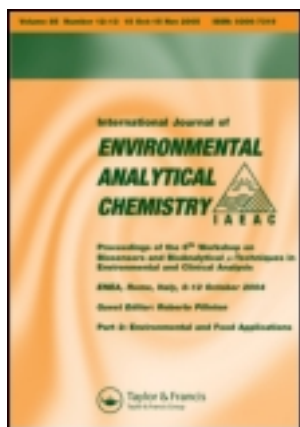


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Interpreting complex trace element profiles in sediment cores from a multi-basin deep lake: the western branch of Lake Como

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The concentration profiles of Co, Ni, Cu, Zn, Sc, Y, As, Cd, Pb, U and the rare earth elements (REE) were determined by inductively coupled plasma–mass spectrometry (ICP-MS) in three sediment cores sampled in the western branch of Lake Como (northern Italy). This hydrographically closed branch has a complex morphology, with a maximum depth of 425 m and an approximate length of 30 km and it is affected to different extents by direct discharges and atmospheric depositions. The present study is the first attempt to deeply investigate trace element profiles in the sediments of this lake. The concentration trends of cores sampled in different zones were compared and the different patterns were interpreted on the basis of local runoff and/or global atmospheric sources. The concentrations of Cr, Zn, Pb, Cd and Cu, which are representative proxies of anthropogenic activities, were found to increase moving toward the tip of the branch, where human activities are concentrated. A distinction between atmospheric, runoff and crustal contribution to element levels in the sediment cores was proposed based on both profile analysis and principal component analysis (PCA).

Keywords: lake sediment core; trace elements; inductively coupled plasma–mass spectrometry; Lake Como; principal component analysis

1. Introduction

Vertical concentration profiles of trace elements in lake sediments have been widely used to monitor lake water quality and to assess long-term trends in anthropogenic emissions in the environment [1,2], making it a reliable archive of natural and anthropogenic changes (e.g. work by Birch *et al.* and Handong *et al.* [3,4] but also see work by Boudreau [5] for issues related to element mobility in sediments).

The crustal material that is weathered on (dissolved) and eroded from (particulate) the Earth's surface is the principal natural source of elements in the environment, with volcanic activity playing also an important role. Industrial activities and the burning of industrial or domestic wastes are conversely the principal anthropogenic sources. Assessing the relative contribution of the two sources, i.e. natural vs anthropogenic, is of the utmost importance if local and/or global anthropogenic changes are to be addressed. As an example, Nriagu [6] found that the atmospheric anthropogenic emission of elements such as Cd, Cu, Ni, Zn and Pb exceed natural sources since the beginning of

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the last century, clearly showing the impressive changes human activities have had on the cycling of these elements.

Unfortunately, the issues connected with multi-basin, complex lakes were never addressed, although morphological, geological and limnological features play a dramatic role in the extent of element sequestration in sediments. The morphology, the different sedimentary environments and the presence of multiple sources, some of which of local origin, make it difficult to understand trace element patterns in lake sediment cores. A sediment core sampling campaign was therefore carried out in winter 2002 in the western branch of Lake Como, for which only a few, mainly old (>10 years), scientific studies are available [7–14]. Moreover, only two sediment core sampling campaigns were conducted [12,13].

The goal of this study was to elucidate the relation between trace element profiles and different sub-basins of such a complex system. Accordingly, the concentration trends of cores sampled in different basins were compared and the different patterns were interpreted on the basis of local runoff and/or global atmospheric sources with the aid of principal component analysis (PCA). Elemental concentrations were determined by inductively coupled plasma–mass spectrometry (ICP-MS) preceded by microwave assisted digestion.

2. Experimental

2.1 Geographical and geological setting

Lake Como is a typical south-Alpine lake, located in Northern Lombardy. It is characterised by a N-S direction and a particular λ shape. It is the second deepest lake in Europe (max. depth 425 m) and the third Italian lake in extension (142 km²). The basin of Lake Como is mainly characterised by crystalline basement in the northern part, by limestones in the Como branch and by dolomites in the Lecco branch [15,16]. The lake has a complex morphology, being composed of three main sub-basins, corresponding to the three branches of the λ (see Figure 1). The northern branch has two main tributaries, Adda and Mera rivers, whereas the only effluent, Adda River, is located at the southern tip of the eastern branch. The western or Como branch is instead hydrographically isolated and possibly affected by a slow water renewal. Moreover, this part of the lake is strongly influenced by river runoff, sewage discharge and industrial wastes from the city of Como. In particular, the sewage treatment plant effluents are directly discharged into the lake inside the city of Como and represent the main fluvial contribution of both micronutrients (phosphorous and nitrogen) and trace metals to the western branch of Lake Como. During the period July–December 2007, the trace metal contents of these effluents (mean annual flow rate 0.7 m³ s⁻¹) was determined on a weekly base and yielded to the following results (concentration in $\mu\text{g L}^{-1}$): Cr 3.0, Co 1.1, Ni 5.2, Cu 4.6, Zn 39, Cd 0.04, Pb 1.1, U 0.77 (35 samples, percentage relative standard deviation in the range 30–70%, beside cadmium 120%, see Dossi *et al.* [17]).

2.2 Sampling and sample pre-treatment

Three sediment cores were collected in November 2002: sampling locations are reported in Figure 1. The core labelled CO-02 (length 130 cm) was sampled in the Plateau sub-basin at a depth of 160 m. The core CO-09 (length 96 cm) was collected in the Como sub-basin at a depth of 190 m; the core CO-13 (length 85 cm) was sampled in the Como sub-basin, near to

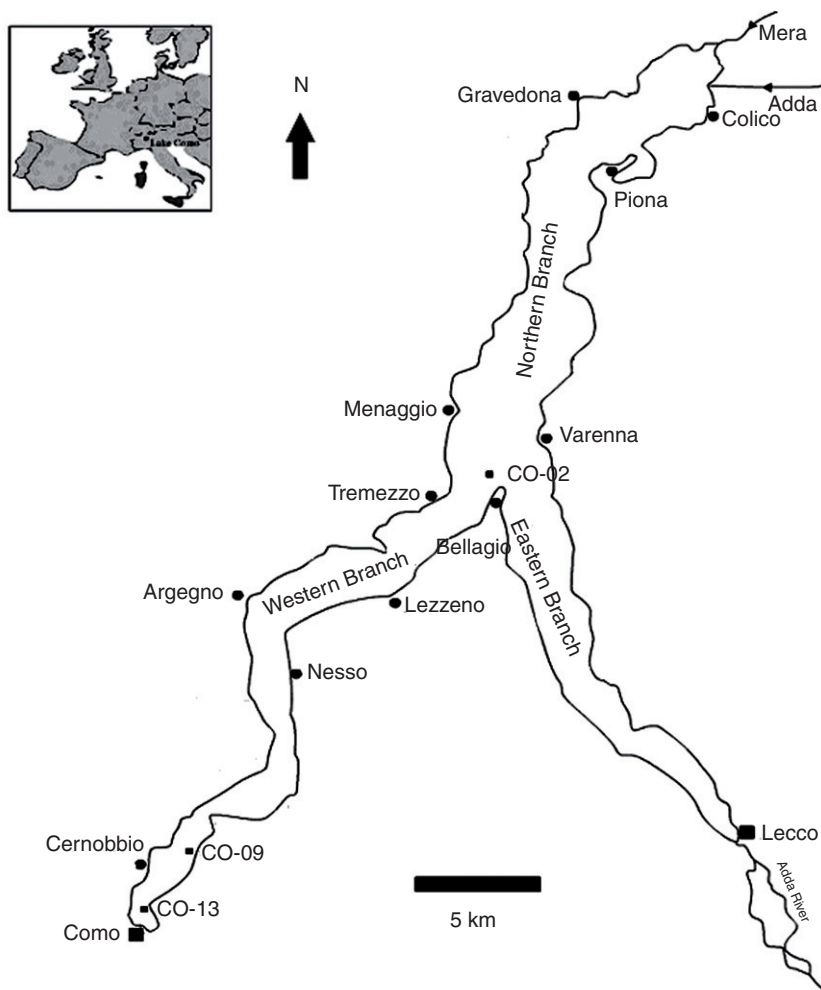


Figure 1. Map of Lake Como and sampling site CO-02, CO-09, CO-13.

the Como harbour, at a depth of 20 m. A gravity corer with an inner diameter of 67 mm was used for sediment collection: the cores were halved inserting transversally two thin plastic sheets and conserved refrigerated until sub-sampling. The sub-samples were collected from the interior of the core using a PTFE knife to avoid the contamination due to coring operations. The CO-02 core was sliced at 1 cm intervals (130 samples), CO-09 was sliced at 2 cm (45 samples) and CO-13 at 5 cm (19 samples). Sub-samples were stored in pre-cleaned plastic vessels, dried at 40°C for two days to constant weight, powdered in an agate mortar and kept in a desiccator before analysis.

2.3 Trace element determination

2.3.1 Solutions and reagents

Pure concentrated acids (HCl 36% and HNO₃ 69% Suprapure from Fluka) and ultrapure water from a Millipore Milli-Q system (18 MΩ cm resistivity, <5 ppb TOC) were

Table 1. Heating program for the digestion of the sediment samples.

Time (minutes)	Power (W)
2	250
1	0
2	250
2	400
5	500
1	0
5	600

used throughout. Solution preparation and sample manipulation were executed in a class 100 laminar flow hood. LDPE (low density polyethylene) sample and reagent bottles were washed and stored in 2% nitric acid; bottles were thoroughly rinsed with ultrapure water before use.

2.3.2 Sample digestion

Around 50 mg of the sediment sample was weighted in a PTFE vessel and *aqua regia* (1.5 mL of HCl and 0.5 mL of HNO₃) was added. The vessels were capped and placed in a Milestone MLS-1200 Mega microwave digester: the heating program is reported in Table 1.

After cooling, the sample digest was diluted 1 : 10 by weight with ultrapure water and stored in LDPE bottles before analysis.

2.3.3 Trace element quantification

Trace metals were determined by inductively coupled plasma–mass spectrometry (Thermo Elemental, mod. X-Series^{II}). Optimisation of the instrumental parameters was performed daily as recommended by the manufacturer with a 10 µg L⁻¹ multi standard solution, while the mass calibration of the quadrupole was verified weekly. As a result, low limits of detection, low levels of oxides (CeO⁺/Ce⁺ < 2%) and double charged ions (Ba⁺⁺/Ba⁺ < 3%) were achieved. The standard solutions used for external calibration were prepared by serial dilution of a 10 mg L⁻¹ multi-element standard solution (Merck, ICP multi-element standard solution VI). The following isotopes were measured: 45Sc, 52Cr, 59Co, 60Ni, 63Cu, 66Zn, 75As, 89Y, 111Cd, 208Pb and 238U. For the rare earth elements (REE) determination, the following isotopes were used: 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb and 175Lu. The selection of the isotope for every element is a compromise between sensitivity (isotopic abundance) and lack of isobaric interferences and was suggested by the manufacturer. The following correction equation was used to correct the signal registered at *m/z* 75 because of the well-known ⁷⁵ArCl interference:

$$^{75}\text{As} = ^{75}\text{C} - 3.127 * (^{77}\text{C} - 0.815^{82}\text{C})$$

where ⁷⁵C, ⁷⁷C and ⁸²C denote the counts registered at *m/z* 75, 77 and 82, respectively (see EPA method 200.8 as an example).

The interferences on REE determination due to oxide formation were checked with a procedure similar to the one devised by Aries *et al.* [18], except that an internal standard was not used for correction. Briefly, oxide formation was calculated on a standard solution of a single rare earth element obtained by diluting a concentrated 10 mg/L standard from Carlo Erba. Correction equations were then calculated for each interfered isotope, taking into account both isotopic abundances and oxide interferences. As an example, ^{157}Gd is interfered by ^{157}PrO (praseodymium is monoisotopic and is not interfered by REE oxides). The analysis of a standard solution containing Pr only evidenced that 1.84% ^{157}PrO is formed under our experimental conditions. The correction equation for Gadolinium was thus calculated as

$$^{157}\text{Gd} = ^{157}\text{C} - 0.0184 \cdot ^{141}\text{Pr}$$

where ^{157}C denotes the counts registered at m/z 157.

Analogously, correction equations were calculated for ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb and ^{175}Lu and applied to correct the signals of interfered isotopes in the analysed samples (see Results and discussion).

The standard reference material BCR-CRM 701 lake sediment (European Community Bureau of Reference [19]) was used for quality assurance purposes. This material was randomly analysed during sample analysis according to the entire procedure, i.e. desiccation, digestion, dilution and final determination. Moreover, a blank was analysed for every mineralisation batch and the detection limits (LOD) were calculated according to the IUPAC recommendations [20]. It should be noted that the determined concentrations are *aqua regia* extractable trace elements.

2.4 Data treatment

PCA [21] was performed as implemented in the software 'The Unscrambler' version 9.6 (CAMO, Oslo, Norway). Principal components were computed using the NIPALS algorithm: loadings and scores of the first two components were discussed. Segmented cross-validation was used as the validation method.

Autoscaling was performed prior to calculations in order to give all variables the same chance in the estimation of the components, as they showed dissimilar ranges of variability and figures differing by orders of magnitude.

Data below the limit of detection were replaced with half of the detection limit (LOD/2). The alternative choice to replace them with numbers lying between 0 and LOD did not change score and loading plots.

3. Results and discussion

3.1 Quality assurance

A quality assurance scheme was adopted for checking the entire procedure. As reported in the experimental section, the standard lake sediment BCR-CRM 701 was analysed randomly together with Lake Como sediment samples in addition to a procedural blank for every mineralisation batch. Regarding the quantification method, standard addition and external calibration curve were preliminary tested on both BCR and Lake Como samples. As a result, no significant difference was evidenced in the slope of the two calibration curves and accurate results were achieved by both methods, proving that matrix effects

Table 2. Indicative values in BCR and found concentrations for 10 independent analyses of the BCR-CRM 701 sample. Results are reported as mean \pm standard deviation. Long-term repeatability is in the 3.4–6.3% range.

	Cr (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)
Expected values	272 \pm 20	103 \pm 4	275 \pm 13	454 \pm 19	11.7 \pm 1	143 \pm 6
Found	267 \pm 13	101 \pm 3	270 \pm 7	458 \pm 24	11.0 \pm 0.7	143 \pm 5

Table 3. LOD liquid: LOD in the solution derived from the digestion; LOD sediment: LOD in the solid sample, assuming 0.050 g of sample were digested. Ten independent blank analyses were used for the calculations.

Element	LOD liquid ($\mu\text{g L}^{-1}$)	LOD sediment (mg kg ⁻¹)
Sc	0.64	0.32
Cr	3.8	1.9
Co	<LOD _{instrumental} (0.009)	<LOD _{instrumental} (0.004)
Ni	2.0	1.0
Cu	0.19	0.10
Zn	2.4	1.2
As	<LOD _{instrumental} (0.084)	<LOD _{instrumental} (0.042)
Y	0.011	0.006
Cd	<LOD _{instrumental} (0.002)	<LOD _{instrumental} (0.011)
Pb	0.21	0.11
U	0.045	0.023
REE (mean)	<LOD _{instrumental} (0.003)	<LOD _{instrumental} (0.0015)

are negligible. Accordingly, external calibration was used. The results, limited to the elements analysed in the BCR sediment [19] are reported in Table 2: it is evident that no statistically significant difference could be determined between experimental and expected concentrations. Moreover, the relative percentage standard deviations (RSD%) were in the 3.4–6.3% ($n = 10$), showing that the procedure ensured good precision too.

Regarding the determination of rare earth elements, the interferences due to oxide formation were found to be limited in accordance with literature data (see the work by Ivanova *et al.* [22]). The corrections were lower than 8% in all of the cases and lower than 5% for 90% of the samples. This result was due to the low rate of oxide formation and the choice of the isotopes to be analysed.

The limits of detection (LOD) of the investigated elements were also calculated according to the IUPAC recommendation [20] (Table 3). As a result, the digestion reagents and procedure did not contribute to the blank level for cadmium, arsenic and the rare earth elements: for these elements, the LODs were calculated using the standard deviation of a low level standard. The latter are indicated as LOD_{instrumental}, denoting they are figures of merit of the instrument.

3.2 Core analysis results

As a first step, the sedimentation rates of the three cores were assessed (see Figure 1 for core location). Bibliographic data indicate that the sedimentation rate in Como basin is 1.4

(1978 survey, see Parise *et al.* [12]) or 1.6 cm y^{-1} (1992 sampling campaign, see Chiaudiani and Premazzi [13]), while lower values were estimated in the upper (1.1 cm y^{-1}) and eastern basin (1.0 cm y^{-1} , see Chiaudiani and Premazzi [13]). Nevertheless, the sedimentation rate in the plateaux region has never been determined and was thus estimated to obtain a time scale for core CO-02 (see Fanetti [23]). Accordingly, the ^{137}Cs activity was measured in 1 cm sections of this core: two well distinguished maxima were observed in the 3–4 and 10–11 cm strata and were attributed to the Chernobyl accident (1986) and to 1963 as during this year the maximum fallout due to nuclear testing was registered in the northern hemisphere (see Appleby [24], p. 171). A sedimentation rate of 0.22 cm y^{-1} for the upper 4 cm and 0.30 cm y^{-1} for the 4–11 cm interval was therefore calculated. The plateau sub-basin thus showed a sedimentation rate approximately four to five times lower than the other basins of the lake (see Fanetti [23] for a more detailed geolimnological discussion).

3.2.1 Analysis of concentration profiles

The concentration profiles of selected elements for the three cores are reported in Figures 2–4, respectively.

As a first consideration, the concentrations of lead, zinc, cadmium and uranium showed a significant increase in the upper section of the cores, although different levels of contamination were evident in the three sites (see the foregoing section for an explanation). The lower part of the cores showed concentrations similar to pre-industrial (before 1850) levels in European and American lake sediments [25]. The rise in trace element concentration can be attributed to anthropogenic inputs from both the atmosphere and direct river discharges, as is well documented by literature data [3,4,26], a dramatic change in sedimentation rate and/or natural inputs being highly unlikely. In particular, the observed trends for zinc, lead and cadmium were in good agreement with the estimated atmospheric emissions (see the EMEP Workshop data [27] for an estimate of European emissions): a steady increase in contamination since the beginning of the industrialisation period, with a sharp decrease in the very last strata for Cd and Pb was registered in the core profiles. The decrease of lead concentration was due to the banning of leaded gasoline, in 2001 in Italy (with a steady decrease in selling since 1992) and in 2000 in most of the other European countries [28]. The decrease of cadmium levels was explained by the introduction of more stringent regulations on the atmospheric emissions caused by fossil fuel combustion and waste incineration. The latter represented the most important sources of cadmium to the atmosphere in the last 30 years (see the EMEP Workshop data [27]). The rise in uranium concentration, which has been seldom reported, was well correlated to the onset of atmospheric contamination by this metal since the second half of the last century, as recorded in the ice cores sampled in Mont Blanc (see Barbante *et al.* [29]).

Core CO-02 results will be discussed in more detail, as exhaustive data with 1-centimetre resolution were available (1 cm corresponds to around four years in the upper 11 cm, see Figure 2). Lead, zinc, cadmium and uranium showed a characteristic enrichment in the upper 11 cm strata: the concentrations of these metals increased on average 2.7, 2.0, 3.6 and 1.5 times, respectively, in the last 40 years (mean concentration in the upper 11 strata/mean concentration in the lower 120 cm). On the other hand, copper, chromium, nickel and arsenic showed much lower figures, in the 1.1–1.2 range. Finally, cobalt, scandium and yttrium were found to be depleted in the upper section: -10% for Co and -20% for

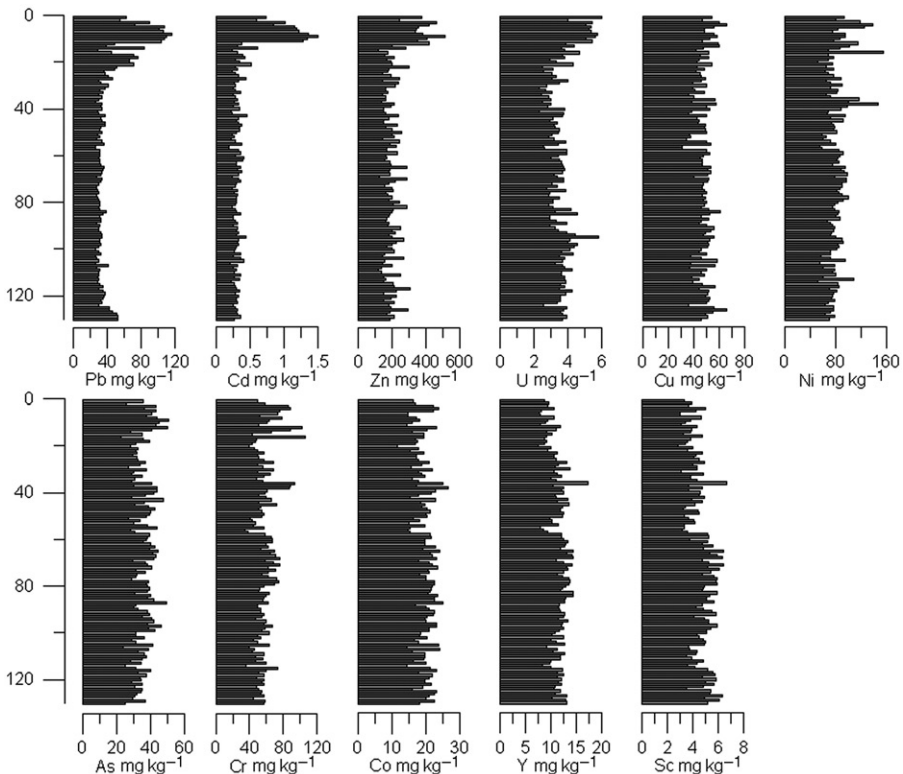


Figure 2. Sediment core CO-02 profiles of selected elements.

Sc and Y. It is worth noting that sudden decreases in metal concentration (e.g. Pb, Cd and Zn in strata 12 and 16) could be attributed to organic matter rich levels, clearly visible in the core. Such a massive deposition of organic matter was effectively able to lower element concentrations in the sediment through a dilution effect.

Lead contamination in the Como basin started earlier than other elements'. A mean concentration of 58 mg kg^{-1} (stand. dev. 17 mg kg^{-1}) was in fact registered in the 12–23 strata, while the mean of 12–130 strata was $35 \pm 10 \text{ mg kg}^{-1}$ (average $\pm 1 \cdot s$). Pb contamination could thus be dated back, assuming an approximately constant sedimentation rate, to the second decade of the nineteenth century. Such an early contamination was also fairly visible for uranium. These two metals, possibly deriving from fossil fuel combustion, were thus the first registered sign of human activities in modern times.

As noted before, lead and cadmium showed a marked decrease in the uppermost six strata, while such a trend is not clearly defined, if at all, for uranium and zinc, indicating that the contamination by the latter metals is all but decreasing.

On the other hand, REE concentrations decreased by 23–35% in the upper 13 strata with respect to the lower ones: averaged data on 10 cm sections are reported in Table 4.

A closer look at REE data for CO-02, suggested that such depletion can be traced back to strata 21–22. Such a pattern was possibly due to the onset of lake eutrophication, which causes the deposition of higher amounts of organic matter, apparently diluting crustal, runoff derived elements like Sc, Y and the REE. Nevertheless, a real decrease in the

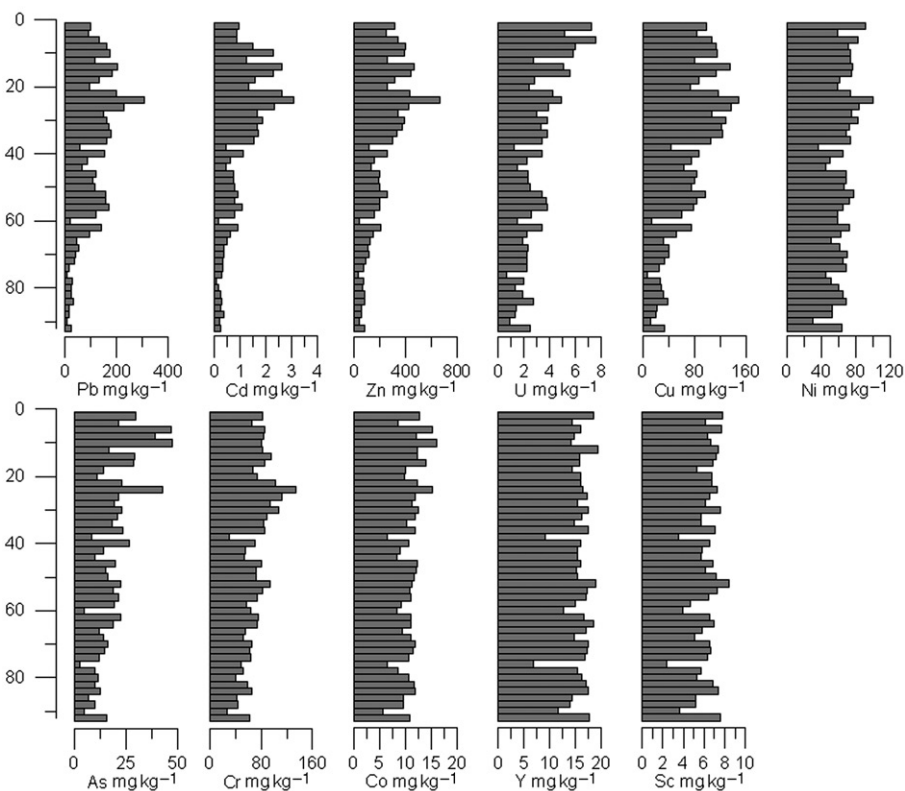


Figure 3. Sediment core CO-09 profiles of selected elements.

exportation of terrigenous elements from the catchment could contribute to a reduced accumulation of these elements in the sediments. The latter feature could be due to the increase in woodland extension owing to changes in soil use (such as reduced pasture and agricultural activities) and/or enhanced land anthropisation. Such a change in population occupation, from pasture to manufacturing, is also in agreement with the concomitant increase in lead concentration, which is a clear proxy of industrial activities. However, the reduction in terrigenous element concentrations is higher than 20% and may be difficultly ascribed to changes in soil use only. The onset of lake eutrophication and the resulting enhanced deposition of organic matter were more likely the major factor causing the observed decrease in terrigenous elements.

3.2.2 Comparison between cores

The comparison of the elemental concentrations in the three cores showed that trace elements were strongly unevenly distributed. Moreover, element specific trends were observed.

Lead, zinc, cadmium and copper concentrations followed the trend $CO-13 > CO-09 > CO-02$, indicating increasing contamination moving from the northern boundary of the Como branch (core CO-02) to sites closer to the city of Como. This feature was

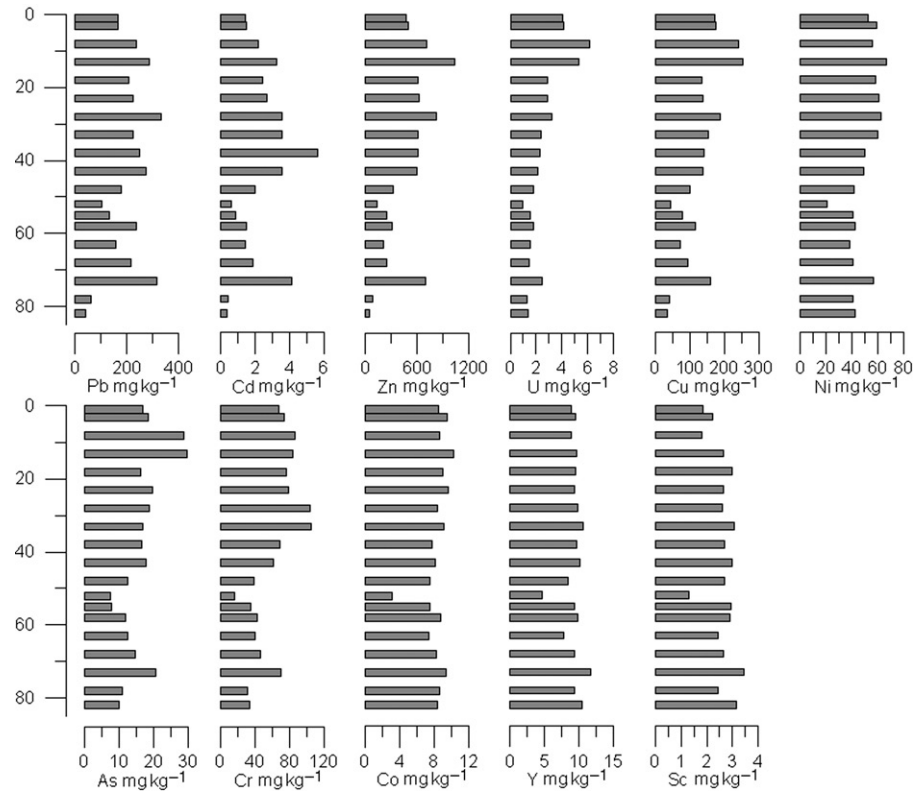


Figure 4. Sediment core CO-13 profiles of selected elements.

attributed to the presence of point sources of contamination in the southern most part of the basin. The latter shows higher population and industrial activity density, resulting in the production of liquid wastes (see, e.g., trace metal concentrations of the sewage treatment plant effluents) and atmospheric emissions. It is also interesting noting that Cd, Zn and Pb showed the same signature in the three cores. In fact, besides showing different total concentrations as reported in the foregoing section, they exhibited the same trends in the three cores (see, e.g., Figure 5 for cadmium). A more detailed analysis was therefore performed to assess whether such metals could share common features. Accordingly, the plots C_{Zn} versus C_{Cd} and C_{Pb} versus C_{Cd} were drawn for each of the three cores and the angular coefficients for the interpolating linear lines calculated. As a result, non distinguishable figures were obtained: the between core difference is less than twice the standard deviation of the angular coefficients of the plots C_{Zn} versus C_{Cd} and C_{Pb} versus C_{Cd} (Cd was chosen as the 'normalising' element). Such a result, i.e. the same Pb, Cd and Zn signature in the three cores, strongly suggested a common source for these metals in the three sampling sites: comparison with particulate matter composition is underway to establish whether this signature may be attributed to atmospheric sources.

Cobalt and yttrium showed an opposite trend when the three cores were compared, increasing their concentration moving away from the city of Como. Such a trend was possibly due to the dilution of terrigenous elements by autigenic organic matter and/or fluvial massive transport.

Table 4. Rare earth element concentrations in the three cores in mg/kg. REEs' content was averaged over 10 cm sections for core CO-02 and along the whole core for cores CO-09 and CO-13 (see text).

CO-02														
Strata cm	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1–10	13.6	28.7	3.39	13.7	2.85	0.55	2.60	0.37	2.05	0.39	0.95	0.15	0.82	0.16
11–20	17.1	36.3	4.25	17.1	3.52	0.68	3.16	0.47	2.42	0.46	1.12	0.20	1.00	0.21
21–30	19.8	42.0	4.89	19.5	3.95	0.76	3.53	0.49	2.63	0.49	1.22	0.19	1.07	0.20
31–40	19.6	41.8	4.82	19.3	3.92	0.74	3.54	0.47	2.63	0.47	1.22	0.18	1.07	0.17
41–50	21.2	44.9	5.16	20.8	4.20	0.79	3.86	0.52	2.78	0.52	1.28	0.20	1.11	0.20
51–60	18.3	38.8	4.48	18.1	3.66	0.69	3.30	0.47	2.46	0.47	1.13	0.20	0.99	0.21
61–70	22.9	48.3	5.55	22.4	4.55	0.87	4.14	0.59	3.02	0.58	1.40	0.26	1.22	0.27
71–80	22.3	46.9	5.33	21.7	4.42	0.84	3.96	0.57	2.92	0.56	1.35	0.25	1.16	0.28
81–90	22.0	47.0	5.29	21.6	4.39	0.84	3.97	0.56	2.90	0.55	1.33	0.25	1.13	0.26
91–100	20.9	44.7	5.04	20.5	4.18	0.79	3.80	0.54	2.77	0.53	1.26	0.24	1.09	0.26
101–110	19.0	40.6	4.67	18.9	3.85	0.72	3.52	0.48	2.58	0.47	1.17	0.18	1.02	0.19
111–120	19.5	41.5	4.78	19.4	3.97	0.76	3.60	0.50	2.60	0.49	1.17	0.20	1.01	0.22
121–130	21.1	44.6	5.04	20.7	4.21	0.81	3.82	0.54	2.68	0.52	1.21	0.25	1.05	0.26
CO-09														
Whole core	19.1	33.8	4.4	17.7	3.7	0.76	3.52	0.48	2.75	0.53	1.45	0.20	1.19	0.17
CO-13														
Whole core	9.7	17.3	2.4	9.7	2.1	0.45	2.1	0.30	1.8	0.34	0.93	0.13	0.78	0.11

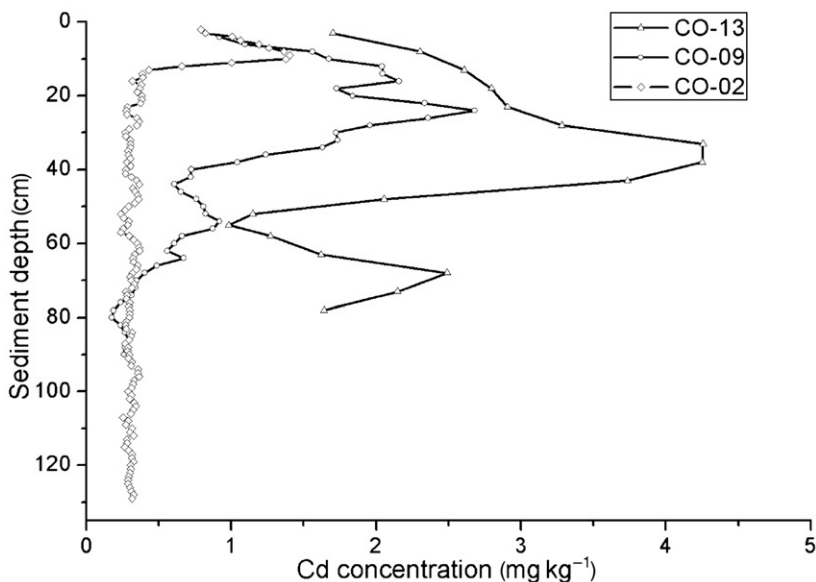


Figure 5. Comparison of cadmium concentration profiles in the three cores (cores CO-13 and CO-09 showed an approximately five-fold sedimentation rate with respect to core CO-02).

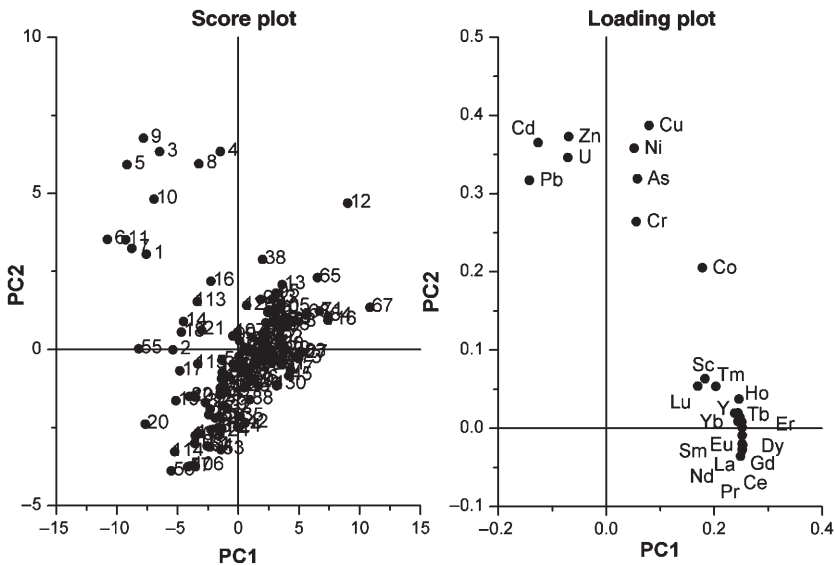


Figure 6. Score and loading plots for core 2 data.

The rare earth elements showed a peculiar trend. Cores CO-13 and CO-09 did not exhibit any depth trend in REE concentrations, with relative standard deviations in the range 9–18%: accordingly, data were reported as averages on the whole core (see Table 4). On the other hand, REE showed depletion in the upper strata in core CO-02. The lack of a similar trend in the other two cores is well explained by their different sedimentation rates. The whole core length of cores CO-13 and CO-09 covered approximately the same time span as the first 20 strata in core CO-02: accordingly, a clear trend was not identified as in these cores the time span covered is too short to evidence the same trend in REE as in core CO-02.

The other analysed elements, scandium, arsenic, uranium, chromium and nickel, showed ambiguous trends when the three cores were compared. In particular, the analysis of arsenic profiles is complicated by its known partial mobility in sediments (see, e.g., Fabian *et al.* [30]).

Because of the great amount of data obtained from the core analyses, PCA was employed to extract useful information, to establish correlations between elements and trends, which were not evident from the analysis of the raw data.

3.3 Exploration of core analysis results by PCA

An exploratory PCA was conducted on each core, including all of the elements shown in Figures 2–4 plus the 14 rare earth elements (25 variables).

The score (strata) and loading (elements) plots for core CO-02 are reported in Figure 6: the first principal component PC1 was highly representative, explaining 61% of the variance of the system, while PC2 had a further 18% variance associated. Variables were clearly separated into three groups by PC1 in the loading plot: Pb, Cd, U and Zn at negative values; As, Cr, Ni and Cu at slightly positive values (<0.08), while Sc, Co, Y and

the REE showed loadings higher than 0.17. This distinction clearly reflected enrichment or depletion in the uppermost strata, as most of the variance of the system was associated with changes in concentrations in this section of the core. PC1 therefore discriminated elements that were enriched (Pb, Cd, U and Zn), moderately enriched (As, Cr, Ni and Cu) and depleted (Sc, Co, Y and the REE) in the section closer to the water-sediment interface (but see Fabian *et al.* [30] for arsenic diagenesis). In addition, elements were grouped according to their origin. Lead and zinc are actually known to receive strong anthropogenic contributions from atmospheric sources (see [31,32] for lake loadings), while Sc, Y and REEs are terrigenous, riverborne elements exported from the catchment. Interestingly, some elements were positioned in between, indicating a moderate enrichment and, possibly, a different source: the enrichment in copper, nickel and chromium is known to have an anthropogenic origin, but their atmospheric contamination is lower than Zn, Cd and Pb (see [33]). Nickel, chromium and copper were shown to be actively exported from catchment and that terrestrial loadings play a major role in their inputs into lakes [32]. Elements were consequently divided in three groups along PC1: anthropogenic, airborne contaminants at negative values, anthropogenic mainly riverborne contaminants at low PC1 values and terrigenous at high PC1 values.

It is also interesting noting that the PC2 axis clearly separated all the anthropogenic derived elements from the terrigenous ones. Pb, Cd, U, Zn, As, Cr, Ni and Cu had a loading major than 0.25, while the REEs, Sc and Y showed figures between 0.1 and -0.05 (cobalt occupied an intermediate position). Accordingly, the upper strata were positioned at high PC2 values in the score plot, indicating that these samples show an enrichment in anthropogenic elements.

The following PCs did not add any relevant information and they were not discussed.

Elemental profiles in core CO-09 and CO-13 were also explored by PCA: score and loading plots are reported in Figures 7 and 8.

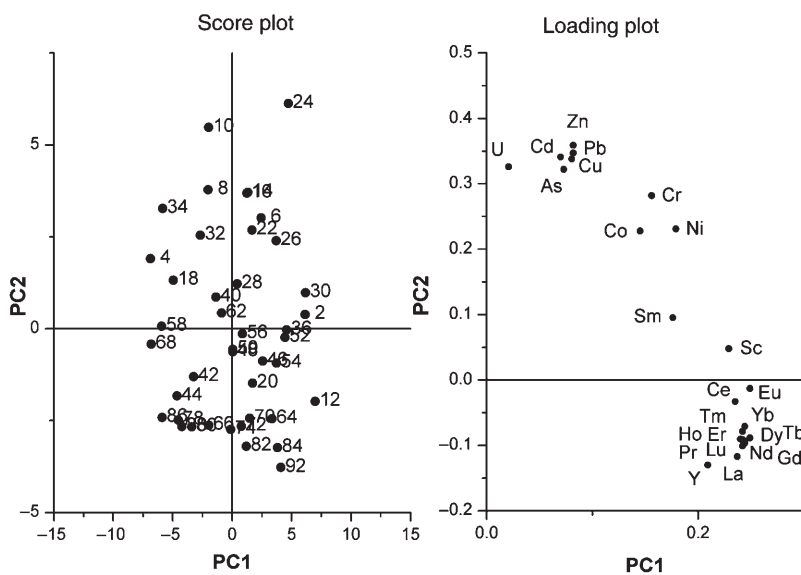


Figure 7. Score and loading plots for core 9 data.

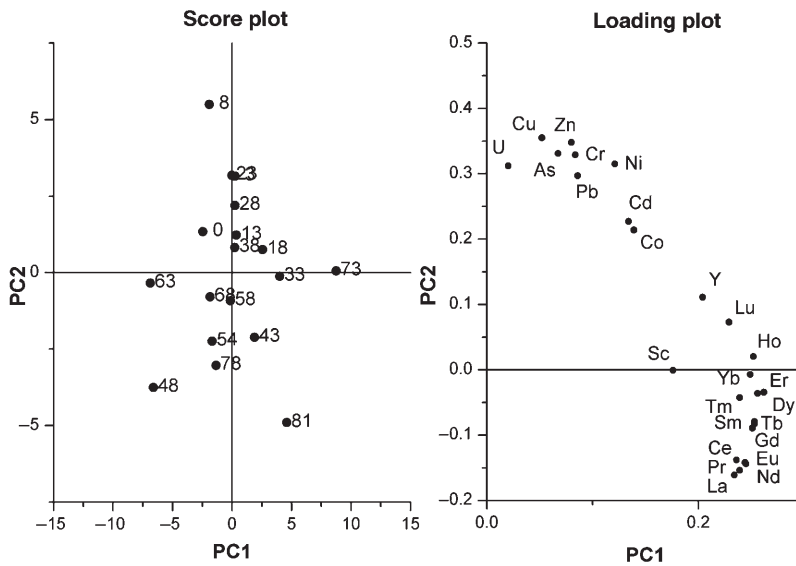


Figure 8. Score and loading plots for core 13 data.

Regarding core CO-09, variables showed a pattern similar to the one described for core CO-02 (see Figures 6 and 7). They were grouped in three clusters along PC1 axis (60% explained variance): low PC1 values (<0.1) including U, Cd, Zn, Pb, Cu and As; medium PC1 values ($0.1 < \text{value} < 0.2$) comprising Co, Cr, Ni and Sm; high PC1 loadings (>0.2): Y, Sc and the REEs (except from Sm). On the other hand, U, Cd, Zn, Pb, Cu and As showed the highest loadings along PC2 (26% explained variance) whereas the REE laid close to PC2 axis (limited contribution to PC2). Accordingly, PC1 mainly reflects changes in terrigenous, crustal elements (REE, Sc and Y), whereas PC2 described the variation of element concentration with sediment depth: elements enriched in the upper strata were grouped at high PC2 values. Almost all of the samples collected in the upper section of the core were in fact located at positive values of PC2 in the score plot.

It is interesting noting that copper and arsenic laid at high PC2 values with Cd, Zn, Pb and U and showed a similar enrichment pattern. Chromium, nickel and cobalt were instead at intermediate values of PC2, with only a slight enrichment in the upper section.

PCA of core CO-13 data (explained variance: PC1 57% and PC2 28%) revealed a pattern similar to core CO-09 and CO-02: terrigenous elements (REE, Y and Sc) were placed at high PC1 values, whereas the elements that showed enrichment in the upper section clustered at high PC2 values with a limited contribution to PC1. Nevertheless, chromium, nickel and cobalt showed a correlation with the elements at high PC2 in this core, indicating enrichment similar to Pb, Zn, Cd, U, Cu and As.

Some general conclusions may be drawn collecting all of the observations made in the foregoing sections.

First, the PC2 axis clearly separated anthropogenic from terrigenous elements. The former were grouped at low loading values, whereas the latter showed higher figures (>0.2). Secondly, the PC1 axis was also able to discriminate terrigenous from anthropogenic elements as the first grouped at highly positive values while the latter showed low positive or even negative loadings. Nevertheless, the PC1 axis was found to be

related to the source of the elements. Actually, the elements were sorted along PC1 axis according to the following sequence: anthropogenic with strong atmospheric loadings (Zn, Cd and Pb), another group of anthropogenic elements (possibly runoff related) like Cu, Cr, Ni and As and terrigenous elements (REE, Sc and Y). Such a pattern was evident in core CO-02 loading plot only, where grouping according to sources is typical of an area affected by atmospheric depositions only and low fluvial loads. Accordingly, airborne elements only showed a marked enrichment in the upper strata. Regarding uranium, no literature data on atmospheric *versus* weathering contribution to lake basins are available: the circumstance that this element grouped with metals receiving strong atmospheric contributions could suggest a similar behaviour, as supported by the detection of atmospheric contamination by this metal (see Barbante *et al.* [29]).

Moving towards the Como basin, higher atmospheric loadings were present whereas river inputs started to play a role as a source of elements. As a result, all the anthropogenic elements showed an enrichment pattern similar to the one of the airborne elements, as is well demonstrated by the progressive coalescence of all the elements, beside the terrigenous ones, in the loading plot of core 9 and 13.

4. Conclusions

This study explored the possibility to extract information from trace metal profiles of sediment cores sampled in different locations in a multi basin lake. The complexity of such data was effectively dealt with by the use of both traditional means, e.g. profile description and comparison, and chemometric tools like PCA. The latter proved a powerful method for the analysis of this complicated system: the elements were grouped according to their origin and/or recent environmental evolution (increased or reduced loading), establishing a remarkable frame for the interpretation of trace element profiles. The possibility to exploit PCA to discriminate between metal sources is clearly attracting and may be employed as a general tool in the study of lake basins once validated through a better knowledge of element loadings into lakes and a larger number of case studies.

Specifically, data from the western branch of Lake Como showed that the asymmetrical distribution of pollution sources and the variation in sub-basin sedimentation rates lead to changes in element fluxes to sediments as high as one order of magnitude, depending on the considered sub-basin. As an example, zinc, lead and cadmium fluxes in the last decade of the twentieth century can be estimated as 0.2, 0.07 and 0.0007 mg m⁻² y⁻¹, respectively, when the southern most basin (Como basin) is considered, whereas flux estimates yielded 0.02, 0.004 and 0.00004 mg m⁻² y⁻¹ for the northern part of the Como branch (plateau region). Lake morphology and circulation together with the distribution of point sources are undoubtedly responsible for the uneven trace metal fluxes to sediments: at present, a quantitative modelling of trace element balance is hindered by the inadequate understanding of both element loadings and water masses circulation.

Further developments in the extraction of useful information from element profiles could cover the use of point sources of these elements as an *in situ* tracer and of atmospheric derived elements as tracers for establishing core correlation. In fact, point emissions could be employed as tracers for present or past circulation studies: the uneven distribution of metals in cores at different distances from the metal source could prove useful in establishing the circulation of water masses, particularly in

paleolimnological studies. A good knowledge of the metal behaviour in the lacustrine environment and reliable data on the local source(s) are nevertheless mandatory for such an approach to be feasible. On the other hand, core correlation could be achieved by matching metal profiles in different cores when traditional limnological means fail in multi-basin lakes. As a matter of fact, the complexity of the morphology, the completely different sedimentary environments, possibly different diagenetic processes (e.g. resuspension and bioturbation) and the presence of multiple sources, some of which of a local origin, commonly hinder the understanding of trace element patterns in lake sediment cores. Metal loading affecting the whole lake like atmospheric, regional scale depositions, could therefore represent a perfect approach for correlating cores coming from different basins, provided the same trend in trace metals is verified.

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