Metals in Sediment Cores from Nine Coastal Lagoons in Central Vietnam

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Abstract: Problem statement: After being dramatically hit by war events, Vietnam is presently experiencing a huge economical and social development. However, very few data, relative to pollution levels and trends, are available for the correct management of critical areas such as coastal lagoons, where many economical activities are linked to high value environmental features. Approach: A set of sediment cores from nine coastal lagoons of central Vietnam (Lang Co, Truong Giang, An Khe, Nuoc Man, Nuoc Ngot, Thi Nai, O Loan, Thuy Trieu and Dam Nai) were sampled in 2008 and analyzed to assess metal and (Al, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, V, U and Zn) and As levels and historical trends. Results: Concentrations are generally low, with the exception of As, which often exceeds ERL guidelines and Ni that does the same at O Loan. In some cases, concentrations-depth profiles account for recent increasing trends but surficial values are still low when compared to both international guidelines and polluted sediments all around the world. Sediment grain size seems to affect the depth distribution of a number of metals and when normalized to the content of silt and clay, values are particularly high at Dam Nai and Thi Nai, due to the very coarse composition of surficial sediments. Conclusion: Metal concentrations in lagoon sediments derive from the composition of rocks and soils in the watersheds. However, recent increasing trends need for further monitoring.

Key words: Trace metals, metal contamination, surficial sediments, coastal lagoons, central Vietnam

INTRODUCTION

Since the industrial revolution, the anthropogenic release of metals into the environment has changed their biogeochemical cycles. Furthermore, high recent fluxes may have led to accumulation in sediment and biota with a consequent threat to both animals and humans beings. Metal contamination and pollution can arise from many sources mostly associated with areas of intensive industrialization (e.g., metallurgy, coal burning and waste incineration, study and fertiliser productions, chlor-alkali plants, reaction catalysts) but there are hundreds of other sources including agriculture, urban sewages, roadways and transportation.

Some metals are necessary for humans in limited amounts (Co, Cu, Cr, Ni) because they are co-factors in enzymatic systems, if present at higher concentrations or other elements are carcinogenic or have toxic effects, at the central nervous system (Hg, Pb, As), kidneys and liver (Hg, Pb, Cd, Cu), or skin, bones and teeth (Ni, Cd, Cu, Cr) (USG, 2011). The directive 2000/76/EC of European community listed 13 elements of highest concern (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn and Tl), the emissions of which are regulated in waste incinerators. Moreover, Cd, Pb, Hg and Ni are included among the priority substances for the classification of water bodies according to the EC (2000) (Directive 2000/60/EC).

Sediments are the ultimate sink for many pollutants, including metals. Most of them display a strong affinity for particles and independently from source and transport pathway, once released into the environment they are involved on the biogeochemical cycles and contribute at the composition of suspended matter that, eventually, will enter the aquatic environment to be stored into sediments.
This adsorption-settling process makes sediments an archive of information on the change of environmental conditions and quality over time. It follows that the study of sediment records can help not only to monitor present concentrations but also to determine past levels, trends and potential toxicity of contaminants e.g., (Bellucci et al., 2005; 2010; Frignani et al., 2005; Giuliani et al., 2011 and references therein). Because of this, we studied sediment cores from nine lagoons in Central Vietnam. The aim was to improve the information about the impact on the environment that may have been caused by both Indochinese War-related events (1945-1975) and recent economic growth. These areas are valuable and important ecosystems, significant tourist attractions and sites for fishing and aquaculture activities; therefore, they represent key environments for the sustainable development of the Vietnamese economy.

**Study areas:** The nine lagoons (Fig. 1) are located in the central Vietnam provinces of Thua Thien-Hue, Da Nang, Quang Nam, Quang Ngai, Binh Dinh, Phu Yen, Khanh Hoa and Ninh Thuan.
They are diverse in typology, scale, shape, size, inlet stability, water features, geographical context and geology of their mainland (Cu, 1995). Their surface area ranges from 2.8-50.6 km² and determines their rating into 4 categories (Cu, 1995): very small (Dam Nai, DN), small (Lang Co, LC; An Khe, AK; Nuoc Man, NM; Nuoc Ngot, NN; and O Loan, OL), medium (Truong Giang, TG; and Thuy Trieu here referred as Cam Ranh, CR) and large (Thi Nai, TN).

The lagoons are fed by water and particulate materials coming from the mainland. The Kontum massif that dominates Central Vietnam, is made of high grade metamorphic rock of calc-alkaline nature, composed by gneiss, amphibolite, schist, migmatite and lenses of marble (Lan et al., 2003). The presence of precious minerals is significant: gold, diamonds, aquamarine and zircon can be found in Quang Nam, Gia Lai and Kon Tum provinces, bauxite is abundant in Dac Lac, graphite in Gia Lai, limestone and silica sand in Thui Trieu and titanite is present along the coast. In spite of this, mining activities are poorly developed; even though, after the “Mineral Law” (circular 1 of the ministry of natural resources and environment - MONRE - dated 23 January 2006), the number of licenses issued by local authorities to exploit mines has increased significantly (Dao et al., 2008; UPFM, 1999). Nowadays, mining at the industrial scale focus only on some non-metals such as coal, apatite and cement raw materials. Broad industrial activities, such as metallurgy or coal mining, are not common in the area, but several development programs are in progress (Perkins and Anh, 2010).

It is a general assumption that environmental quality of the lagoons has been deeply affected over time by anthropogenic pollution, as shown by high concentration of oil, nitrate and coliforms in water (Dieu, 2006; Thom, 2006). However, Giuliani et al. (2008) discussed the distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in the same study areas and found very low concentrations. The highest values were observed at the northernmost locations (LC) indicating the predominance of local sources instead of a widespread distributed contamination. While some cores showed recent decreases, at LC, TG, NM, TN, OL and DN increasing or slightly increasing trends characterized the topmost sediment layers.

**MATERIALS AND METHODS**

The TG Lagoon was sampled in June 2005 and the other lagoons in January 2008 (Fig. 1). In all campaigns, a manual piston corer was used to retrieve the sediment. Cores were immediately extruded and subsampled at intervals 1-4 cm thick, with higher resolution at the top. Sediment sections were kept frozen until the arrival in the lab, then they were freeze-dried and homogenised before analysis.

Porosities were calculated according to Berner (1971), assuming a particle density of 2.5 g cm⁻³. Grain size analyses were carried out by wet sieving, to separate sands, after a pre-treatment with H₂O₂. Silt and clay fractions were determined with the Micromeritic X-ray SediGraph.

For metal analyses, aliquots of 0.5 g were extracted under reflux with 10 mL of 8N HNO₃ and 3 mL H₂O₂ 30% (modified from Bellucci et al., 2002). Solutions were centrifuged and the supernatant solution diluted to 45 100 mL with Milli-Q water. Extracts were analyzed by ICP-QMS (Agilent 7500) fitted with a standard double-pass spray chamber and a v-groove nebulizer (RF power 1,400 W, sample gas 1.20 L min⁻¹, sample flow rate 500 μL min⁻¹, dwell time 20 ms, 3 points per peak). Accuracy was tested through the analysis of Certified Reference Materials NIST 2709 (soil) for leaching extraction, resulting within the confident limit of 95%. Precisions, estimated by replicate analyses of the same sample, were between 7-13%. All concentrations are expressed with respect to dry weight.

Statistic analyses were performed with the software package Statistica.

**RESULTS**

**Sediment features:** Figure 1 shows the depth profiles of sand contents in cores taken in 2005-2008. In general, fine sediments characterize all lagoons except DN (with sand always > 50%) and TG (where the sand content reaches up to ca. 60%). The core from TN shows an upward constant increase of the coarse component (up to ~60% at the surface), whereas at CR, sand reaches a peak value (65%) between 35 and 20 cm depth and remains 48% at the top. In synthesis, each core is characterized by a different grain size composition and depth distribution. The sediment from DN is characterized by a high content of shell tests (ranging from 3-18%) that weakens any interpretation.

Table 1 show that carbonic content and C/N ratio in surficial samples of lagoon cores are comprised in the intervals 0.52-3.72% and 7.68-19.2, respectively. δ¹³C values range from -26.5 to -22.3.

**Metal concentrations:** Table 1 summarize the results listing minimum, maximum, surficial and median values for Al, As, Cd, Cr, Cu, Fe, Hg, Li, Mn; Ni, Pb, Ti, U, V and Zn.
Maximum surficial metal concentrations pertain to OL (Ag, Al, Cr, Cu, Ni, Ti, V, Zn), CR (Hg), TN (As, Mn, Fe and AK (Cd, Pb, U). The As maximum in the sandy surficial sediment at TN is particularly surprising, due to the general strong affinity of As for iron coatings and fine particles (Belliucci et al., 2002; Anawar et al., 2003). U values are close to natural ones (ca. 4 μg g⁻¹; Turekian and Wedepohl, 1961; Wong, 1983) at NM, DN, and SN, but are slightly higher at LC, TN and OL, whereas the concentration at AK is surprisingly elevated (ca. 24.4 μg g⁻¹).

Metal concentration-depth distributions within the nine cores display similarities and differences that will be highlighted in the Discussion.

**DISCUSSION**

Depositional settings and organic matter origin: Grain size patterns account for major changes in the depositional settings that may be due to the decrease (e.g., AK, DN e N) or increase (e.g., NN, TN and CR) of water hydrodynamics over time (i.e., from deep to surface sediments), or to anthropogenic activities increasing fine particles remobilization. Indeed, the change at TN could have been influenced by a beach nourishment close to the sampling site related to the development plans in the area.

The plot of Fig. 2 accounts for different organic matter contributions to the lagoons. CR shows the highest value of C/N and the lowest of δ¹³C, suggesting a prevailing continental contribution. Indeed, C/N higher than 10 is considered as an indication of terrestrial contributions (Cunha et al., 2006), while δ¹³C values for mangrove C3 plants vary from -33 to -24‰ (Zieman et al., 1984; Lallier-Vergès et al., 1998). The same origin can be assumed for TN and LC, whereas
OL, NM and NN have a mixed terrestrial/marine influence, with C/N ≤ 10 and δ^{13}C from -24 to -22‰, characterising both marine algae and terrestrial C4 plants (Fry and Sherr, 1983; Gearing et al., 1984; Kato et al., 2000; Boonphakdee et al., 2008). On the other hand, values for TG and DN account for light marine influence. This high variability is typical of such study areas, tropical coastal brackish water lagoons bordered by large rice fields (C4 plants) and characterized by the presence of ponds, shellfish aquaculture farms and mangrove plants. In addition, a mixed contribution, due to intrusion of saltwater in the lagoon during low tide and from paddy soils, mangroves and ponds, cannot be excluded.

Trace metal levels and their potential toxicity: Most metal concentrations (e.g., Al, Fe, Mn, Cr, Cu, Ti, V and Zn) are rather low, even below the background levels measured in soils and near-shore muds as reported by Turekian and Wedepohl (1961) and Wong (1983). This, especially for Al and Fe, is a consequence of the analytical method (hot acid leaching) that does not account for the fraction contained in the crystal lattices of mineral particles. However, a comparison with literature data obtained with similar methods is shown in Fig. 3 for As, Cr, Hg, Ni, Pb and Zn in surficial samples of the lagoons. Reference data were separated into three major groups, to account for different anthropogenic pressures and environmental settings: industrial/urban areas (Tanner et al., 2000; Zago et al., 2001; Berg et al., 2001; Bellucci et al., 2002; 2003; Bertolotto et al., 2003; Adamo et al., 2005; Ferraro et al., 2006; McCready et al., 2006; Marmolejo-Rodriguez et al., 2007; Harikumar and Nasir, 2010; Nikolaidis et al., 2010), coastal areas (Taher and Soliman, 1999; Dauphaveler and Rognerud, 2001; Zabetoglou et al., 2002; Sericano et al., 2002; Preda and Cox, 2002; Bertolotto et al., 2003; 2005; Kishe and Machida, 2003; Cuong and Obbard, 2006; Farkas et al., 2007; Nobi et al., 2007; Romano et al., 2010) and lagoons (Bellucci et al., 2002). The values measured in Vietnamese lagoons are by far among the lowest (up to one order of magnitude) of the entire set for all elements considered, being lower but comparable to other coastal systems. This would suggest a still very low, if any, anthropogenic contribution.

The potential threats to biota of Vietnamese lagoon sediments can be evaluated through the comparison of measured concentrations with internationally accepted Sediment Quality Guidelines (SQGs) that define values above which adverse effects can be observed (Table 1). Using Threshold Effect Levels (TEL) and Probable Effect Levels (PEL) for marine sediments (Burton, 2002), which appear to be the most restrictive limits (Table 1), all As concentrations in Table 1 exceed the lower limit except for NN, where TEL is exceeded only at the bottom of the core (55-59 cm depth). TEL limits are overcome also by Ni at TN, OL and LC, Cr at TN, OL and LC, whereas NM shows values close to threshold level for Ni and Cr. Moreover Ni at OL reaches levels higher than PEL. These situations raise the possibility of occasional adverse effect on biota and suggest the need for a monitoring project and possibly, a reduction of the loadings to the lagoons. Attention is also needed for those chemicals that do not exceed the guidelines but show recent increasing trends (Table 1) that may account for a growing anthropogenic pressure.

Environmental factors driving trace metal patterns: An R-mode Factor Analysis, extracted by PCA and Varimax as factor rotation, was used to obtain a first order information about what parameter (among grain size, mineral composition, redox conditions and anthropogenic inputs) eventually drives the metal patterns. Four factors account for 81.3% of total variance and Table 2 lists their score coefficients.

| Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|----------|----------|----------|----------|
| SILT     | 0.25     | 0.20     | -0.02    | 0.73     |
| CLAY     | 0.77     | 0.34     | 0.18     | 0.07     |
| Geometric mean | -0.63 | -0.32 | -0.20 | -0.49 |
| Geometric sorting | 0.28 | 0.14 | 0.18 | -0.75 |
| Mode (μm) | -0.58 | -0.47 | -0.36 | 0.05 |
| Be       | 0.62     | 0.71     | 0.16     | 0.01     |
| Al       | 0.87     | 0.44     | 0.00     | 0.00     |
| Ti       | 0.88     | 0.20     | -0.34    | 0.00     |
| V        | 0.94     | 0.18     | 0.06     | -0.05    |
| Cr       | 0.96     | -0.03    | 0.12     | 0.11     |
| Mn       | 0.81     | 0.09     | 0.28     | -0.30    |
| Fe       | 0.88     | 0.19     | 0.15     | -0.29    |
| Ni       | 0.96     | 0.01     | -0.14    | 0.03     |
| Cu       | 0.93     | -0.09    | 0.05     | 0.19     |
| Zn       | 0.94     | 0.10     | 0.23     | 0.10     |
| As       | 0.02     | -0.14    | 0.88     | -0.17    |
| Ag       | 0.74     | 0.52     | -0.17    | -0.10    |
| Cd       | -0.06    | 0.91     | -0.13    | -0.06    |
| Pb       | 0.03     | 0.66     | 0.51     | 0.20     |
| Hg       | -0.16    | -0.19    | -0.23    | 0.00     |
| Li       | 0.73     | 0.16     | 0.55     | 0.17     |

Eigen values; extracted by principal components

| Values | Eigenvalue | % Total variance | Cumulative Eigenvalue | Cumulative (%) |
|--------|------------|------------------|-----------------------|----------------|
| 1      | 11.70      | 53.2             | 11.7                  | 53.2           |
| 2      | 2.70       | 12.3             | 14.4                  | 65.5           |
| 3      | 1.88       | 8.54             | 16.3                  | 74.0           |
| 4      | 1.60       | 7.28             | 17.9                  | 81.3           |

Table 2: Factor score coefficients and Eigenvalues from R-mode Factors Analysis on metal levels, grain size parameters (geometric mean, sorting, mode, silt and clay percent content) from cores sampled in nine Central Vietnam coastal Lagoons.
Fig. 3: Values of selected metals (As, Cr, Hg, Ni, Pb and Zn) in surficial sediments of different environment: industrial areas, coastal zones, lagoons

No factor accounts for TG samples because this core lacks of some parameters. Factor 1 accounts for c.a. 53.2% of the variance and represents the main mechanism that drives the element distributions with the predominance of Ag, Al, Cr, Cu, Fe, Mn, Ni, Li, Ti, Zn, V and clay content. These parameters are commonly associated with calc-alkaline minerals typical of the area (NLA, 1995; Cu, 1995; Thuy et al., 2000), suggesting the presence of terrigenous inputs with a rather constant mineralogical sediment composition. Factor 2 accounts for 12.3% of the variance and is controlled by Be, Cd and U. In this case, while Cd and U may be associated to the use of contaminated phosphate fertilizers (Al-Shawi and Dahl, 1999; McBride and Spiers, 2001) and thus can indicate a specific anthropogenic influence, Be is mostly linked to terrigenous input, behaving as a vicariate element of Al.

Factor 3 accounts for 8.54% of the variance and shows significant loading (> 0.7) of As. This element, present at high levels in most of the lagoons, could be generated from natural processes (e.g. weathering of metamorphic rocks or arsenic-bearing minerals by dissolution due to variations in redox conditions) as reported in (Berg et al., 2001), but also anthropogenic activities can play a role because of deposits of gold mining wastes (Berg et al., 2001; Matschullat, 2000), metal smelting processes, ceramic production, timber treatment, burning of fossil fuel and/or arsenic containing pesticides (Ngoc et al., 2009; Yudovich and Ketris, 2005).

Finally, factor 4 (7.28% of the variance) is controlled by silt and negatively correlated with geometric sorting, thus indicating the influence of course content patterns.
The geochemistry of Central Vietnam is dominated by calc-alkaline rocks with high grade metamorphism (Al-Shawi and Dahl, 1999; Thuy et al., 2000) that can evidently influence the geochemistry of major elements in sediments (Shimmield and Mowbray, 1991). Actually, the good relation Al versus fines or clay content (Table 3) and many metals (Table 2) confirm the hypothesis of a prevailing alumina-silicate input into four of the nine lagoons (AK, NM, CR, TN). On the contrary, LC, TG, NN and OL show an independent trend of Al and fines, with little variation of grain size down core. Even though we have to assume that each core is representative of the relative lagoon, sampling locations may have influenced the metal patterns. In this regard, it is important to note that, while the first four cores are located near the tributary estuary, the remaining ones are far from a direct river influence. Consequently, a normalization vs. Al, considered a natural element linked to clay minerals, was performed in order to assess the influence of sediment composition variations over trace metal depth profiles. Figure 4 shows some examples relative to the normalization of selected metals in some lagoons. In many cases, the normalization strongly modifies the metal pattern.
When metal values become more constant than the original ones, a similarity is evidenced that suggests a natural origin. On the contrary, when Al concentration is nearly constant throughout the core the pattern remains the same, thus indicating a non-natural control mechanism. When there is no relationship between the two parameters, the profile is oddly modified. In our case the depth distributions of most metals become linear, even if the correlation with Al is not statistically significant, whereas, Hg and Cd fall in the second or third case, depending on the lagoon (Fig. 4). Moreover diagenetic effects cannot be excluded, in that a subsurfacial peak often survives after normalization for all metals (included the redox sensitive Fe and Mn). This feature is particularly evident in cores from LC, NM, TN, CR where Fe and Mn show evident subsurfacial peaks (e.g., at 10-25 cm depth in core CR, Fig. 4) that accounts for an accumulation of metals in a subsurfacial oxic layer.

Setting differences and trace metal sources: In general, metals can reach the lagoons via direct river discharge, runoff of agricultural soils, roads and/or urban settlements and atmospheric dry and wet deposition, thus affecting the composition of sediment in the lagoons. Nowadays, the presence of industrial activities around the Vietnamese lagoons is still very scarce, but it should be noted that the area was once occupied by military bases during the war (Young et al., 2004) and many different mines (gold, diamonds, ruby, bauxite, florite) are to be found in the mainland and along some coast tracts (Kusnir, 2000; MWC, 2007). Moreover, all the lagoons host medium/little economic settlements, are heavily exploited for fisheries and aquaculture activities, as they have many artificial ponds for shrimps and mollusks and are constantly crossed by small motor boats. The hypothesized origin from phosphate fertilizers for Cd and U (see above) is likely, but also urban sources can be relevant. Indeed, one of the most important sources from increasing urbanization is linked to motor vehicles: roadways and automobiles now are considered to be one of the largest suppliers of Zn, Cu and Pb with smaller amounts of many other metals, such as Ni, Cd and Cr that are also found in road runoff and exhausts Fairfaxcounty, 2007. Nevertheless, the measured contaminant concentrations previously discussed do not indicate a harmful situation, with metal patterns mostly driven by natural mineral composition of parent rocks. In these environments different soil composition may cause background variations among the lagoons.

It is interesting to understand which are the main differences among the nine study sites. Thus, a two way Cluster Analysis was carried out using metal composition and core samples as variables and cases, respectively. Because some cases, lacks of some parameters, the statistical calculation indicates that TG and some DN levels are not suitable for factor analysis. The plot (Fig. 5) identifies two main groups, with some minor differences within. The distribution is mainly driven by the metal contents, which previously have been described by factor 1 of the Factor Analysis and secondly by As, Hg and Cd, Pb and U previously described by factors 2 and 3.

In the first group DN seems differ more from NM, NN and CR topmost levels, in the second group AK and CR downcore levels and OL differ more from LC and TN.

As for DN, the shell content may have affected the result distribution. On the contrary, the division of CR samples in the two main groups points out that a clear depositional change occurred in the recent years as already shown by the strong change in grain size pattern. High concentration of Ni, Cr and Fe, Mn and Ti (Table 1) due to the presence of mafic and ultramafic minerals (olivine, spinel, amphibole as intrusions located in the margin of the Kon Tum Block) and occurrence of Titanite and Zircon in the area as reported in both Al-Shawi and Dahl (1999) and Dung (2006) could explain the higher mutual similarity of some lagoons (LC, OL, TN), moreover, high levels of Al, originated from K-feldspate, Plagioclase, could strengthen the group of LC, AK, TN and OL. However, it is probably the higher concentration of As, Cd and Pb in AK and some levels of CR that drives the main differences in the cluster analysis (Fig. 5). The results, suggest that at some places both natural and anthropogenic processes determined metal patterns and trends. However, recent small increasing trends are visible, the most important being located at AK, NN and OL, even though concentrations remain rather low. This may be due to recent anthropogenic influences. Regarding the high levels of as and U, these metals exist in nature because of intrusive formations as granite and granodiorite with molybdenum occurrences.

### Table 3: R² of Al vs fines and Al vs clay content in cores sampled in nine Vietnam coastal lagoons

| Sample | R² Al vs fines | R² Al vs clay |
|--------|----------------|---------------|
| LC     | 0.085          | 0.713         |
| TG     | 0.019          | 0.017         |
| AK     | 0.795          | 0.663         |
| NM     | 0.729          | 0.630         |
| NN     | 0.082          | 0.279         |
| TN     | 0.880          | 0.812         |
| OL     | 0.004          | 0.493         |
| CR     | 0.962          | 0.976         |
| DN     | 0.656          | 0.843         |

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Actually, hot streams are common in the area while the economic sectors, especially industries, are at a very low level of development. However, it should be also noted that the identification of productive processes responsible for the input of metals to the environment needs further in situ investigations, specifically designed to discriminate between urban related inputs and those linked to the productive and industrial activities located in the area. It will be also important to assess the relative importance of soil natural composition in comparison with the influence of anthropogenic contaminants.
CONCLUSION

Nine sediment cores taken from central Vietnam coastal lagoons, were analyzed to understand patterns and historical trends of a series of metals. Results can be summarized as follows:

- Concentrations are generally low if compared with literature values of other lagoons worldwide. However, As, Cr and Ni showed values exceeding TEL guidelines that can occasionally cause adverse effect on biota.
- There is no clear trend in metal values among the lagoons. In many cases the soil composition and the selective action of hydrodynamics determine element values. Anthropogenic inputs are limited, due to the lack of large industrial settlements. Probably the most important deliveries are from agriculture soils, fishing activities, urban development and traffic. Understanding and locating the main sources is a task for the future.
- A first-order information to understand which parameters drive metal patterns was obtained from R-mode Factor Analysis. The main factor influencing element distributions is the terrigenous input associated with clay minerals (Ag, Al, Li, Fe, Mn, Cr, V), but also, the anthropogenic contribution due to the land use by agriculture can be distinguished (Cd, U). Moreover, a mixed origin of some elements (As and Hg) is related both to natural processes (e.g. weathering of metamorphic rocks, arsenic-bearing minerals by dissolution and so on) both to anthropogenic activities (deposits of gold mining wastes, metal smelting processes, ceramic production and so on). Finally the residual contribution seems to be associated to coarse sediment patterns.
- Element concentration-depth profiles are often driven by granulometric and compositional changes, especially those related to clay contents. In a number of cases, a minor effect can be attributed to early diagenesis.
- Cluster Analysis carried out to understand which are the main differences among the nine study lagoons, identifies two main groups: one is mainly characterized by metals associated with calc-alkaline minerals and clay.
- Content, whereas in the other the higher concentration of As, Cd and Pb in, AK and CR, are probably due to a mix of natural anthropogenic sources.
- Since an increasing trend is observed in some cases, possibly as a consequence of growing industrialization and urbanization, designing a monitoring program is certainly advisable.

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