

Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece

Eleni Pertsemli, Dimitra Voutsas*

Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece

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Abstract

The distribution of heavy metals in two lakes of high ecological significance, Doirani and Kerkini, located in Northern Greece was studied. Eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined in water, total suspended solids, fine and coarse sediments. Moreover, the modified BCR fractionation scheme was employed in sediments and suspended solids to determine soluble, oxidisable, reducible and residual fractions of metals. The Lake Doirani presents higher metal concentrations in aqueous phase than Lake Kerkini; Cd, Cu, Ni, Pb and Zn are above the chronic freshwater quality criteria for aquatic life. In both lakes, Fe and Mn are the most abundant elements in total suspended solids whereas Cd the less abundant. The Lake Kerkini exhibits higher concentrations of all the examined metals in sediments comparing to the Lake Doirani, however the concentrations are lower than the sediment quality guidelines. Cd in sediments is mainly in soluble fraction, Pb and Cu exhibit significant oxidisable fractions whereas, Cr and Fe associated mainly with residual fraction.

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1. Introduction

The 2000/60/EC Directive in the field of the water policy aims at the maintaining and the improving of aquatic environment in the Community by establishing a framework for the protection of surface water. Heavy metals are among the pollutants that should be monitored in order to obtain a coherent and comprehensive overview of quality status for a certain aquatic system. Heavy metals in aquatic environment are distributed among aqueous phase, suspended particles and sediments. Suspended particles play an important role controlling the reactivity, transport and biological impacts of metals and other substances in aquatic environment and provide a crucial link for chemical constituents between water column, bed sediments and food chain [1]. Sediments also play an important role as a sink and possible source of trace metals. Many studies have been focused on the investigation of the total metal content in particulate matter. However, information on total concentration alone does not offer sufficient information about mobility, bioavailability and toxicity of

metals. Their behavior in aquatic environment depends also on the physicochemical forms they occur. Sequential extraction is a well established approach for the investigation of different forms of trace metals in soils and sediments. Several sequential fractionation procedures have been suggested to identify element distribution in “operationally” defined pools; from water soluble to recalcitrant forms immobilized in mineral lattices. The five step protocol developed by Tessier et al. is the most widely used while many modified procedures with different reagents or operational conditions have been proposed [2–5]. Considering the diversity of procedures and the lack of uniformity of indifferent protocols, the Community Bureau of Reference (now Standards, Measurements and Testing Programme) proposed a standardized/harmonized three step sequential extraction protocol for metals in soil and sediments. However, some sources of uncertainty such as irreproducibility and inaccuracy in application of the BCR sequential extraction procedure to sediments lead on to modifications of the initial protocol and to the proposal of a modified BCR scheme [3,4,6,7].

The present study investigates the distribution of heavy metals in Lakes Kerkini and Doirani, Northern Greece. For this purpose the concentrations of eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined in water, total suspended matter,

* Corresponding author. Tel.: +30 2310 997858; fax: +30 2310 997747.
E-mail address: dvoutsas@chem.auth.gr (D. Voutsas).

fine and coarse sediments. Moreover, the modified BCR fractionation scheme was employed in sediments and suspended solids to determine operationally active forms. Distribution coefficients of metals between water and particulate phases were calculated and discussed.

2. Materials and methods

2.1. Studied lakes

Lake Doirani ($41^{\circ}13'N$, $22^{\circ}44'E$) is located North to Thessaloniki at an altitude of 142 m, in the border between Greece and FYROM (Fig. 1). The present lake is the remnant of a larger pleistocene lake formed in a karstic terrain. The surface area of the lake is now about 28 km^2 , 15 of them are within Greek territory. Underwater springs and surface runoff from the catchment are the main water sources. The depth range from 5.0 to 8.5 m. Agriculture and cattle raising are the main activities on the Greek side of the catchment area. The shore of FYROM side is mainly used for recreational purposes. The Lake Doirani is an eutrophic–hypertrophic lake exhibiting temporarily nitrogen (autumn–winter) or phosphorus (spring–summer) as limiting nutrient [8].

Lake Kerkini ($41^{\circ}12'N$, $23^{\circ}09'E$) is a large, artificial reservoir that was created on the site of a former natural swamp, after the construction of a dam across the Strymon River (Fig. 1). The surface area of the lake varies from 54 to 72 km^2 , the max-

imum depth is 10 m, however large fluctuations, more than 5 m, in water level caused by the irrigation practices are observed. Lake Kerkini receives large quantities of sediment from the River Strymon and plays an important role in providing flood control, maintenance of water quality, water storage, recharge and discharge of groundwater. Moreover, Lake Kerkini is along the migratory flyway for birds' enroute and supports the largest mixed nesting colony of water birds in Greece. For this reason, it is considered as a protected aquatic system according to International Convention of Ramsar.

2.2. Sampling and analysis

Surface water and sediment samples were collected from Lake Doirani (D) and Lake Kerkini (K) during three sampling campaigns. The water samples were collected in glass bottles and kept cool in the field. Sediment samples were collected using an Eckman sampling device. At each site three subsamples of water and sediments were collected and mixed, to ensure that the sample was representative for this site. The sediments were put in air-sealed plastic bags and kept cool in the field. Dissolved oxygen and pH were measured in the field.

After transportation to the laboratory water samples were filtered through $0.45\text{ }\mu\text{m}$ membrane filter for separation of total suspended solids (TSS). Filtered samples were acidified using nitric acid. Filter loaded with TSS was dried at 70°C and kept for metal analysis. The sediments were also dried at 70°C ,



Fig. 1. Map of the studied lakes, Doirani and Kerkini, Northern Greece (sampling sites are shown).

Table 1
The mBCR sequential extraction procedure

Step	Reagents/conditions	Fraction	Extracted phases
1	Acetic acid 0.11 mol/L pH 2.85, 16 h	SOL: soluble	Soluble forms, exchangeable metals and metals bound to carbonates
2	Hydroxyl ammonium chloride, 0.5 mol/L, pH 1.5	RED: reducible	Metals bound to iron and manganese oxyhydroxides
3	Hydrogen peroxide, 8.8 mol/L, 2 h at 85 °C, ammonium acetate 1 M at pH 2.0	OXI: oxidisable	Metals bound to organic matter and sulfides
4	Aqua regia	RES: residual	Metals bound in lithogenic minerals

homogenized and size fractionated using stainless steel sieves in a mechanical sieving apparatus. Two grain size fractions were separated: the sand fraction (100–1000 μm , coarse fraction) and silt/clay fraction (<100 μm , fine fraction). Water content, loss on ignition and carbonate content measurements were based on weight losses after drying and combustion of the sediments at 105, 550 and 900 °C, respectively.

TSS and sediments were subjected to modified BCR sequential extraction procedure. The metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in aqueous samples and in extracts obtained from BCR procedure were determined by employing flame (FAAS) or flameless (GFAAS) atomic absorption spectrometry (Perkin-Elmer 2380 FAAS system coupled with a HGA-400 Graphite Furnace system). The dissolved metals in water were determined by GFAAS system. The detection limits were 0.05 $\mu\text{g/L}$ for Cd, 0.5 $\mu\text{g/L}$ for Pb and Mn, 1 $\mu\text{g/L}$ for Cr, Cu, Fe and 2 $\mu\text{g/L}$ for Ni and Zn. FGAAS was also employed for the determination of Cd, Cr, Cu, Ni, Pb and FAAS for the determination of Fe, Mn and Zn in suspended solids and sediments. Reagent-matched standard solutions were prepared in the same matrix as the extracting reagents for calibration curves. Quality control was assured by the analysis of duplicate samples, reagent blank, procedural blanks and standard reference materials. The standard reference material SRM 2704 (river sediment) was used for total element analysis; percentage recoveries ranged from 85% (for Cd) to 105% (for Ni). The standard reference material CRM 601 (lake sediment) was used to verify the accuracy of the sequential extraction method. The recovery rates for heavy metals ranged from 82% (for Pb in soluble fraction, BCR step 1) to 110% (for Cr in residual fraction, BCR step 4). Analytical precision, expressed as relative standard deviation (R.S.D.), was in general better than 12%.

2.3. BCR sequential extraction procedure

The modified BCR sequential extraction scheme was used for metal fractionation [6,7,9]. TSS, coarse and fine sediments were subjected to sequential chemical extraction by 0.11 M acetic acid, 0.5 M hydroxylammonium chloride at pH 1.5 and hydrogen peroxide followed by 1 M ammonium acetate at pH 2 (Table 1). The extracts were centrifuged and the supernatants were filtered through a 0.45 μm membrane filter. This extraction procedure fractionates metals into: (a) *acid soluble phase* (fraction SOL) that is made up of exchangeable metals and metals bound to carbonates, easily released to the water column, (b) *reducible phase* (fraction RED) which consists of metals bound to iron and manganese oxyhydroxides and can be released under changes in redox conditions and (c) *oxidisable phase* (fraction OXI) that represents the metal bound to organic matter and sulfides and can be released under oxidizing conditions. The residue from the BCR procedure was further digested with aqua regia extracting *residual fraction* (fraction RES) that contains the metals bound strongly in lithogenic materials.

3. Results and discussion

3.1. Dissolved metals

Similar pH and DO values have been measured in both lakes. The waters showed a slightly to fairly alkaline character with pH values ranged from 7.8 to 9.0 in Kerkini and 7.6 to 9.5 for Doirani. The concentrations of DO showed large variability ranging from 4 to 12 mg/L.

The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in water from Lake Kerkini and Doirani are shown in Fig. 2. The

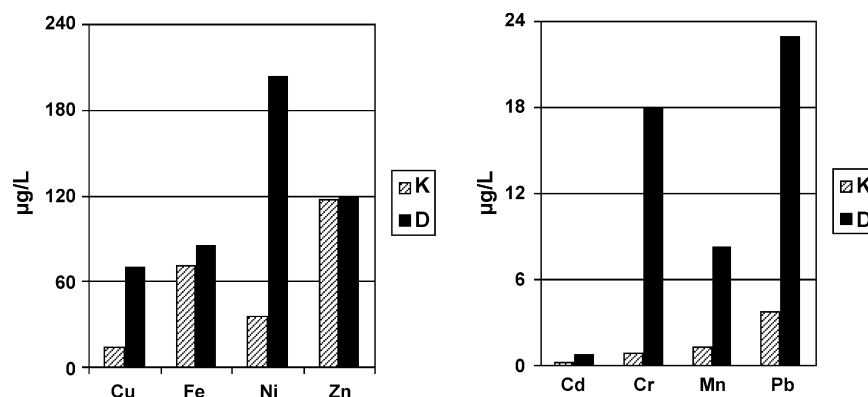


Fig. 2. Dissolved metals in Lakes Kerkini (K) and Doirani (D), Northern Greece.

Table 2
Concentrations of dissolved metals ($\mu\text{g/L}$) in various lakes

Lake, Country	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Lake Doirani, Greece [10]	0.1–0.4	1–17	1–13	29–690	14–160	1–6	1–6	6–66
Lake Volvi, Greece [10]	0.1–0.4	1–22	1–9	20–582	9–90	1–4	0.3–5	4–99
Lake Koronia, Greece [10]	0.1–0.6	1–27	1–18	20–1311	8–384	1–9	1–5	2–126
Lake Megali Prespa, Greece [10]	0.1–0.2	1–19	2–5	16–103	1–14	1–22	1–12	2–12
Lake Mikri Prespa, Greece [10]	0.1–0.2	1–15	2–7	24–238	9–46	1–10	2–8	5–20
Hazar Lake, Turkey [24]			dl–18	120–430	4–25	dl–12		38–71
Ataturk dam lake, Turkey [25]			10–40			500–900		40–140
Lake Texoma, USA [26]	2–249	2–8	11–104	35–430	1–152	1–12	15	12–246
Lakes, USA [27]	dl–0.11						dl–1.04	dl–14
Lake Balaton, Hungary [13]	$1-5 \times 10^{-3}$		0.22–0.59			0.33–0.71	0.04–0.33	0.22–1.9
Freshwater quality criteria [11]								
CMC, acute	2.0	570/16 ^a	13			470	65	120
CCC, chronic	0.25	74/11 ^a	9			52	2.5	120

dl: Detection limit; CMC: criterion maximum concentration; CCC: criterion continuous concentration.

^a Cr(III)/Cr(VI).

Lake Doirani presents higher metal concentrations in aqueous phase than Lake Kerkini, especially for Cr, Cu, Mn, Ni and Pb, suggesting different geological substrate, different composition of feeding waters and possible impacts from pollution sources. The concentrations of Cd, Cr, Fe and Mn in Lake Doirani are within the values previously reported (Table 2) [10]. However, Cu, Ni, Pb and Zn exhibited higher concentrations, possibly due to pollution events. The concentrations of Cd, Cu, Ni, Pb and Zn in Lake Doirani are above the chronic freshwater quality criteria for aquatic life (Table 2) [11]. The concentrations of dissolved metals in Lake Kerkini are similar to those reported for the Strymon River which is the feeding water system [12]. Although, a direct comparison with other lakes is not always possible due to different geological background, the concentrations of heavy metals in other lakes located in Northern Greece and in other countries are reported in Table 2. Generally, the concentrations of metals determined in studied lakes are within the range reported for the other lakes.

3.2. Metals in suspended particulate matter

Suspended particles comprise sediments and seston which are suspended in the water column, either permanently or, more usually for sediments, temporarily and in a state of exchange with the bed sediment reservoir. The episodic resuspension, deposition and generation of particles, coupled with their high reactivity, ensure that they can play a key role in the availability, transport, recycling and fate of metals in the aquatic environment. Changes in physicochemical parameters, adsorption–desorption reactions and mixing processes influence the particulate metal concentrations [1,13]. The total concentrations of metals in total suspended solids (as sum of four fractions extracted by employing the BCR fractionation scheme) are shown in Fig. 3a. Fe and Mn are the most abundant elements in particulate matter. The concentration of metals in TSS follows the order: Fe > Mn > Ni > Zn > Cu > Pb ~ Cr > Cd. The Lake Kerkini exhibits higher concentrations of particulate Cu, Fe and Mn than Lake Doirani. Similar fractionation patterns were

observed in both lakes (Fig. 3b and c). Pb was found mainly in residual fraction (70–80%), Cd, Cr, Fe, Ni and Zn (in Doirani) exhibited significant oxidisable fractions (50–90%) whereas Cu and Mn exhibited significant soluble fractions (47–65%).

The distribution coefficients (K_d) of metals defined as the ratio of the metal concentration in particulate matter ($\mu\text{g/kg}$) to the dissolved metal concentration ($\mu\text{g/L}$) have been calculated. K_d depends on the nature of suspended solids or sediments, geochemical parameters of the water and specific characteristics of each element [14,15]. The logarithmic values of K_d are shown in Fig. 6a. The log K_d values ranged from 1.1 to 4.9 L/kg. Mn and Fe exhibited the higher values. The ranking of log K_d values in Lake Kerkini is Mn > Fe > Cr > Cu > Pb > Ni > Cd > Zn and in Lake Doirani Mn ~ Fe > Cd > Zn > Ni ~ Pb > Cr > Cu. The lower association with particulate matter was observed for Cr and Cu in Lake Doirani and for Cd and Zn in Lake Kerkini.

3.3. Metals in sediments

The total metal concentrations (as sum of four fractions extracted by employing the BCR fractionation scheme) in fine and coarse sediments are shown in Fig. 4. The Lake Kerkini exhibited higher concentrations of all the examined metals. The concentrations of metals in sediments from both lakes followed the order: Fe > Mn > Zn > Cr > Ni > Cu > Pb > Cd. Fine fraction was usually more enriched than coarse (except for Pb and Cd in Doirani). It must be noticed that the fine sediments in Kerkini exhibited higher organic content than coarse sediments (4–11 and 2–4.5%, respectively). Lower organic content was found in Doirani, with no significant difference between fine and coarse sediments (1–1.8 and 0.8–2%, respectively).

The concentrations of heavy metals in sediments from other lakes as well fresh water sediment quality guidelines expressed as probable effect level (PEL) or threshold effect level (TEL) values are shown in Table 3. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in sediments are lower than the proposed PEL or TEL values (Table 3). Only Ni exceeded the proposed TEL value [16].

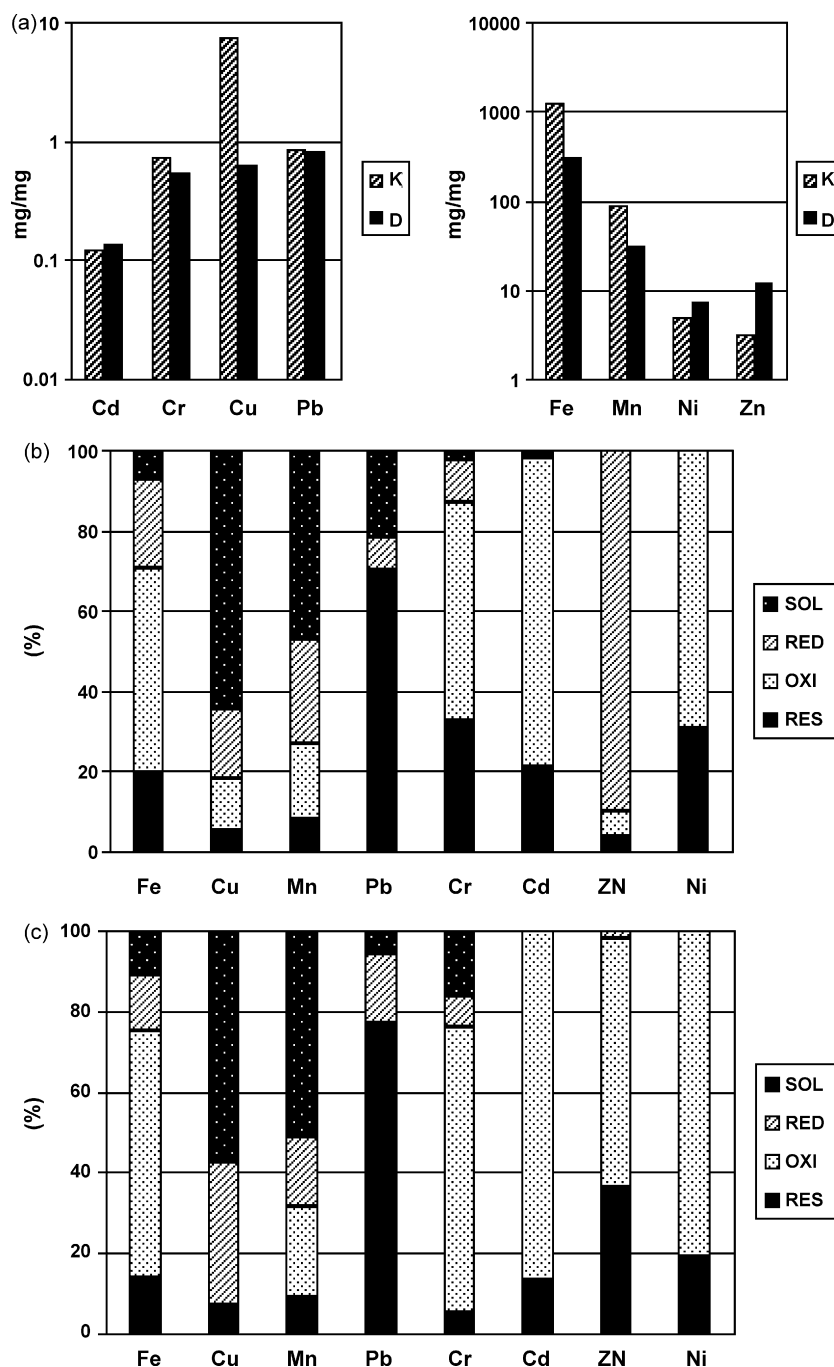


Fig. 3. Heavy metals in suspended particulate matter from Lakes Kerkini and Doirani, Northern Greece: (a) total concentrations of metals; (b and c) metal distribution according to BCR fractionation scheme in Lake Kerkini and in Lake Doirani, respectively.

Most metals occurred at higher concentrations in sediments than in TSS. Fe and Cr were found at 35–40-fold, Mn at 5–10-fold and Pb, Ni at 2–5-fold higher concentrations in sediments. However, similar concentrations in sediments and in TSS were observed for Cd (in Doirani) and Cu (in Kerkini).

The distribution of heavy metals in different phases extracted according to BCR fractionation scheme is shown in Fig. 5. Similar patterns for the examined metals were observed in both lakes. The ranking of metals in different BCR fractions according to their percentage contribution is the follow-

ing: $Cd > Mn > Cu > Zn > Ni > Fe > Pb > Cr$ in soluble forms, $Zn > Cu > Fe > Mn > Cd > Ni > Cr > Pb$ in reducible fraction, $Pb > Cu > Ni > Cr > Zn > Fe > Mn > Cd$ in oxidisable fraction and $Cr > Fe > Ni > Zn > Cd > Mn > Cu > Pb$ in residual fraction. The dominant proportion (63–68%) of Cd in Kerkini was found in soluble fraction, which indicates that Cd is mainly occurred in exchangeable forms and bound to carbonates. Other studies also reported that Cd in sediments is associated with labile fractions [5]. Mn was distributed in all four fractions; a significant amount was found in the soluble fraction (25–46%). Mn

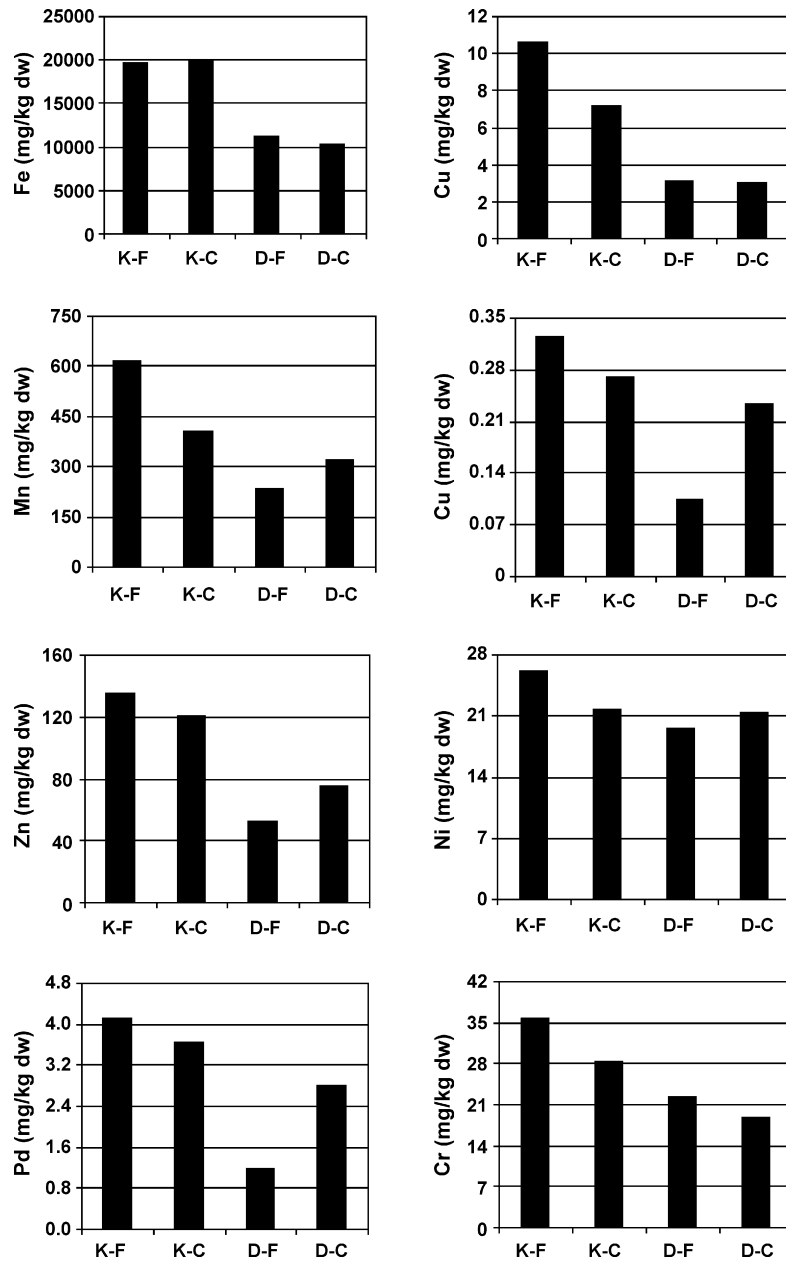


Fig. 4. Heavy metals in sediments from Lakes Kerkini and Doirani, Northern Greece (K-F, K-C: fine and coarse sediments in Lake Kerkini; D-F, D-C: fine and coarse sediments in Lake Doirani).

in this fraction retained on sediment surface by relatively weak electrostatic interactions and may be released by ion exchange processes and dissociation of Mn carbonate phase [5,17,18]. Ni and Zn showed similar patterns, distributed almost equally in all phases. Soluble fraction for Zn and Ni ranged from 8–22% and 10–20%, respectively. Pb dominated by the oxidisable fraction (69–94%) coinciding with organic and sulfur compounds. Cu also showed considerable fraction in oxidisable forms. Cu can easily form complexes with organic matter due to the high stability constant of organic copper compounds. This is consistent with the results reported by other investigators [17–19]. Cr and Fe showed similar fractionation profile with significant residual fraction ranging from 58 to 76% for Cr and 35 to 65%

for Fe, followed by the oxidisable fraction. Metals in residual fraction associated mainly with aluminosilicate minerals and therefore are unlikely to be released to aqueous phase. A negligible amount of Fe was found in the soluble fraction compared to the total concentration showing that this metal is unlikely to pose a direct and significant threaten to the aquatic environment. Similar results have been reported by other investigators [5,20,21].

The distribution of metals in different phases according to BCR procedure offers an indication of their availability which in turns, assess the risk connected with the presence of metals in aquatic environment. Risk assessment code (RAC) gives an idea of the possible risk by applying a scale to the percentage of

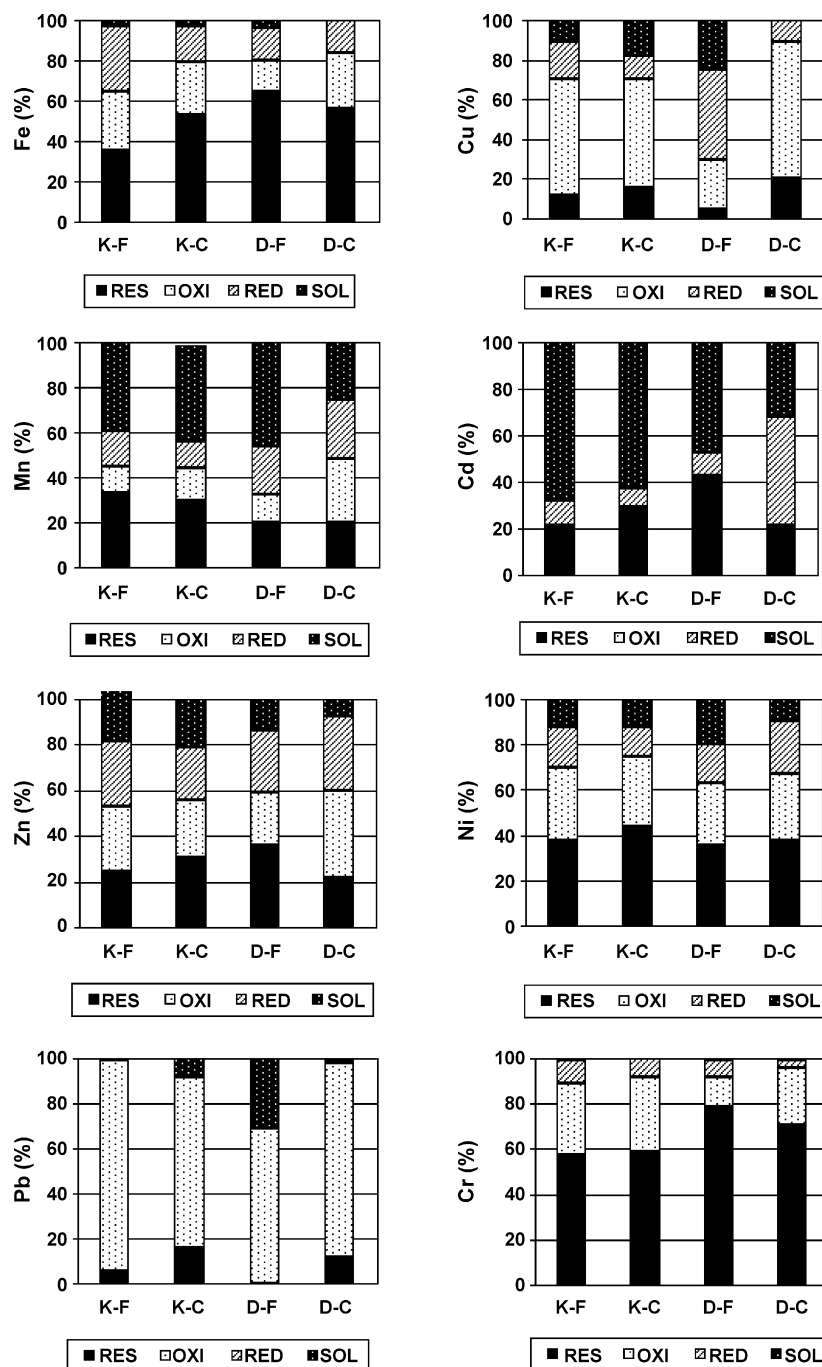


Fig. 5. Metal distribution in sediments according to BCR fractionation scheme (K-F, K-C: fine and coarse sediments in Lake Kerkeni; D-F, D-C: fine and coarse sediments in Lake Doirani).

metals presented in exchangeable and carbonate fractions, i.e. labile phases. According to RAC if this fraction is <1% there is no risk for the aquatic system, 1–10% exhibits low risk, 11–30% medium risk, 31–50% high risk and >75% very high risk [22,23]. In this study, Cd seems to pose high risk due to high availability and toxicity. Mn and Zn exhibited significant labile fractions posing medium to high risk.

The distribution coefficients of metals, defined as the ratio of the metal concentration in sediments ($\mu\text{g}/\text{kg}$) to the dissolved metal concentration ($\mu\text{g}/\text{L}$) are shown in Fig. 6b. The

values of $\log K_d$ ranged from 1.6 to 5.9 L/kg. Similar ranking of $\log K_d$ values were found in both lakes; Fe, Mn and Cr presented the higher distribution coefficients whereas, Cu the lower ($\text{Mn} \sim \text{Fe} > \text{Cr} > \text{Zn} \sim \text{Cd} \sim \text{Pb} > \text{Ni} > \text{Cu}$ in Lake Kerkeni and $\text{Fe} > \text{Mn} > \text{Cr} > \text{Zn} > \text{Cd} > \text{Ni} \sim \text{Pb} > \text{Cu}$ in Lake Doirani). Cu and Ni were found to have the lower K_d values in Lake Balaton, Hungary, whereas Cd and Pb exhibited the highest values. Generally, the partitioning coefficients of examined elements are low and, within the range reported for natural water [15].

Table 3
Concentrations of heavy metals ($\mu\text{g/g}$) in sediments

Lake, Country	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Lake Volvi, Greece [28]	0.74–1.0	20–25	12–16	2.9–3.8	84–157		10.5–14.4	48–75
Lake Koronia, Greece [28]	0.97–1.0	27–37	15–19	5.2–5.7	581–682		16.3–24.5	72–100
Lake Lochnagar, UK [29]	0.4–6						30–400	50–250
Hazar Lake, Turkey [24]		17–79	10–64	3.7–30 ^a	85–625	38–130		46–210
Ataturk dam lake, Turkey [25]			15–23			44–140	1	59–61
Lake Palas, Turkey [30]	2.8–4.8	22–58	dl–51	0.2–1 ^a	98–863			10–47
Lake Texoma, USA [26]	1–3	12–51	9–136	8–32 ^a	145–643	6–31	5–15	33–242
Lake Balaton, Hungary [13]	0.1–0.7	5.7–66	0.7–36		160–760	4.4–55	2.4–160	13–150
Kolleru Lake, India [21]	dl–0.27	44–66	270–572			0.2–2.2	2.5–5.1	356–622
Lake Macquarie, Australia [31]	<0.1–0.2	7–45	6–17			11–57	5.5–17	12–68
Sediment quality guidelines [16]								
PEL	3.5	90	197			35.9	91.3	315
TEL	0.60	37.3	35.7			18	35	123

dl: Detection limit; PEL: probable effect level; TEL: threshold effect level.

^a g/kg.

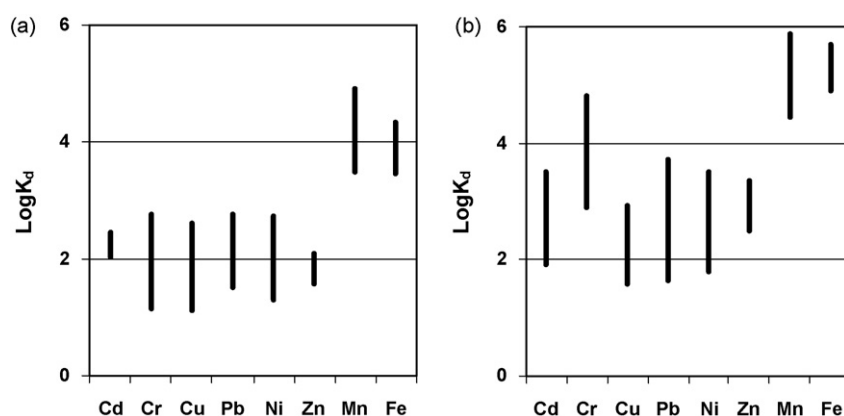


Fig. 6. Distribution coefficients ($\log K_d$) of metals in Lakes Kerkini and Doirani, Northern Greece: (a) ratio of the metal concentration in suspended particulate matter ($\mu\text{g/kg}$) to the dissolved metal concentration ($\mu\text{g/L}$); (b) ratio of the metal concentration in sediments ($\mu\text{g/kg}$) to the dissolved metal concentration ($\mu\text{g/L}$).

4. Conclusions

Eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined in water, total suspended solids, fine and coarse sediments of two Lakes, Doirani and Kerkini, located in Northern Greece. Doirani exhibited higher concentrations in water, above the chronic freshwater quality criteria, for Cd, Cu, Ni, Pb and Zn. Kerkini exhibited higher concentrations of all the examined metals in sediments, although lower than sediment quality criteria. Fe and Mn are the most abundant metals in suspended particulate matter.

The modified BCR fractionation scheme was employed to determine soluble, oxidisable, reducible and residual metal fractions in sediments and suspended particulate matter. Metals in suspended particulate matter and sediments exhibited different fractionation profiles. In suspended matter, Pb was found mainly in residual fraction, Cd, Cr, Fe, Ni and Zn exhibited significant oxidisable fraction, Cu and Mn significant soluble fraction. In sediments, Cd exhibited significant soluble fraction, Pb and Cu significant oxidisable fraction whereas Fe and Cr were found mainly in residual fraction.

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