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Factors Regulating the Distribution of Elements in the Sediments of a Seasonally Anoxic Lake in Tropical Taiwan

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ABSTRACT

Sixteen metals, both total and acid-leached, and their binding formations were quantified for the sediment column of the seasonally anoxic Great Ghost Lake. Since marked variation in the content of organic matter plays a major role in regulating the distribution of metals in sediments, this study provided insight into the relationship between organic matter and metals in a naturally anoxic water environment. Metals, Al, Cs, Mg, Rb and V, had significant negative correlations with total carbon content (TC) and occurred less often in mobile fractions. These findings indicate that these metals came from lithogenic sources and did not change much during early diagenesis. As a result, signals of these elements, whose origins can be traced back to long-range transport dust, were better preserved. Acid-leached contents of Cs, Mg and Rb also had negative correlations with TC, while both total and acid-leached As and Cd had good positive correlations with TC. Large portions of both As and Cd, were observed in mobile fractions (especially As) and came from organic sources and/or were incorporated into organic matter during early diagenesis (especially Cd). Long-term variations in redox conditions of the lake were induced by climate changes and might have influenced distributions of Sr and redox-sensitive Mn and V in mobile fractions. In addition to natural processes, enrichment of Pb and Cd near the core top was from anthropogenic aeolian sources. Finally, recent aeolian fluxes of Al, As, Ba, Br, Ca, Cd, Ce, Cl, Cr, Cs, Cu, Er, Eu, Fe, Ga, Gd, K, La, Lu, Mg, Mn, Na, Nd, Ni, Pb, Rb, Si, Sm, Sr, Ti, Tm, V, Yb, Zn and Zr were estimated and large amounts of micronutrient Fe (~60 μg cm^{-2} yr^{-1}), of aeolian origin, was also noted.

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1. INTRODUCTION

The variable water chemistry in lakes favors the study of geochemistry of an aquatic environment. The Great Ghost Lake (GGL) is seasonally stratified and anoxic (Chen and Wang 1990; Wang and Chen 1990). Undisturbed sediments of the lake serve as an archive of dust fallout. Chen et al. (1993) found that the high mountain lake contained coarse, organic carbon-rich sediments with periodic appearances of a fine, organic carbon-poor layer. These dark and coarse-grained sediments were characterized by a single mode of 80 μm or larger, and were formed in the watershed. The fine, bright sediments, however, were characterized by a single mode of 10 μm or smaller and were of aeolian origin. Since dust storms from China have been found to affect Taiwan (Liu and Lin 2004; Chiang et al. 2004; Yuan et al. 2004; Chou et al. 2004; Lee and Liu 2004; Lin et al. 2004), the occurrence of gray colored sediments and bimodal particle size distribution (Fig. 1) suggest that dust storms were more frequent in China at about 1350AD (Chen et al. 2001).

The hypolimnion lake is anoxic most of the year but not during the winter turnover (Wann et al. 1997). The anoxic conditions promote anaerobic mineralization processes in anoxic bottom waters and underlying sediments (Stumm and Morgan 1981; Kuivila and Murray 1984; Sigg et al. 1991; Balistrieri et al. 1992a; Balistrieri et al. 1992b; Hamiltontaylor et al. 1996) and affect distributions of metals in sediments (Carignan and Nriagu 1985; Wann and Chen 1996; Schaller et al. 1997; Wann et al. 1997). During winter turnover, dissolved oxygen enters the anoxic hypolimnion and oxidizes the dissolved reduced species, especially redox-sensitive Fe and Mn. Fe and Mn oxides are both good scavengers in the water column and able to remove other dissolved species (Balistrieri et al. 1992b; Hamiltontaylor et al. 1996; Xue et al. 1997; Wann et al. 1997). Elements removed by Fe and Mn oxides are released from sediment, when reductive dissolution of oxides occurs during stagnation (Davison et al. 1982; Davison and Woof 1984; Davison 1985; Balistrieri et al. 1992a; Balistrieri et al. 1992b).

Since climatic changes can affect the state of lake stagnation, these changes might play a significant, albeit indirect, role in regulating distributions of redox-sensitive elements in sediments of an anoxic lake. Previous studies on sediments of GGL by Chen et al. (1993), Lou et al. (1997) and Chen et al. (2001) examined their relationships with climatic changes, whereas Wann et al. (1995) and Wann and Chen (1996) only examined surface sediments and Wann et al. (1997), the Fe cycle. This study examined characteristics of the same lake but focused on factors regulating the distribution of elements in the sediment column based on core samples, which had not previously been the subject of a systematic study.

Transformation and re-mobilization of metals during early diagenesis are the major processes regulating the distribution of metals in anoxic sediments. These processes were evaluated to assess the contribution of aeolian metal fluxes. Transformation and mobility of metals depend on their specific chemical forms or binding formation in sediments. Therefore sequential extraction procedures were used to determine the forms of binding (Tessier et al. 1979; Salomons and Forstner 1980; Quevauviller et al. 1997) A 3-step sequential extraction proce-

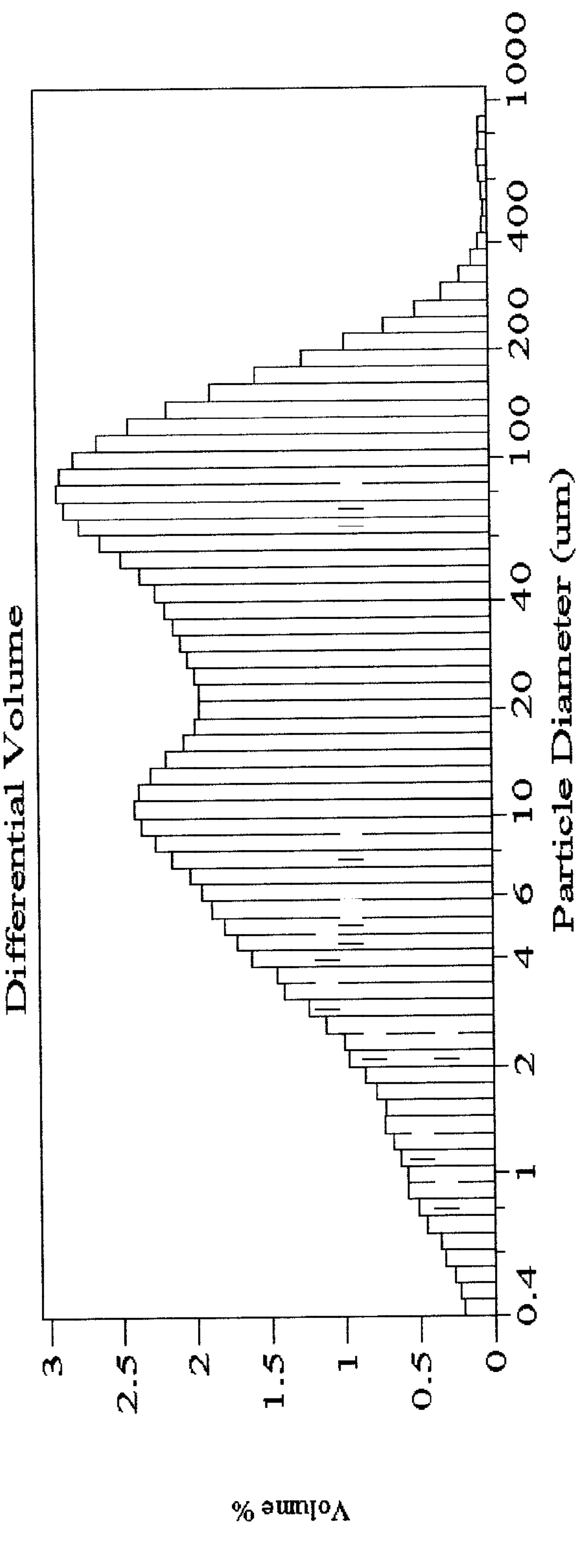

Fig. 1. The grain size distribution of a typical gray, bi-modal sediment sample.

dure was applied, using a protocol recommended by the Standard, Measurements and Testing Programme (SM&T), formerly known as the European Communities Bureau of Reference (BCR) (Quevauviller et al. 1997; Mester et al. 1998; Quevauviller 1998). This protocol uses certified reference material (CRM) 601, which was developed to enable worldwide comparisons of test results from studies of metal-binding forms in sediment columns. (Quevauviller et al. 1997). Although there are problems in using results of sequential extraction to simulate natural processes (Martin et al. 1987), this procedure provides further insight into particulate fractions and more detailed information, with which to evaluate the transformation and mobility of metals in sediment columns.

Due to its isolation, GGL is only slightly affected by local anthropogenic activity (Wann et al. 1995; Wann and Chen 1996). The atmosphere provides most of the anthropogenic material found in the lake (Chen et al. 2001). Anthropogenic activity, such as the burning of fossil fuels, garbage and leaded gasoline, has significantly increased the flux of certain elements into the atmosphere (Li 1981; Patterson and Settle 1987; Nriagu 1989; Hsu et al. 2004). Consequently, this aeolian material has become the principal factor controlling distribution of a number of elements in the lake sediments. The wide variation in the total organic carbon content of sediments is another important factor which regulates the distribution of elements. This study examined the correlations between organic matter and other elements. Analysis of the distribution and forms of elemental species, as well as relationships among elements and organic carbon, was undertaken in this study to develop a better understanding of (1) the extent to which climate and other factors regulate the distribution of elements in sediments; (2) the relationships between metals and organic matter; and (3) the geochemical and diagenetic processes in a seasonally stratified and anoxic lake sediment column.

2. STUDY AREA AND METHODS

Located at 22°52'N, 120°51'E, GGL is an oligo-mesotrophic body with an area of 11.25 ha, a volume of 1.67×10^6 m^3 and an altitude of 2150 m. It is the deepest (40 m; averaging 15.4 m) and best preserved, natural lake in Taiwan. There is very little human perturbation at this remote location and due to an absence of wind mixing or bioturbation, the lake sediments are interlaminated and well preserved. Argillite and slate are the major types of rock, surrounding the lake.

A plastic barrel was the gravity corer used to collect sediment samples. Cored sediments were immediately sealed with wax, after recovery, and then processed at a laboratory, where fishing line was used to prevent any possible metal contamination (Chen et al. 1993). The extent of oxidation was negligible, as indicated by an absence of color change, when sediments were exposed during the process.

During the leaching procedure, 15 ml of 1.6 N nitric acid was used to treat 0.3 g of dried sediment, which was shaken over night (Ng and Patterson 1982; Giblin et al. 1990) in a 50 ml centrifuge tube. The leachate was separated by centrifugation, removed with a quartz pipette and stored in pre-cleaned polyethylene bottles until the metals were measured. To determine the total metal content, a microwave system with an acid mixture of 42% HNO_3 and 17% HF was used to digest 0.3 g of dry sediment. ELAN 5000 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), coupled with a Ryton spray chamber and cross-flow nebulizer were used to measure metals. A peristaltic pump, with a flow rate of 1 ml min^{-1}, was then used to nebulize sample solutions.

The LECO CS-244 elemental analyzer was used to determine total carbon (TC), total nitrogen (TN) and total sulfur (TS) content of sediments. LECO CS-244 elemental analyzer was also used to determine the total inorganic carbon content of sediment, after the samples were incinerated at 450°C for 6 hours to remove organic carbon. The content of total organic carbon (TOC) was taken to be TC-TIC. Wann et al. (1995) provided details on trace metal determination and the National Institute for Environmental Studies (NIES) No. 2 Pond Sediment (NOAA 1995) provided calibrations for each set of sample treatments and metal determinations, including those for the metalloid, As. The measurement of Al, As, Cd, Ce, Cr, Cs, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sr, V and Zn were roughly ± 15.9, 10.7, 7.3, 9.5, 8.4, 7.1, 3.2, 5.3, 4.5, 4.1, 2.1, 10.5, 4.1, 11.5, 1.7 and 3.8%, respectively, based on replicate analysis.

A 3-step sequential extraction procedure (Mester et al. 1998) was used to determine metal contents of different fractions in sediments. According to Mester et al. (1998), the fractions of metal separated by the 3-step procedure are i) the exchangeable/carbonatic fraction (Step 1), ii) the easily reducible fraction (Step 2), and iii) the oxidisable fraction (Step 3). 0.5 g of dry sample in a 50 ml centrifuge tube was used in the procedure, with CRM 601 - lake sediment measured to control the quality of measurements. The tube was shaken at 45 rpm for 16 hrs with a vertical rotary shaker. The extract was separated by centrifugation at 10,000 rpm for 30 mins and was later removed with a quartz pipette to measure the metals with ICP-MS. Details of the sequential extraction steps mainly followed Mester et al. (1998).

3. RESULTS AND DISCUSSIONS

93 cm core was collected from the middle of GGL was studied. Lake cores collected, exhibited a distinctive lamination and correlated well with each other.

3.1 Organic Carbon and Weather Pattern

Distribution of TC, TN, TS, TC/TN ratio and water content in sediments are shown in Fig. 2. Since the content of inorganic carbon was usually very small (less than 0.2%), the TC measured was nearly equal to the total organic carbon (TOC). Low TC values correlated well with brighter sediments, whereas higher values correlated with darker ones. TC content vary markedly from 2.0 to 19.3 %. With a few exceptions, the TC-values generally increased with depth. This was in direct contrast to the usual trend that was found in the shallow and oxic Little Ghost Lake, in the same area (Lin 1992). Kuivila and Murray (1984) and Birch et al. (1996) showed that total organic carbon decreases with depth as a result of decomposition and remineralization of buried organic matter.

The variation in the TC content of sediments in GGL was generally a result of the variation in particulate input. Chen et al. (1993) and Lou et al. (1997) reported that the brighter

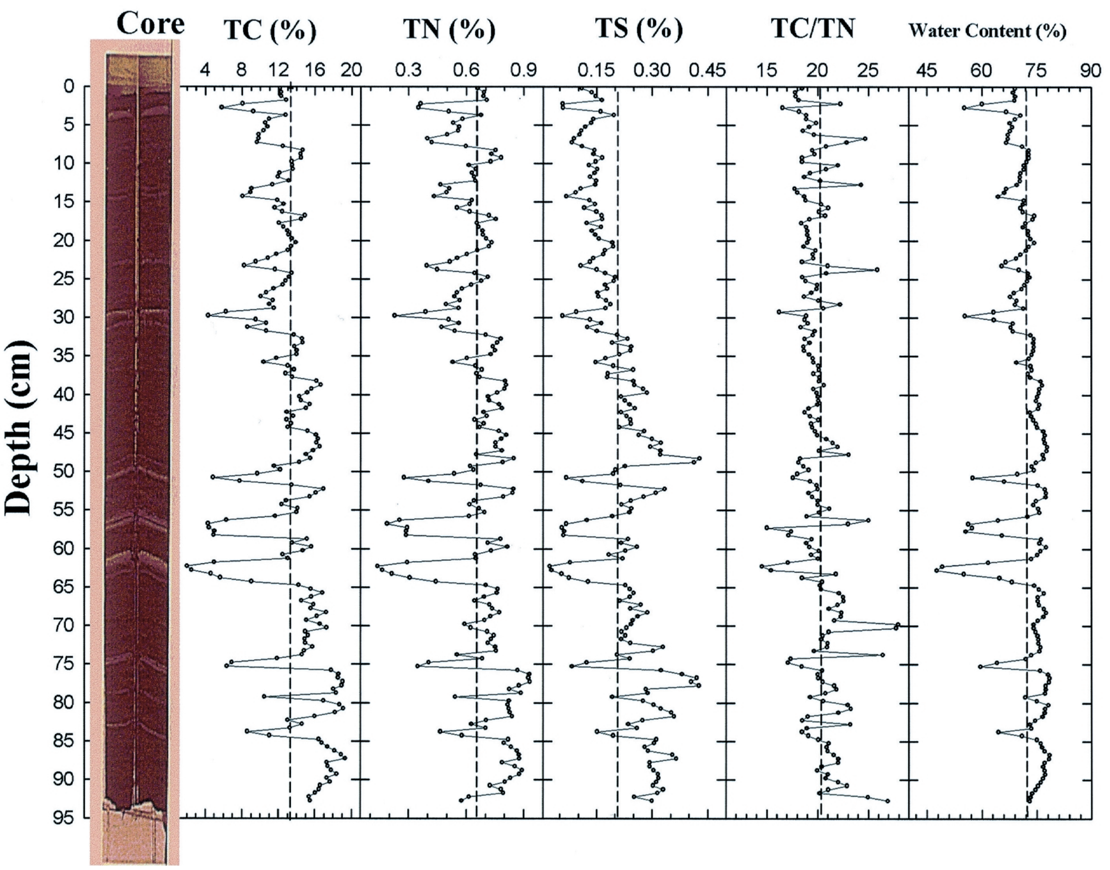

Fig. 2. Distribution of total carbon (TC), total nitrogen (TN), total sulfur (TS), TC/TN ratio and water content in the sediments of GGL (modified from Lou et al. 1997).

sediments, with lower TC and smaller particle size, were consistent with cool, dry periods, while darker sediments, with higher TC and larger particle size, correlated with warm, wet periods. During dry periods, when water levels were low, less TC particles entered sediments from the shore, leading to lower TC values (Chen et al. 1993; Lou et al. 1997). At the same time, the aquatic carbon with relatively low TC/TN ratios, of about 10, (Huang 1992; Huang and Chen 1994) became significant sources of TC. In addition, lower lake water volume, during dry periods, might have increased concentrations of nutrients, which resulted in larger numbers of aquatic organisms in water and sediments and lead to lower TC/TN ratios in sediments.

During wet periods, TC content of soil from the catchment area was high and the soil became the major source of sediments, with high TC content. The TC/TN ratios of terrestrial plants in this area were about 26 - 30. Consequently, the TC/TN ratio was also higher in the sediments deposited, during wet periods. This finding was supported by a good positive correlation between TC and TC/TN (Fig. 3). The TN and TS content ranged from 0.14% to 0.93% (averaging 0.65%) and from 0.02% to 0.43% (averaging 0.21%), respectively. The water content ranged from 47.6% to 78.5% (averaging 72.0%). Figure 3 reveals strong positive correlations between TN, TS and TC, and the intercepts of the regression lines are very close to zero. Since TC is nearly equal to the TOC, this implies that carbon, in sediments, and perhaps nitrogen and sulfur as well, were mainly derived from organic sources, including aquatic and terrestrial ones. A high positive correlation between TC and water content is also shown in Fig. 3. This might have been due to increased porosity of organic matter.

Terrestrial and aquatic plants have different C/N/S ratios, with terrestrial plants having higher TS but lower TN content, when compared with aquatic plants. In this study, the TC/TN ratio was found to increase, whereas the TC/TS ratio was found to decrease as TC increased (Fig. 3). A high TC/TN ratio with a low TC/TS ratio when TC content was high implies that in warmer periods (higher TC), the amount of organic matter supplied to the sediments by terrestrial plants increased. For the same reason, TS/TN ratio was also higher when TC content was higher (Fig. 3). Furthermore, anoxic conditions during warm, wet periods might lead to higher TS content in sediments due to sulfide mineral deposition.

3.2 Factors Regulating Metal Deposition

Distribution of TC and total metals for dry weight is shown in Fig. 4. Most metal concentrations were similar to those found in other lakes (Forstner and Wittmann 1983; Das et al. 1995; Birch et al. 1996) and to standard values in shale (Turekian and Wedepohl 1961). Figure 4 shows that Al, Cs, Fe, Mg, Ni, Rb and V have a negative correlation with TC content.

Correlation amongst elements was supported by correlations between total metals and TC content shown in Table 1. The negative correlation coefficient between Al-TC, Cs-TC, Fe-TC, Mg-TC, Ni-TC, Rb-TC and V-TC was good for each. However, the same metals also had good positive correlations with each other (Table 1). This trend suggests that Al, Cs, Fe, Mg, Ni, Rb and V in sediments were derived mainly from lithogenic sources and were diluted by deposition with organic matter. Chemical forms of metals determined by sequential extraction from the sediment column have confirmed this finding (Fig. 5). These metals occurred mainly in the residual fraction (total metal content for the sum of the three components obtained from the 3-step extraction procedure) and mostly in the hard-to-reduce fractions such as that for refractory organic matter and within a crystal structure of primary and secondary minerals. The majority of primary and secondary minerals in sediments were quartz, feldspars and clay minerals (Chen et al. 1993).

Few metals, with the exception of Fe and Ni, occurred in the mobile fractions of sediments, i.e., exchangeable/carbonatic, easily reducible and oxidisable fractions. This finding was similar to that of Mester et al. (1998). Metals in these fractions represented sorbed, precipitated or coprecipitated (on carbonates, hydrous Fe/Mn oxides and sulfides) and complex forms in

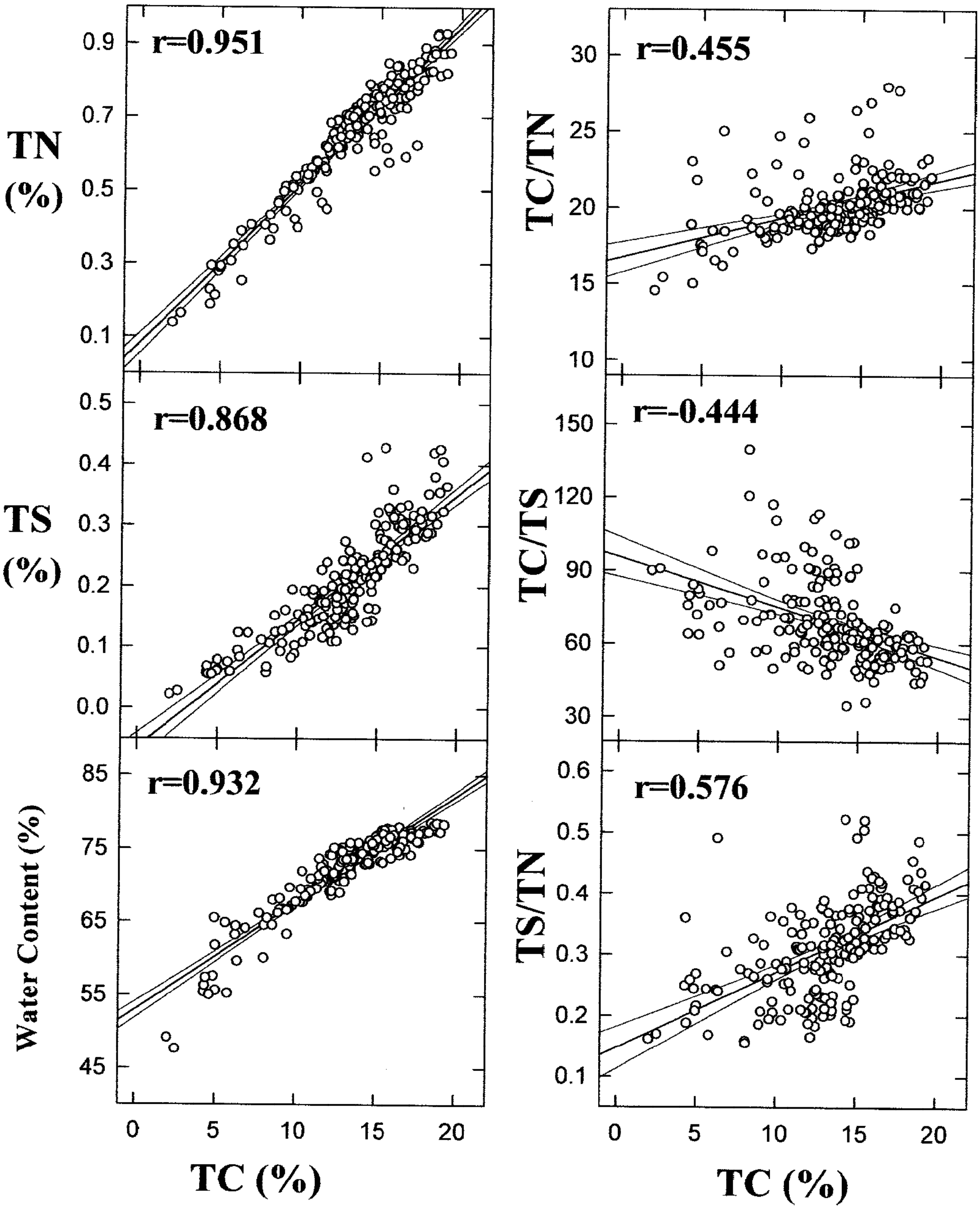

Fig. 3. Correlations between total carbon (TC) and total nitrogen (TN), total sulfur (TS), water content, TC/TN, TC/TS and TS/TN in the sediments of GGL. The regression line and its 95% confidence range are marked.

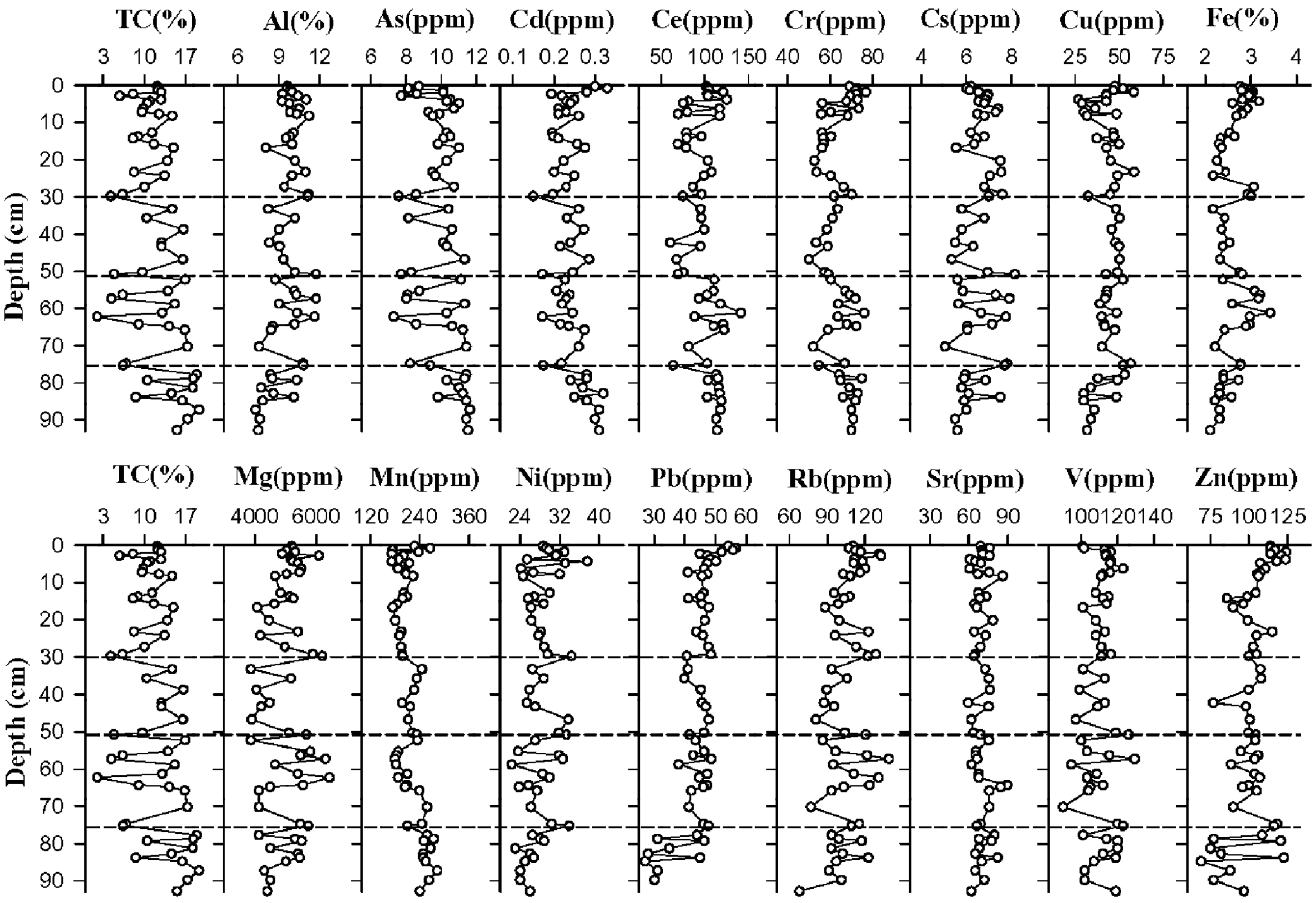

Fig. 4. Distribution of total carbon (TC) and total metals (Al, As, Cd, Ce, Cr, Cs, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sr, V and Zn) in the sediments of GGL (TC is shown in both the upper and lower panels so that its relationship with metals can be better seen. Thin horizontal dashed lines are drawn to show the correlation of some peaks).

Table 1. Correlation coefficients (r) between total carbon (TC) and total metals in the sediments of GGL. Bold values are significant at the $a = 0.05$ level (n = 48).

	TC	Al	As	Cd	Ce	Cr	Cs	Cu	Fe	Mg	Mn	Ni	Pb	Rb	Sr	V	Zn
TC	1	**-0.735**	**0.772**	**0.648**	0.252	-0.182	**-0.810**	0.156	**-0.518**	**-0.857**	**0.295**	**-0.474**	0.023	**-0.832**	0.233	**-0.687**	-0.257
Al		1	**-0.671**	**-0.489**	0.032	0.254	**0.828**	-0.155	**0.489**	**0.786**	-0.221	**0.356**	0.112	**0.721**	-0.185	**0.660**	**0.405**
As			1	**0.369**	0.111	-0.270	**-0.615**	0.028	**-0.478**	**-0.723**	0.093	**-0.380**	-0.066	**-0.668**	0.049	**-0.425**	-0.228
Cd				1	0.244	0.150	**-0.546**	0.220	-0.259	**-0.507**	**0.384**	-0.183	**0.446**	**-0.407**	0.222	**-0.399**	0.099
Ce					1	**0.666**	0.015	0.040	0.245	-0.006	0.118	**-0.444**	0.105	0.171	**0.365**	-0.137	**0.335**
Cr						1	0.217	-0.101	**0.710**	**0.397**	-0.062	-0.016	**0.411**	**0.572**	0.123	0.241	**0.491**
Cs							1	-0.097	**0.418**	**0.715**	-0.189	**0.343**	-0.021	**0.807**	-0.018	**0.785**	**0.443**
Cu								1	-0.188	-0.231	**0.352**	0.160	0.232	-0.186	0.031	-0.066	0.167
Fe									1	**0.725**	**-0.288**	**0.360**	**0.328**	**0.708**	-0.171	**0.443**	**0.325**
Mg										1	-0.219	**0.383**	0.140	**0.848**	-0.204	**0.625**	**0.361**
Mn											1	-0.066	-0.064	-0.264	**0.478**	-0.195	0.211
Ni												1	0.269	**0.397**	**-0.315**	**0.416**	**0.409**
Pb													1	0.182	-0.030	0.121	**0.403**
Rb														1	-0.020	**0.692**	**0.550**
Sr															1	-0.167	0.126
V																1	**0.398**
Zn																	1

sediments, which were probably affected by diagenesis and/or changes in water chemistry. A significant portion of Fe initially occurred as mobile Fe oxides. Anoxic conditions in sediments produced reductive dissolution of Fe (III) oxides and thereafter, dissolved Fe^{2+}, which could interact with the other species, especially organic substances. This interaction could transform Fe from easily reducible fractions to oxidisable forms and account for large amounts of Fe observed in the oxidisable fraction (Fig. 5).

As ($r = 0.772$) and Cd ($r = 0.648$) displayed good positive correlations with TC content. The correlation coefficient between As and Cd ($r = 0.369$) was low, butstill significant (Table 1). The chemical forms of metals derived from sequential extraction could also explain these results (Fig. 5). Figure 5 reveals that large amounts of these two metals were in mobile fractions. As also occurred in residual fractions, and since it occurred in oxidisable fractions as well, a complex or incorporation of As, with the organic matter was evident. Cd, on the other hand, is chiefly observed in exchangeable/carbonatic fractions, indicating Cd was sorbed with organic matter.

Total Ce, Cr, Cu, Pb, Sr and Zn concentrations did not correlate with TC ($r < 0.26$; Table 1). Total Ce, Cu, Mn, Pb and Sr did not have significant correlations with metals from lithogenic sources (Table 1), which suggests that few of these metals were associated with both organic and inorganic mobile fractions of sediments. On the other hand, total Cr and Zn had significant positive correlations with metals from mainly lithogenic sources (Table 1), which suggests that Cr and Zn were associated with inorganic minerals in sediments. Surface sediment was enriched with Cd and Pb (Fig. 4). Enhanced concentrations of Cd and Pb were also reflected in their correlations with TC (Table 2). The source of these metals was probably from anthropogenic, aeolian particles. Anthropogenic input of Pb has been previously reported, as indicated by a low Pb-206/Pb-207 ratio in surface sediment (Wann et al. 1995; Wann and Chen 1996).

Distribution of total carbon and acid-leached metals (extracted with 1.6 N HNO_3) is shown in Fig. 6. Acid-leached As, Cd, Cr, Cu, Mn, Sr and V showed significant positive correlations with TC, as well as with most metals (Table 2), which suggests that these acid-leached metals were associated mainly with organic matter. With the exception of residual fractions, As, Cr and Cu occurred mainly in oxidisable fractions (Fig. 5), so they might be a complex of or incorporated into organic matter, and this could explain positive correlation coefficients between TC and these metals (Table 2). Since Cd, Mn and Sr were mainly in exchangeable/carbonatic fractions, they could be sorbed with organic matter. Correlation between acid-leached metals, Al, Cs, Mg, Ni and Rb, were positive with each other but were negative with TC (Table 2). Most of these metals were in the residual and oxidisable fractions (Fig. 5), suggesting that acid-leached Al, Cs, Mg, Ni and Rb in sediments were mainly associated with mobile inorganic phases.

Concentration of metals in mobile fractions (Step1 + Step2 + Step3; Fig. 5) and in acid-leached fractions (Fig. 6) compared well, except for Al, Ce, Cs and Cu. Concentrations of these in acid-leached fractions were about three times that of mobile fractions. This indicates that large amounts acid-leached content of these four metals could not be released by the 3-step procedure. A large amount of Al (~1.3%), which has a significant negative correlation ($r = -0.288$; Table 2) with TC, was found in acid-leached fractions. This finding suggests that

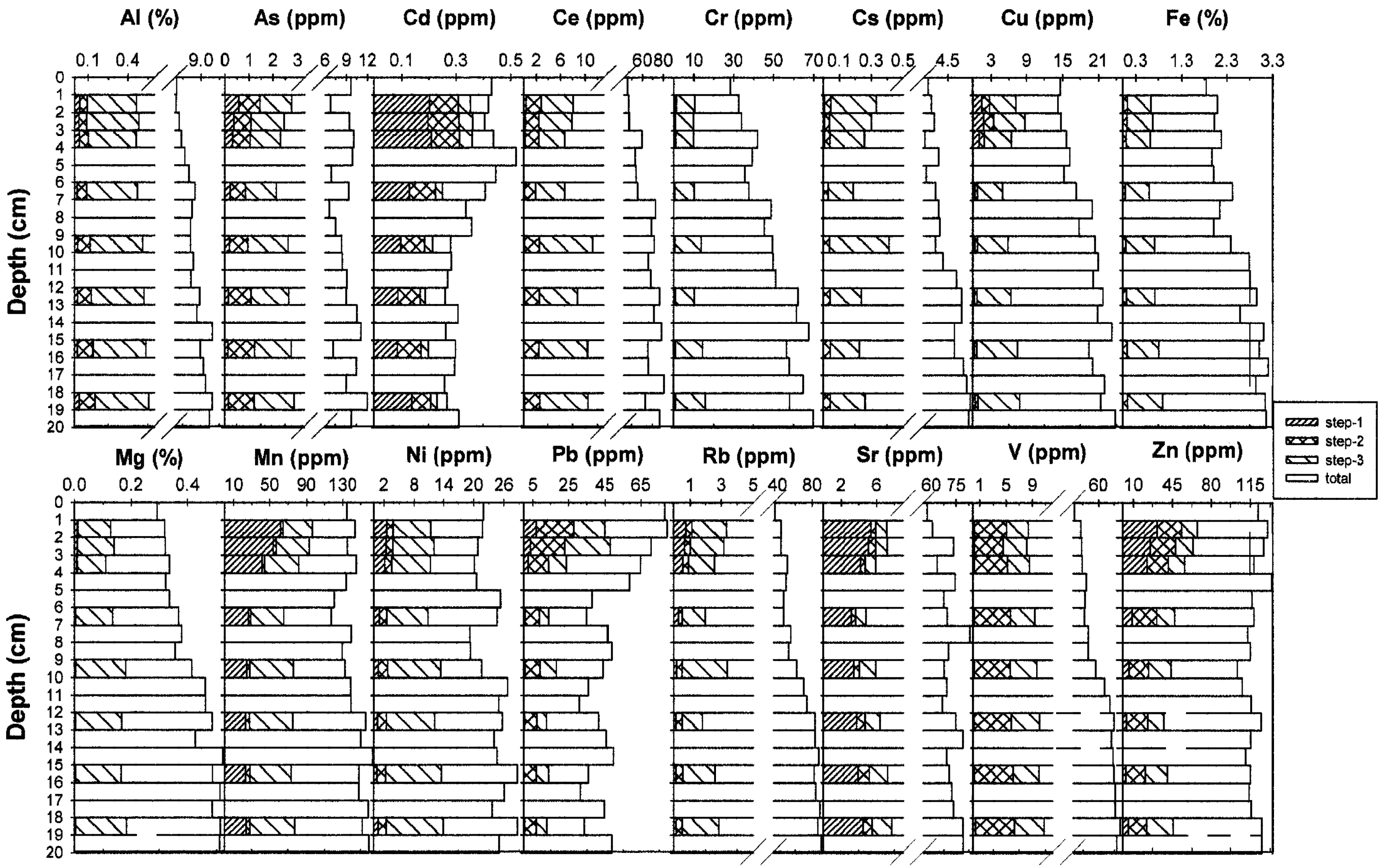

Fig. 5. Metal contents in three different phases as determined by a 3-step sequential extraction procedure in the sediments of GGL (the background is the distribution of the total metal content).

Al was mainly associated with other mobile inorganic fractions, such as Al hydroxides and oxyhydroxides, that are usually found in soil minerals synthesized during pedogenesis. Large amounts of acid-leached Ce, Cs and Cu might also be associated with the Al hydroxides and oxyhydroxides. The acid-leached concentration of metals represented most of the metal content in mobile fractions of sediments, and were more readily determined using this method than by sequential extraction. As a result, large numbers of samples could be analyzed quickly. Sequential extraction provided more detail but this procedure was tedious, which limited the number of samples that could be analyzed.

The correlations between TC and acid-leached Fe (about 40% of total Fe content) were not significant at $\alpha = 0.05$ (Table 2), but large amounts of Fe content (about 30% of total Fe) was found in oxidisable fractions (Fig. 5), which was the main fraction represented. Acid-leached Fe probably contained oxidisable fractions, at least in part, and/or other organic fractions that could not be released by sequential extraction. However, complicated interactions between Fe^{2+}, Fe (III) oxides, organic substances and clay particles in the water column and sediments can also result in associations of Fe and organic carbons (Tipping 1981; Forstner and Wittmann 1983; Salomons and Forstner 1984; Wann and Chen 1996; Wann et al. 1997). This could also explain why large amounts of Fe were found in oxidisable fractions and correlations between TC and acid-leached Fe were positive. Negative correlations between TC and total Fe were found because Fe was mainly derived from lithogenic sources and exists in residual fractions (Fig. 5). Lithogenic and organic matter were the two major components of sediments and an increase in one must be accompanied by a decrease in the other.

Poor correlations between TC and total and acid-leached Ce, Pb and Zn were found in sediments (r = 0.252 and 0.162 for Ce, r = 0.023 and -0.257 for Pb, r = -0.100 and 0.153 for Zn, respectively). In this case, poor correlations occurred mainly because more than 50% of total metal content was in residual fractions, except for a few surface samples. Small amounts of Pb and Zn were found in oxidisable fractions, which was even less than that for the other two mobile fractions, and explain poor correlations between their acid-leached values and TC. Figure 5 shows that, with the exception of residual fractions, Ce, Pb and Zn were mainly in easily reducible and oxidisable fractions. Figure 5 shows that surface enrichment of Zn (not obvious in Pb) was also found in exchangeable/carbonatic fractions.

Distribution of acid-leached Cd and Pb (Fig. 6) and their correlations with TC (Table 2) also demonstrated enrichment near the surface. This was mainly due to atmospheric anthropogenic input (Wann et al. 1995; Wann and Chen 1996). Surface enrichment of Pb due to atmospheric anthropogenic input was mainly found in easily reducible fractions. Results derived from the study of a water column in which the annual Fe cycle plays a major role as a sink for atmospheric Pb (Wann et al. 1997), supports findings from this study.

The relationship between total metals and total carbon and acid-leached metal/total metal (extractable ratios) are shown in Fig. 7. In sediments Al, Cs, Mg, Rb and V, possess low extractable ratios, which clearly correlate negatively with TC (or TOC). These metals were relatively stable in this environment and occurred mainly in immobile fractions of sediments, i.e., in mineral lattices and in refractory organic matter. Relatively mobile metals, on the other hand, were associated with higher extractable ratios and higher organic carbon content.

The correlation coefficient between total V and TC was negative (-0.69), but the correla-

Table 2. Correlation coefficients (r) between total carbon (TC) and acid-leached metals in the sediments of GGL. Bold values are significant at the $a = 0.05$ level (n = 48).

	TC	Al	As	Cd	Ce	Cr	Cs	Cu	Fe	Mg	Mn	Ni	Pb	Rb	Sr	V	Zn
TC	1	**-0.288**	**0.871**	**0.706**	0.162	**0.542**	**-0.806**	**0.461**	0.203	**-0.735**	**0.453**	**-0.408**	-0.100	**-0.775**	**0.703**	**0.862**	0.153
Al		1	-0.264	0.065	0.258	-0.052	**0.436**	**0.403**	0.161	**0.522**	-0.172	**0.549**	**0.555**	**0.369**	-0.178	**-0.328**	**0.382**
As			1	**0.677**	**0.348**	**0.468**	**-0.668**	**0.495**	0.186	**-0.546**	**0.624**	-0.174	-0.027	**-0.726**	**0.746**	**0.819**	**0.378**
Cd				1	**0.326**	**0.318**	**-0.351**	**0.504**	0.103	**-0.397**	**0.423**	-0.041	**0.395**	**-0.403**	**0.608**	**0.551**	**0.522**
Ce					1	0.102	0.146	**0.438**	-0.023	0.217	**0.290**	**0.416**	**0.297**	0.074	0.235	**0.298**	**0.637**
Cr						1	**-0.428**	**0.533**	0.062	**-0.407**	0.207	-0.037	-0.230	**-0.492**	**0.380**	**0.741**	0.034
Cs							1	-0.221	-0.070	**0.738**	**-0.418**	**0.578**	**0.330**	**0.900**	**-0.626**	**-0.713**	0.151
Cu								1	0.185	-0.147	**0.320**	**0.306**	**0.380**	-0.214	**0.415**	**0.475**	**0.533**
Fe									1	-0.105	-0.243	-0.028	0.278	0.049	-0.160	0.087	0.023
Mg										1	-0.239	**0.633**	0.188	**0.654**	**-0.486**	**-0.616**	0.144
Mn											1	-0.016	-0.151	**-0.567**	**0.875**	**0.500**	**0.383**
Ni												1	**0.426**	**0.488**	-0.178	**-0.317**	**0.565**
Pb													1	**0.354**	-0.029	-0.197	**0.477**
Rb														1	**-0.742**	**-0.769**	0.052
Sr															1	**0.702**	0.278
V																1	0.131
Zn																	1

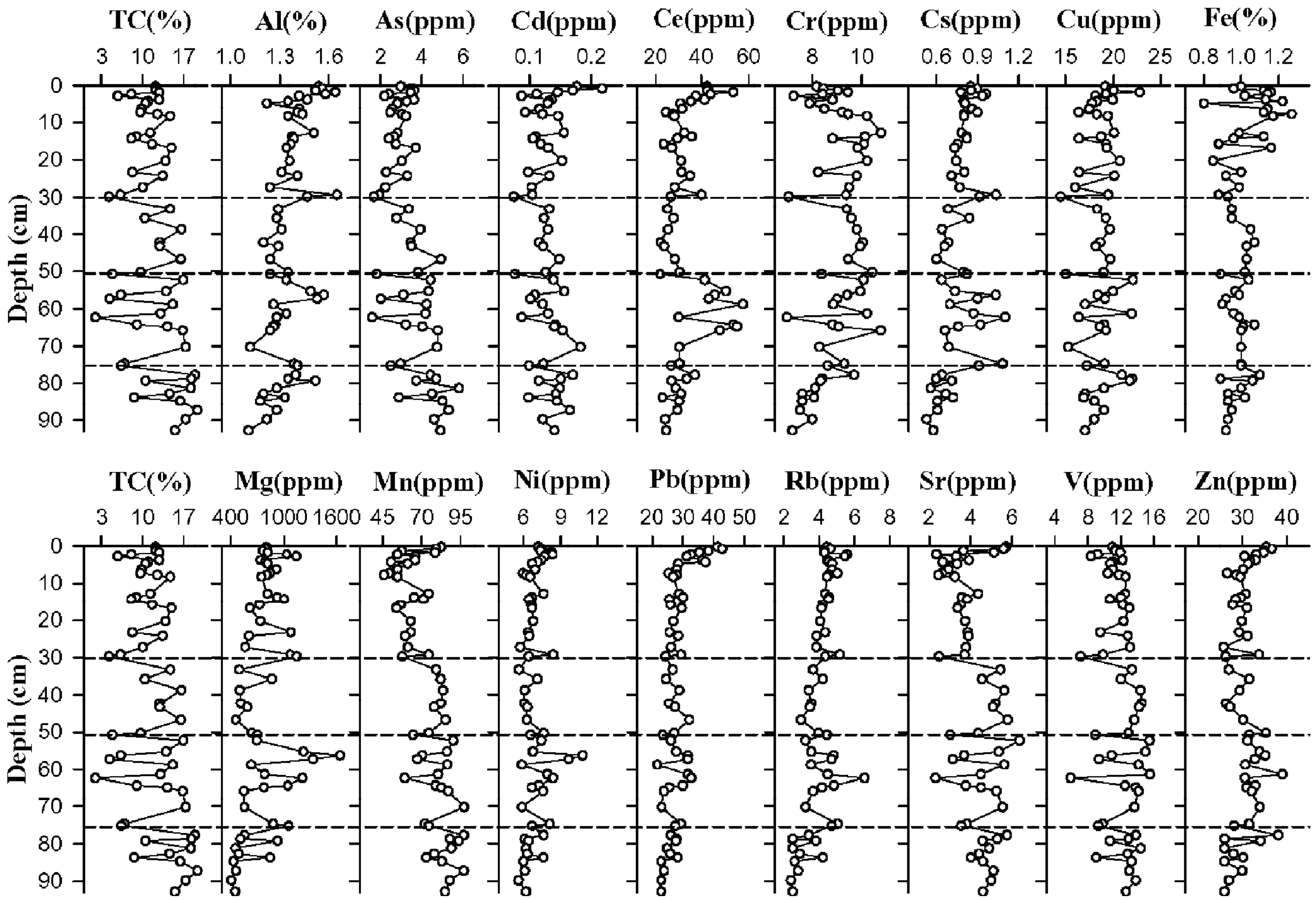

Fig. 6. Distribution of total carbon (TC) and acid-leached metals (Al, As, Cd, Ce, Cr, Cs, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sr, V and Zn) in the sediments of GGL (TC is shown in both the upper and lower panels so that its relationship with metals can be better seen. Thin horizontal dashed lines are drawn to show the correlation of some peaks).

tion coefficient changed to positive (0.862) between acid-leached V and TC. This high correlation contradicts that of other immobile metals, especially Cs and Rb, whose total and mobile fractions negatively correlated with TC. It is not known if acid leachable V has a broader source base during drier periods (lower TC). On the other hand, certain processes could explain differences between V and other conservative, nonmobile metals. Weathering of exposed rocks could oxidize V^{3+} to VO_4^{3-}, a highly soluble species in oxic water. In anoxic

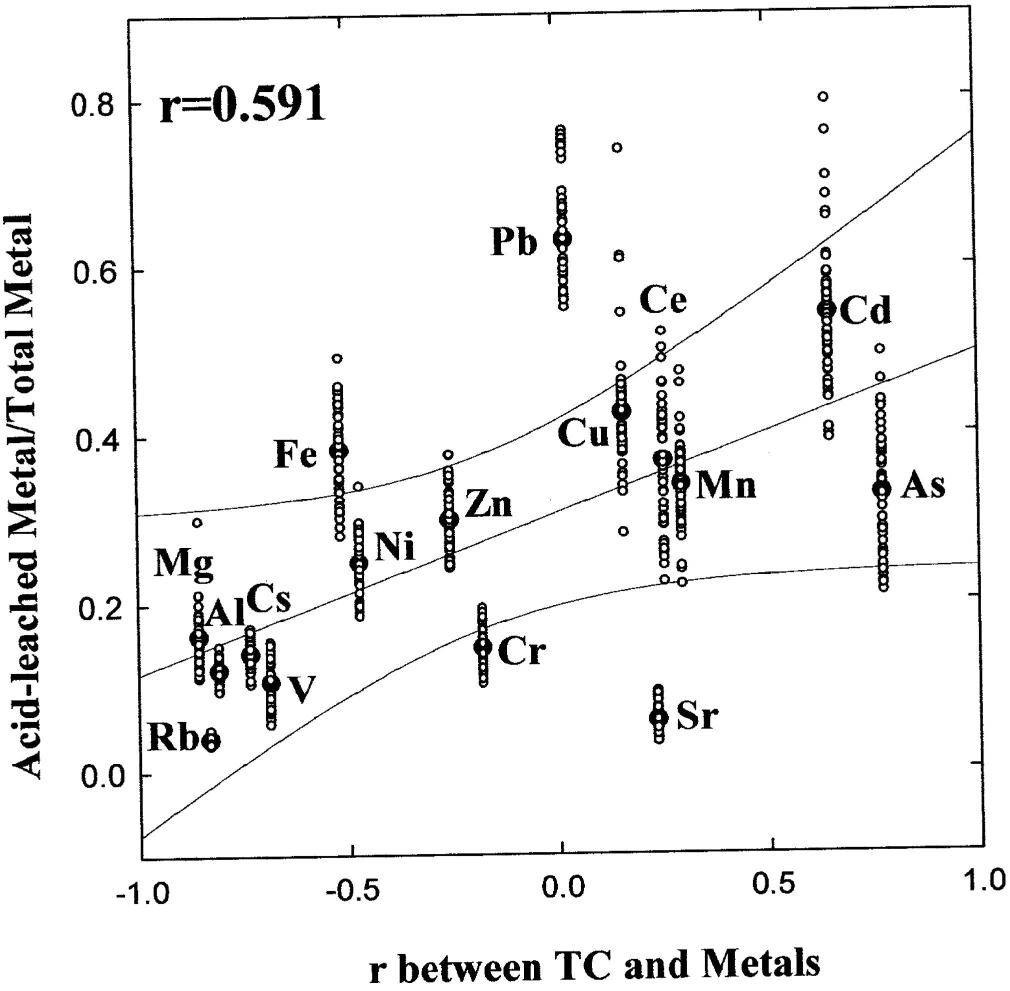

Fig. 7. Correlation between the ratios of acid-leached metal/total metal and the correlation coefficients (r) of total carbon and total metals. The r egression line obtained from the average of acid-leached metal/total metal and its 95% confidence range are marked.

water, $VO_4{}^{3-}$ is transformed into VO^{2+} which is easily associated with particles (Premovic et al. 1993). Since the Great Ghost Lake is seasonally stratified and anoxic, dissolved $VO_4{}^{3-}$ can be transformed into VO^{2+} during anoxic stratification and then combine with organic matter or other surface particles in anoxic bottom waters. The reduction of $VO_4{}^{3-}$ to VO^{2+} by humic substances under anoxic conditions, with subsequent formation of vanadyl organic complexes, has been demonstrated previously (Wilson and Weber 1979; Templeton III and Chasteen 1980; Francois 1988). In addition to effects of changing water redox conditions, sediment input and water redox conditions in GGL were also highly influenced by climatic changes. During warm, wet periods, high water level and increased water stratification enhanced anoxic conditions and resulted increased VO^{2+} being incorporated into high-TC sediments. In contrast, during cool, dry periods, little VO^{2+} was transformed to associate with the low-TC sediments in oxic conditions. Low V was observed in oxidisable fractions in low-TC sediments, whereas high V was observed in oxidized fractions in high-TC sediments.

Distributions of total carbon and acid-leached Mn and their relationships in sections from 0 to 30 cm and from 30 to 84 cm are shown in Fig. 8. In the upper 30 cm of sediments, the average acid-leached Mn concentration (~62.6 ppm) was lower than those in deeper layers (~79.3 ppm), with poor negative correlations with carbon (r = -0.13). In contrast, there was good positive correlation (r = 0.88) between organic carbon content and acid-leached Mn in sediments below 30 cm. Both Mn and Fe are redox-sensitive elements. The acid-leached Mn in the sediments represented most of mobile fractions (Step1 + Step2 + Step3) and contained the entire exchangeable/carbonatic fraction. Abundance of Mn indicated that Mn recycle was an important geochemical process in the lake. During warm climatic conditions and high water levels, the development of a thick anoxic hypolimnion favored release of Mn from shallower sediments to the water column. Marked Mn was found in the water column as shown in Fig. 10. High Mn concentrations in deeper parts of the water column were affected by input of reduced Mn from bottom sediments, during summer (May 1993 and July 1988). On the other hand, Fe was mainly affected by diffusion of reduced iron from bottom sediments since Fe oxides are reduced at lower redox potentials.

During the winter turnover, Fe oxides were formed in the water column, removing dissolved reduced Mn. Distribution of Mn in one winter is shown in Fig. 9a and that in March 1992, is shown in Fig. 10. During the development of anoxic hypolimnion, Mn, removed by Fe oxides, was re-dissolved into water, where it could interact with $CO_3{}^{2-}$ to produce $MnCO_3$ (rhodochrosite). This compound was usually found in anoxic sediments during early diagenesis (Berner 1981; Surdam et al. 1984; Sigg et al. 1991). Large amounts of Mn observed in exchangeable/carbonatic fractions (Fig. 5) supports the notion of $MnCO_3$ production. In addition, Ksp calculations of Mn species also suggest that Mn concentrations in anoxic bottom waters of GGL were limited by solubility of $MnCO_3$ during late stage stagnation (Wann et al. 1997). $MnCO_3$ was stable in sediments and did not participate in the redox cycle again. All this led to high content acid-leached Mn in high-organic-matter sediments produced during the warm, wet periods.

As for the cold, dry periods, climatic conditions and low water levels were not suitable for development of anoxic hypolimnion and release of Mn from sediments (Fig. 9b). As a result, less recycled Mn was found in white layers and sediments from 29.5 cm to about 2 cm. These climatic conditions also led to low production of CO_3^{2-} and $MnCO_3$. Accordingly, mobile fractions of Mn in sediments did not increase but, in fact, decreased such that a negative correlation existed between acid-leached Mn and TC. Sediments from 29.5 to 2 cm were deposited from about the 13th to late 19th century (Lou et al. 1997), around the time of the "Little ice Age". More recently, however, climatic conditions have become warmer, and higher acid-leached Mn was also found in sediments above 2 cm.

Distribution of acid-leached Sr (Fig. 11) was similar to that of acid-leached Mn in sediments, and their positive correlation was quite substantial at r = 0.875 (Table 2). In the upper 29.5 cm of sediments, acid-leached Sr content was also lower than that in deeper layers. Its correlation with TC was also poor (r = 0.273, where r is 0.07 if samples above 2 cm are excluded). There was however strong positive correlations (r = 0.956) between TC and acid-leached Sr in sedi-

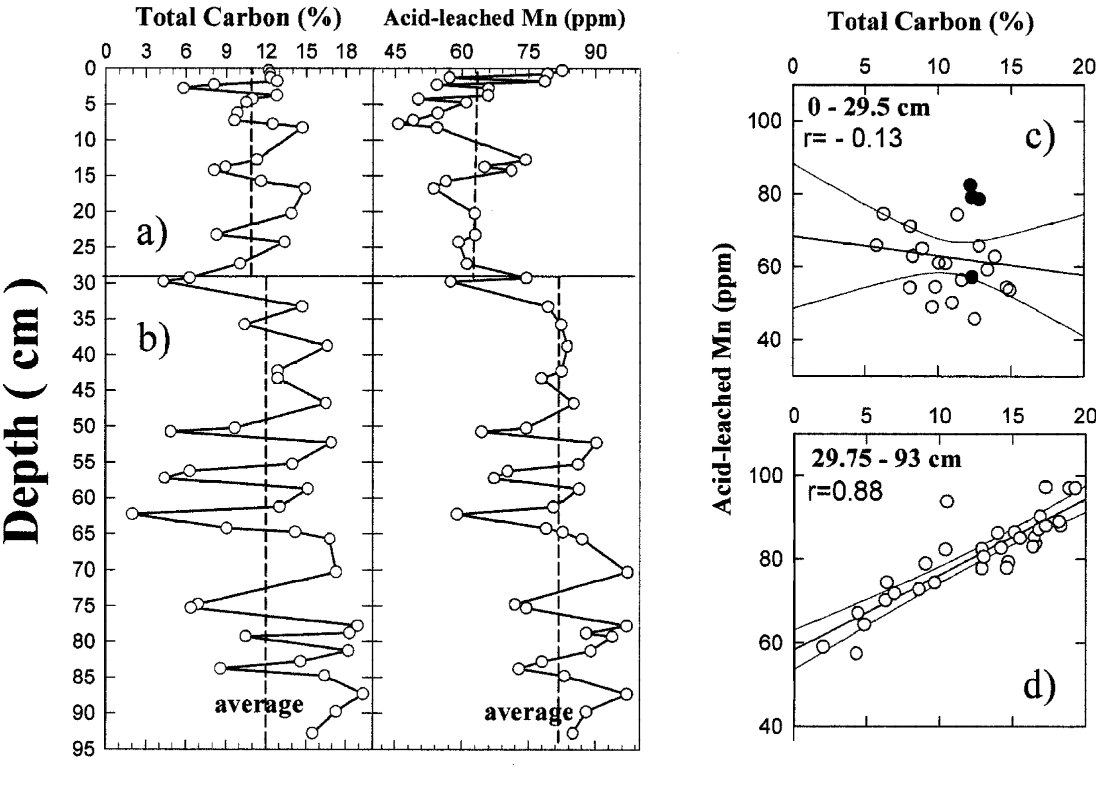

Fig. 8. Distribution of total carbon and acid-leached Mn in the sediments of GGL from (a) 0 to 30 cm and from (b) 30 to 93 cm, as well as correlations between total carbon and acid-leached Mn from (c) 0 to 30 cm and from (d) 30 to 93 cm. Dark circles represent those above 2 cm; r is -0.40 if these 4 points are excluded. The regression line and its 95% confidence range are marked.

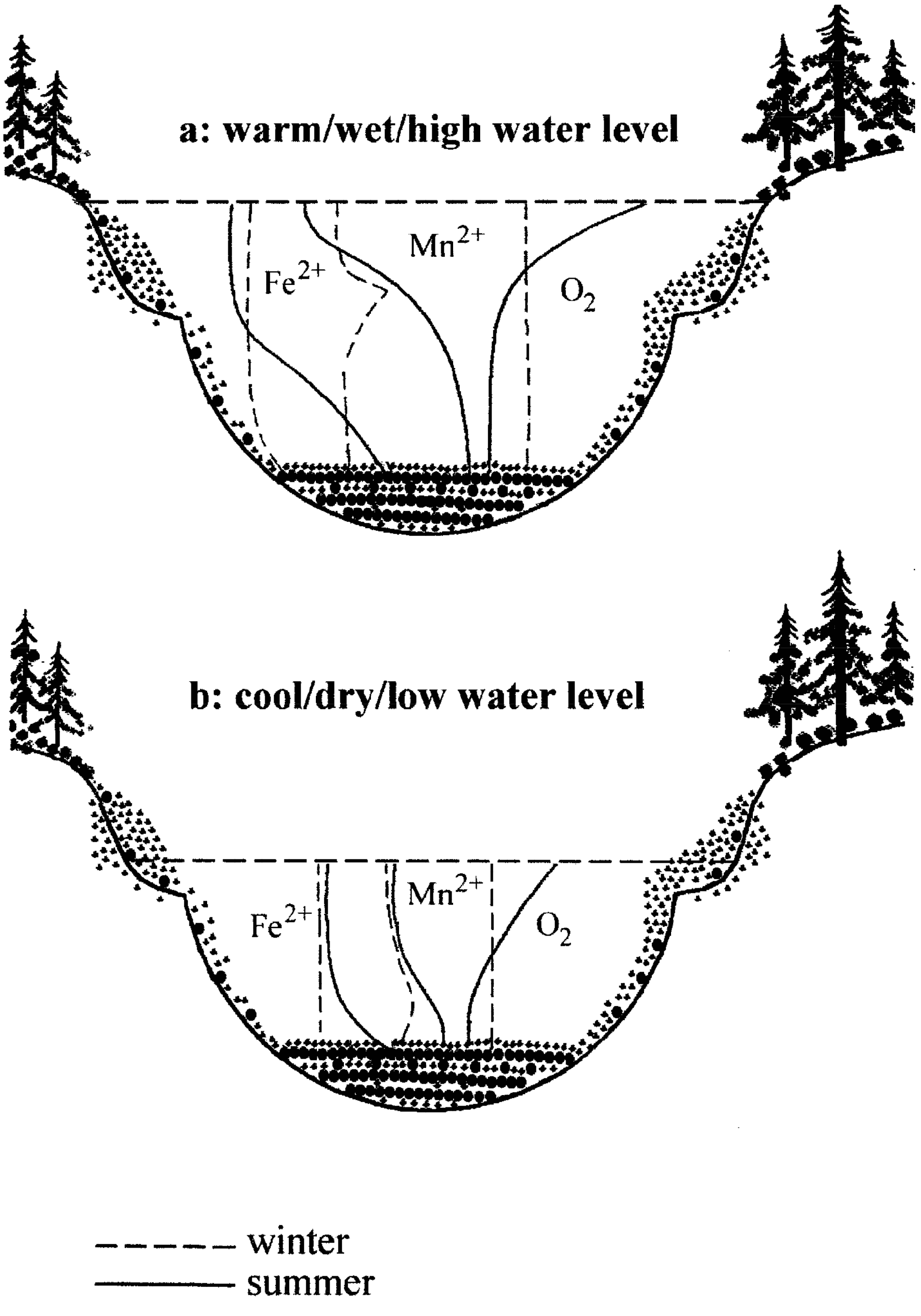

Fig. 9. Hypothetical distribution of dissolved oxygen, Fe^{2+} and Mn^{2+} in summer and winter in GGL during the (a) warm/wet and (b) cool/dry periods.

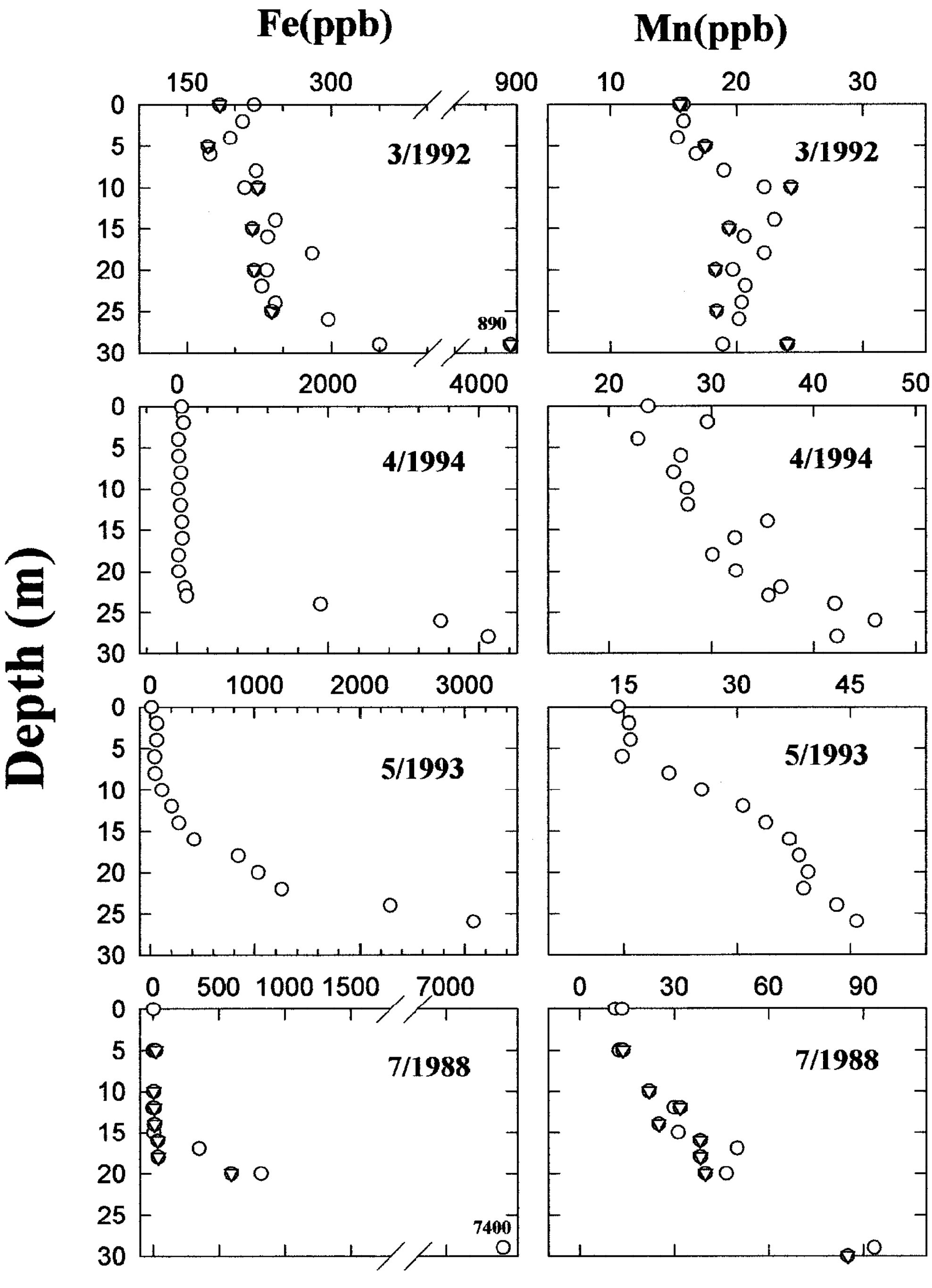

Fig. 10. Distribution of total dissolved Fe and Mn in GGL, where circles and triangles are the results obtained from different stations. Note the change in scales (taken from Wann et al. 1997).

ments below 29.5 cm. Sr is a IIA element with a strong tendency to form $SrCO_3$ and formation was similar to $MnCO_3$ in sediments. Similarities between Mn and Sr were even closer when their distributions in mobile fractions were examined (Fig. 5).

To summarize, long-term variations in redox conditions in the lake were mainly controlled by local climate changes. A surplus of Mn, Sr and V were incorporated into high-TC sediments produced in relatively anoxic conditions during warm, wet periods. During the cool, dry periods, the relatively oxic water column limited increases in these metals in low-TC sediments. As a result, low TC and low acid-leached Mn, Sr and V were associated with cool, dry periods. The reverse was true during warm, wet periods. Climate change clearly plays a major role in regulating distributions of metals in sediments, especially redox-sensitive ones.

Early diagenesis and changes in redox conditions can clearly affect distributions of certain elements in sediments of GGL. Nevertheless, well-preserved sediments still serve as a repository of aeolian flux of dust. Following the procedure of Chen et al. (2001), elements of aeolian flux near the tops of three cores are given in Table 3. A total of 35 elements are listed, including some unpublished data of Wann (2000). These include Al, As, Ba, Br, Ca, Cd, Ce, Cl, Cr, Cs, Cu, Er, Eu, Fe, Ga, Gd, K, La, Lu, Mg, Mn, Na, Nd, Ni, Pb, Rb, Si, Sm, Sr, Ti, Tm, V, Yb, Zn and Zr. Many of these elements were found in aerosols in Taiwan (Wang et al. 2004) and the fluxes compared reasonably well with direct flux measurements in and around Taiwan. Certain toxic elements, namely, As, Cd, Cr, Cu, Ni, Pb and Zn were noted but micronutrients such as Fe and V serve to enhance biological productivity of aquatic environments. All four studies listed in Table 3 show rather large Fe flux indeed.

4. CONCLUSIONS

Variation in particle input with different organic matter content was the major factor regulating distributions of elements in sediments of GGL. Concentrations of Al, Cs, Mg, Rb and V, from mainly lithogenic (including aeolian) sources, were diluted by organic matter in sediments and were found to be low in mobile fractions. Organic matter was the major source of C, N and S, as well as As, and mainly occurred in oxidisable phases. This caused C, N, S and As to correlate well with TC in sediments. Most metals in mobile fractions were correlated well with TC, suggesting that organic matter plays a major role in remobilizing metals during early diagenesis. The annual Fe cycle in GGL also was also found to play a major role in regulating distributions of redox-sensitive elements (such as Fe, Mn and V) in sediments.

Climate-induced changes to the redox cycle in the water column might be partly responsible for distributions of elements and for positive correlations between TC and metals in mobile fractions. This was especially true for redox-sensitive elements. In addition to natural factors, anthropogenic activities affected distributions of metals in sediments through input of aeolian matter. Large amounts of anthropogenic Cd and Pb enriched surface sediments and occurred mainly in and/or transformed into exchangeable/carbonatic and easily reducible fractions, respectively. Finally, aeolian fluxes of micro-nutrients, such as Fe and V can serve to enhance biological productivity in aquatic environments.

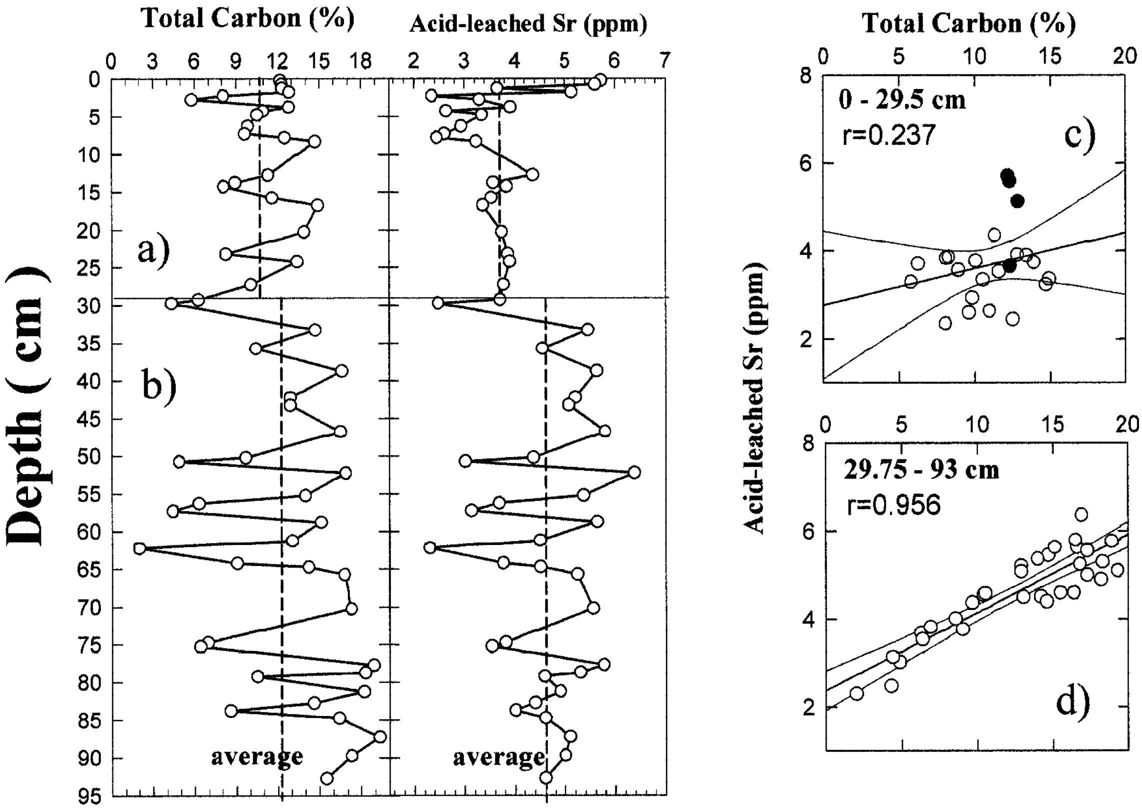

Fig. 11. Distribution of total carbon and acid-leached Sr in the sediments of GGL from (a) 0 to 30 cm and from (b) 30 to 93 cm, as well as correlations between total carbon and acid-leached Sr from (c) 0 to 30 cm and from (d) 30 to 93 cm. Dark circles represent those above 2 cm; r is 0.07 if these 4 points are excluded. The regression line and its 95% confidence range are marked.

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Table 3. Recent Aeolian Flux of Elements (μg cm^{-2} yr^{-1}) in and around Taiwan.

Element	This Study[a]	Wu (1996)	Lin (1996)[b]	Hong *et al.* (2002)[c]
Al	188-194	80.7-291	0.72-480	34.5
As	0.016-0.019	0.04-0.15	---	0.11
Ba	0.451	---	---	0.36
Br	0.027	---	---	---
Ca	0.763	---	---	43
Cd	0.0006-0.0007	nd-1.45	0.0001-0.040	0.016
Ce	0.195-0.214	---	---	0.022
Cl	0.722	---	---	---
Cr	0.145-0.151	0.35-0.83	0.0021-4.0	1.13
Cs	0.119-0.138	---	---	---
Cu	0.098-0.106	0.71-2.23	0.0035-0.23	0.089
Er	0.006			0.00098
Eu	0.0026			0.0011
Fe	55.1-68.5	52.4-182	0.5-180	51.5 (17.2-154.4)[d]
Ga	0.019	---	---	0.041
Gd	0.016			0.0019
K	22.3	---	---	66
La	3.63			0.012
Lu	0.0009			0.00018
Mg	10.8-12.3	21-84.5	4.1-143	181
Mn	0.375-0.478	1.97-4.47	0.01-2.39	0.57
Na	0.276	---	---	40
Nd	0.061			0.0012
Ni	0.059-0.069	0.23-0.67	0.013-1.23	0.092
Pb	0.124-0.176	0.54-3.13	0.0018-1.52	0.6
Rb	0.232-0.355	---	---	0.056
Si	246	---	---	---
Sm	0.013			0.0062
Sr	0.129-0.151	0.42-3.05	---	0.6
Ti	3.56	---	---	---
Tm	0.0009			0.0002
V	0.186-0.210	0.22-0.75	---	0.049
Yb	0.006			0.001
Zn	0.236-0.261	2.33-18.5	0.03-3.24	1.3
Zr	0.194	---	---	0.043

a: data from the three cores, including the single core data published in Chen et al. (2001) and the unpublished data of Wann (2000).

b: calculated from his aerosol composition data using the particle settling speed of Milford and Davidson (1985).

c: flux of atmospheric elements over the East China Sea.

d: flux of atmospheric elements over the Yellow Sea (Hong et al. 1997).

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