mol L}^{-1}$ ):

$$\log K'_{\text{PbL}} = -1.3 (\pm 0.4) \log[\text{Ca}^{2+}] + 15.1 (\pm 0.7)$$

The plot has a slope close to unity, which would be ex-

pected for competition of a divalent metal ion as calcium for the same binding site on the ligands as used by lead. As this effect occurred at calcium concentrations  $>10 \mu\text{mol L}^{-1}$ , the stability constant of the  $\text{CaL}$  species ( $K'_{\text{CaL}}$ ) must have a value of  $>10^5$ . There are no calcium complex stability data available in the literature for ligands in natural waters, but there are data for fulvic and humic acids, which may well be the source of these ligands; these data are then sometimes expressed on a weight basis as the molecular weight of these compounds is not accurately known, making comparison difficult. Nevertheless, our data are consistent with literature data (Pinheiro et al. 1999) showing calcium binding by fulvic acid at the same calcium concentrations.

Relation between lead complexation and the distribution of dissolved lead: The general shape of the lead profile in the water columns of the lakes reflects its atmospheric input followed by scavenging by adsorption on sinking particles (see for instance the profiles for lead in Redo [May and September] and Ladove [September and July] and Neadalsvatn). The rate of scavenging along with the water residence time determine the residence time of lead in the lake and therefore its residual dissolved concentration. It is possible that the scavenging rate is moderated by the organic complexation. The general shape of the profile of lead is similar to that of the ligands in several of the plots in Fig. 4. The lead and the ligands may to some extent have the same source if they are both derived from a mixture of runoff and atmospheric inputs. However, their paths are likely to separate unless there is an association that resists for instance the removal of lead by scavenging. Plots of lead as a function of the ligand concentration showed covariation between the dissolved lead and the ligand concentrations (Fig. 9). Lines for 1:1 covariation have been drawn in the plots for comparison, from which it can be seen that the actual slopes tend to be less than unity, indicating that the complexation does not fully prevent the lead from being scavenged. However, the covariation of lead with the ligand concentration suggests that the scavenging rate of dissolved lead is diminished as a result of the organic complexation. This means that models attempting to calculate the residence time of lead in lakes should incorporate the change in scavenging by complexation reactions.

Source of the ligands: In principle the origin of the ligands can be from humic or fulvic acids, such as from runoff, or produced in situ by phytoplankton in the lakes. The productivity of the majority of these low-ionic-strength lakes is very low, and their transparency high (Sommaruga and Psenner 1997), which tends to be deleterious for phytoplankton (Sommaruga et al. 1997). It has been known for a long time that humic and fulvic substances bind copper and other metals (Buffle et al. 1977), and it is likely that these are the main source of the ligands in the mountain lakes (Xue and Sigg 1999), rather than in situ production by phytoplankton, which may be a more important contributor to low-land lakes like Esthwaite Water (Achterberg et al. 1997). The large difference in complexing ligand concentrations between copper and lead is not necessarily a sign of different ligands: fulvic and humic acids tend to be relatively large

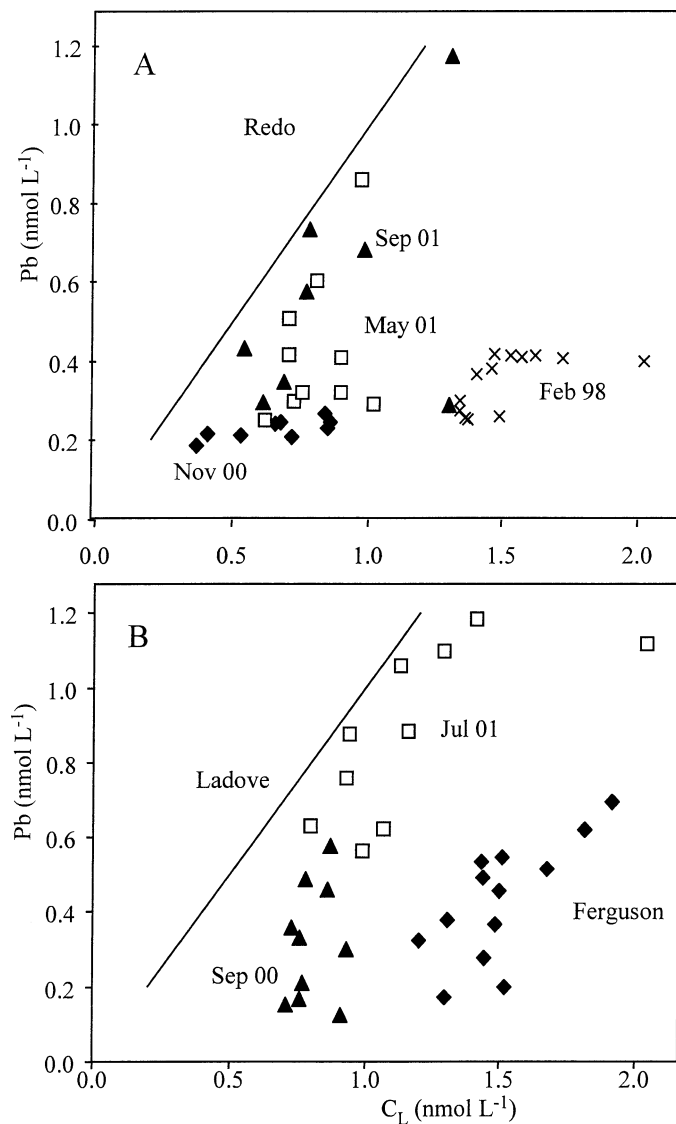


Fig. 9. (A) Concentration of dissolved lead as a function of the ligand concentration for lead in Redo; (B) concentration of dissolved lead as a function of the ligand concentration in Ladove and Ferguson.

compounds that may well form weak as well as strong complexes depending on their configuration. The shape of the water column profiles of the lead- and copper-complexing ligands were similar, but at  $\sim 10\times$  higher levels for copper than for lead. This could suggest that different ligands bind these two metals, but it is also possible that the same humic or fulvic acids bind copper and lead with a different number of sites, or in differing configurations. The agreement in complex stability of the copper species in the lakes in this study and those in the New Zealand study (Averyt et al. 2004) is also consistent with the same, possibly humic and fulvic, substances being responsible for complexation in these waters.

Concentrations of fulvic acids in the mountain lakes can be seen to constitute a major proportion of the DOC (Table 2); calibration was against Suwannee River fulvic acid,

which may not be the correct model of the fulvic substances in these lakes, and in some lakes the fulvic acid amounted to more than the DOC (the DOC values should be used as indicative values only as they were from a database on these lakes consisting of surface water samples collected at different sampling times). The  $\log K'_{\text{CuL}}$  values of 13.5–14 found here (Table 3) for what potentially are fulvic acids in these lakes, are within the same range (12–14) as found for Suwannee River fulvic acid in  $0.01 \text{ mol L}^{-1} \text{ KNO}_3$  (Xue and Sigg 1999). This similarity suggests that fulvic acids are a reasonable model for the ligands in mountain lakes. However, evidence regarding the actual nature of the ligands is still lacking.

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Received: 6 May 2004

Accepted: 16 December 2004

Amended: 18 January 2005