SPATIAL DISTRIBUTION PATTERNS OF HEAVY METALS IN LAKE BOTTOM SEDIMENTS: AN EXAMPLE FROM THE MULARGIA RESERVOIR (ITALY)

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ABSTRACT

Lake Mulargia is one of the reservoirs that provides the bulk of water supply to southern Sardinia. The catchment area comprises terrains abounding in heavy-metal deposits, mostly base-metal sulphides, that give rise to a major group of pollutants in the bottom sediments depositing in the lake.

More than 200 samples of sediments have been collected from all over the lake bottom following a scheme dictated by the drainage system above and beneath the normal water level of the reservoir. Diffractometric analyses have been performed on all samples, and spectrometric XRF analyses on a selected group of samples. Trace element determinations for Co, Cu, As, Cd, Sn, Sb, W, Pb, Zn, Bi and Ba have been done using ICP-MS spectrometry.

The analytic data have been statistically treated, processed using a GIS and represented with maps showing the distribution of each metal so as to highlight those areas where the metals disperse and those where they accumulate.

The chemical and mineralogical compositions of the bottom sediments reflect the source rock type and are strongly affected by the surrounding ore mineral occurrences and mining activity.

INTRODUCTION

Lake Mulargia, a man-made lake, is one of the main water reservoirs for Southern Sardinia. It has a roughly triangular shape, the longest side measuring about 5.5 km. Its maximum surface is about 124 km^2, and its maximum capacity about 350 M cu.m; the dam is 90 m high.

Because of the warm, semiarid climate of the island, the lake is prone to significant level fluctuations. In fact, during the rainy season (late autumn to early spring), the water collected in the reservoir, which flows in both from its own drainage basin and from the nearby Lake Flumendosa, is usually sufficient to attain the maximum possible level, while during the dry season (late spring to early autumn) most of the water is consumed and a large part of the lake bottom dries up. During recurrent drought, rainfall does not sufficient to fill it completely and the water consumption empties it almost totally.

In these conditions, most of the bottom sediments undergo alternate phases of dryness, reworking by the incipient river flows after the first heavy rains, supply of new material (including an important organic fraction), and lastly a "normal" lake bottom situation.

A recent period of exceptional drought enabled us to collect samples of these sediments over almost the entire bottom, with the exception of a comparatively small area near the dam.

The above characteristics, together with the geological features of the drainage basin imply peculiar characteristics of its bottom sediments which will be analysed in the present paper.

GEOLOGICAL AND ANTHROPIC ENVIRONMENT

Lake Mulargia is situated in the central part of the southern half of Sardinia. In this part of the island the most important terrains are crystalline Palaeozoic terms, including regionally metamorphosed volcanics, terrigenous sediments and minor carbonatic lenses, often cut by important porphyry dikes. Hydrothermal alteration is also widespread, and is accompanied by sulphide mineralisation (Fe, Cu, Pb, Zn, As, Sb, W, Au). In particular, one of the tributaries of Lake Mulargia drains an old Sb-W-As mine, and the surrounding metavolcanics ("porphyroids") commonly host disseminated Fe (As) sulphides.

This crystalline basement is overlain by non metamorphic terrains, which include Permian clastic lacustrine sediments, Jurassic conglomerates, clays and carbonatics rocks, Eocene conglomerates, Miocene marls and Plio-Pleistocene basalts. All these post-Palaeozoic formations are still sub-horizontal and form the tops of the higher relieves (Figure 1).

Besides the mining excavations, other factors associated with human activity obviously come into play. As mentioned, Lake Mulargia receives the water from Lake Flumendosa, trough a tunnel, which is situated near the eastern end of the northern side. The latter lake drains a much wider basin; however its geological setting is similar to that of Lake Mulargia. One major difference consists in the presence of several mixed-sulphide ore bodies (including an old mine) inside the lake itself.

Another important aspect of human influence on these waters is represented by waste waters, mostly domestic, discharged by several villages in the main valleys. These waters supply important quantities of organic substances. Another contribution is given by agricultural and pastoral activity around the lakes and their tributary valleys, and in the parts of their bottoms which regularly emerge during the dry season. A last factor influencing the bottom sediments of these lakes is the progressive deforestation of the generally steep slopes of the valleys. This induces an active erosion and sedimentation in these basins. Sediments a few metres thick already accumulated, in about thirty years, in the central parts of the main lakes.

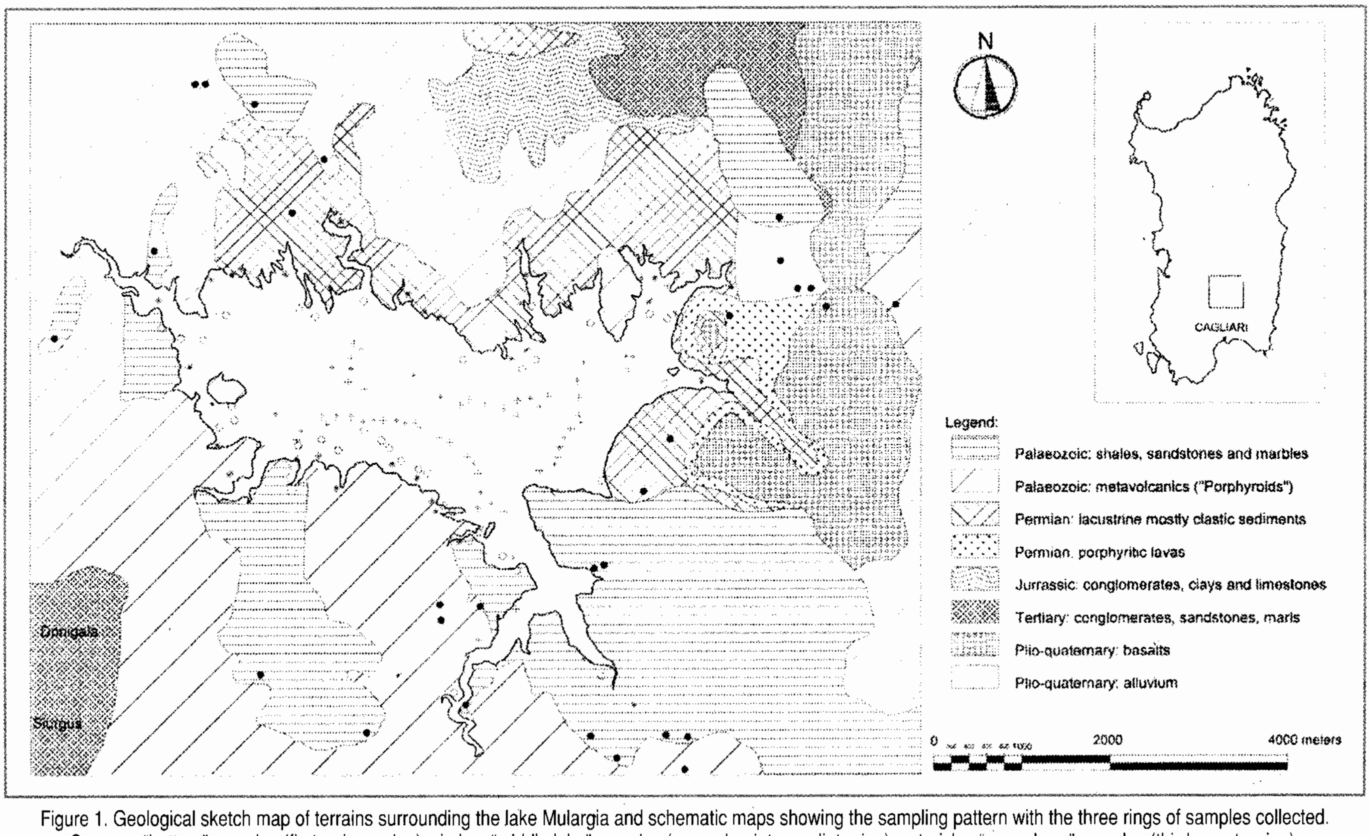

Figure 1. Geological sketch map of terrains surrounding the lake Mulargia and schematic maps showing the sampling pattern with the three rings of samples collected. Crosses: "bottom" samples (first or inner ring); circles: "middle lake" samples (second or intermediate ring); asterisks: "near shore" samples (third or outer ring). Dots represent the sampling sites in the rocks surrounding the lake.

SAMPLING

Given the above characteristics of the studied basin and the exceptional drought of the late eighties, the sample collection was performed in 1990 in the deepest part of the lake, and in 1991 in the marginal parts (Fiori et al., 1993).

Since old maps were also available, it was possible reconstruct the submerged drainage framework. Therefore it was decided to collect the sediment samples following the streams entering the lake (Figure 1).

In the central part of the lake bottom, along the old Rio Mulargia bed and locally along a few important tributaries, the thick sequences of sediments, cut by the most recent water flow, were sampled as stratigraphical columns, while laterally, on leaving the axial zone of the bottom, the total sediment thickness, which never exceeds 20 cm, was collected as a single sample. Inter-stream (pure "lacustrine") sediments were also collected; normally they do not exceed 5 cm in thickness.

Following this scheme, three "rings" were sampled: the first represents the central bottom area, the second concerns the intermediate zone, and the third consists of stream sediments along the border of the lake at its maximum level. A total of 140 sampling sites was sampled this way, and more than 200 samples were collected.

To verify the influence of the surrounding terrains, a further sampling was performed on the different rock types above cited. For this purpose, rock samples were collected, in the main rock facies around the lake.

SAMPLE PREPARATION AND ANALYSIS

The samples, averaging some 300 g in weight, were first dried, then split into two parts, one of which was stored for possible further controls. The second half was split again, and a quarter was sieved to -2 mm, and the finer fraction finalised for analysis. The above mesh size was chosen in keeping with an earlier sampling campaign conducted by the EEC Institute of the Environment to study the major and a few minor elements, to enable comparison of results, at least to some extent. On the remaining quarter particle size analysis was performed on most samples. The following analyses were then performed:

- diffractometric analysis on all samples, to determine the distribution both of the most common and of some minor minerals which characterise the local sources of clasts;
- XRF analysis on a group of selected samples for characterising the distribution of the major and a few minor and trace elements in different parts of the lake bottom; and
- chemical analysis, by means of AAS and ICP-MS, of the trace elements typically contained in the surrounding rocks and ore deposits. Besides the rock samples, all the superficial samples collected in the lake bottom, as well as several of the complete columns sampled in the thick sediment accumulations, were analysed.

As for chemical analyses, a group of trace elements was chosen (Ag, As, Bi, Cd, Co, Cu, Mo, Pb, Sb, Sn, W, Zn), on the basis of their possible presence both in the surrounding rocks and mineralisations, and in human products.

All these elements were analysed in a first group of samples, representing the inner part of the lake bottom, in the -0.125 mm fraction. In order to use other analyses made by the EAF (regional water authority responsible for lake management), and because recurrent nugget effects were observed, in the following, it was decided to analyse the whole -2 mm fraction.

DATA TREATMENT

The results of the diffractometric analyses, i.e. the mineralogical assemblages observed in the -2 mm fractions, have been mapped. For the samples of the inner ring of the lake, the -0.125 mm fractions have also been studied and mapped in the same way. Obviously, no quantitative treatment is possible in this kind of determination. For this reason it has not been considered in the present paper.

As to the chemical analyses, kriging was performed on the analytical values of the major elements and the results mapped.

The analyses for trace elements in the lake sediments were treated using statistic methods and their populations were defined. Correlations, covariances and factor scores were also studied. The samples of the surrounding rock types, though not enough to define clear statistics for each lithological group, are taken into account in the following in order to explain the behaviour of certain metals.

For most of the considered elements, the statistical analysis applied on the samples of the three rings taken as a whole showed that at least one main population exists, sometimes normal, sometimes lognormal. In other instances, two populations have been detected; only in one case no population exists at all. However each ring has also been studied independently, in order to detect whether statistically homogeneous behaviours exists at the different lake levels.

The statistical parameters given in Table 1 concern, for each element, the main population or the population characterised by a higher mean value in the case of two populations of equal importance, for the total sample distributions.

DISCUSSION

In this paragraph only a few elements, exemplifying the main types of behaviour observed, will be discussed. Namely, Zn, for the mobile metals, and W, for the metals related with clastic processes, have been chosen from among the elements typically abundant in the lake basin and displaying sufficiently defined populations. Two other important elements, for the sake of their toxicity, are As and Cd; the former also displays a good statistical behaviour, while the latter is the only studied element

Element	Population	Median (ppm)	Mean (ppm)	St. dev./ Var.coeff.	Anomaly thresholds (ppm)		
					Possible	Probable	Sure
Zn	Lognormal	92.5	87.2	1.5	130.6	195.5	292.7
W	Normal	2.1	2.1	0.8	2.9	3.7	4.5
Pb	Lognormal	56.5	56.5	1.2	68.6	83.4	101.3
Co	Lognormal	16.6	16.6	1.3	21.6	28.	36.2
As	Lognormal	68.4	67.3	1.3	87.7	114.2	148.8
Cu	Lognormal	31.2	30.7	1.5	45.	66.	96.8
Sb	Normal	4.9	5.1	2.	7.1	9.1	11.
Sn	Normal	3.	3.	1.	4.	5.1	6.1
Cd	Lognormal	0.4	0.4	2.2	0.9	1.9	4.1

Table 1. Main statistical parameters for some studied metals. Anomaly thresholds are respectively given by: mean plus 1, 2 and 3 standard deviations (normal); mean by variation coefficient to the 1st, 2nd, and 3rd power.

denoting statistical "disorder". Since samples from the deepest part of the lake, near the dam (situated at the southern tip of the lake, on the right, just north of the big branching) have not been collected, the metal distributions in the vicinity of the dam are mere extrapolations automatically calculated by Inverse Distance Weighted (IDW).

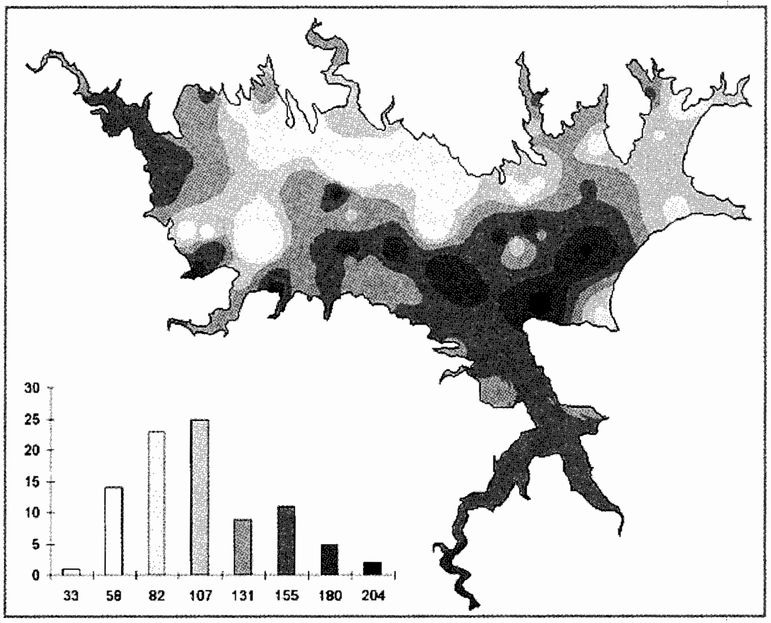

Figure 2. Distribution of Zn according to the frequency classes of its histogram.

Zn clearly exhibits good lognormal behaviour (Table 1), due to its high mobility, which has enabled its almost even distribution, with progressive enrichment in the increasingly deeper parts of the lake (Figure 2). Accordingly, the anomaly maps, referred to the three rings (Figure 3a-b-c) and to the total population (Figure 3d), show that in geographic terms the anomalies match substantially those derived from the treatment of the inner ring data. They appear to occur well away from the main streams, in front of the Lake Flumendosa tunnel outlet and in the vicinity of the dam.

W behaves in a different manner; its total population is normal (Table 1), its distribution shows decreasing values from a few precise sites near the northern shore (Figure 4), and accordingly its anomalies appear more intense in the vicinity of the outlets of some streams rather than in the inner part of the lake (Figure 5 a-b-c-d).

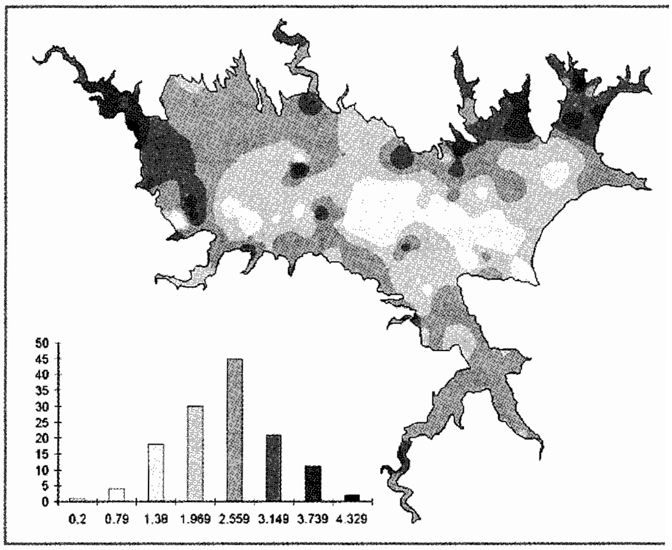

Figura 4. Distribution of W according to the frequency classes of its histogram.

As displays peculiar characteristics; its total population (Table 1, Figure 6a) is lognormal, as for Zn, but its distribution in the sediments rather resembles that of W, because the highest As values, along with the major anomalies, occur near shore; however these values appear to be related to sulphide occurrences in the vicinity of the lake rather than to stream outlets.

As shown by Figure 6b, the total population of Cd does not display any of homogeneity, nor any similarity with the Zn distribution, as was to be expected. However its distribution within the lake has been studied in the same way as the other elements, and at least in the first ring an acceptable lognormal distribution has been observed: this indicated that at least in the deepest sediments a statistical control on Cd deposition exists.

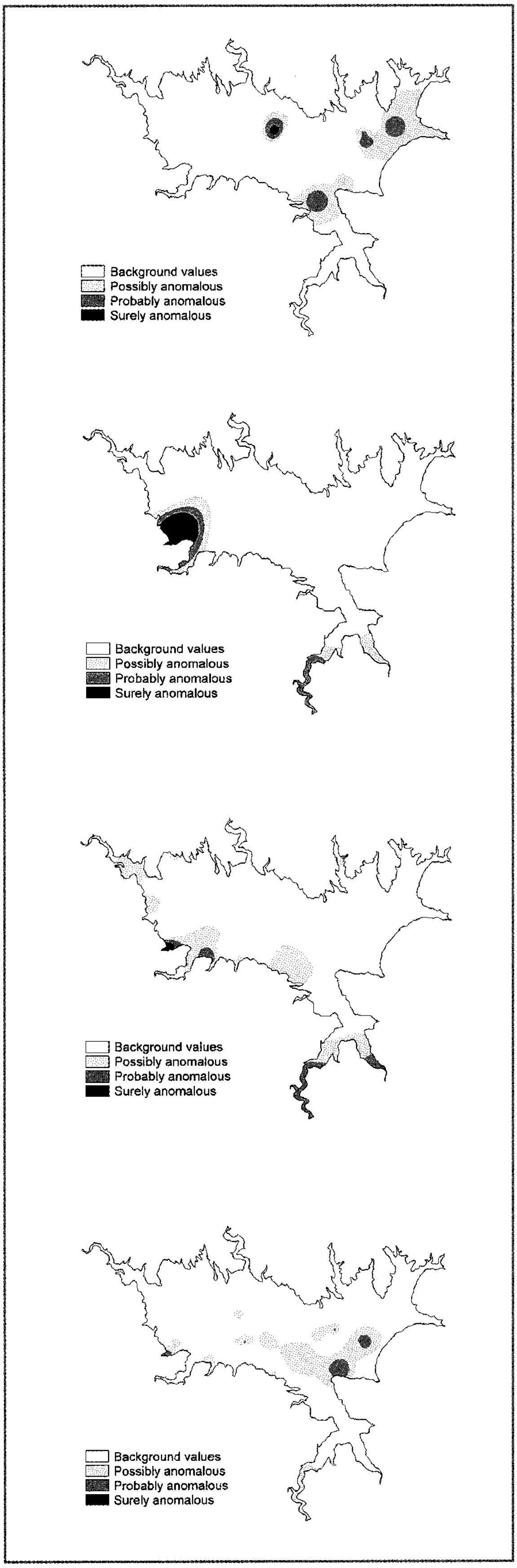

Figure 3. Distribution of Zn according to the anomaly thresholds given in table 1: a) inner ring; b) intermediate ring; c) outer ring; d) total population.

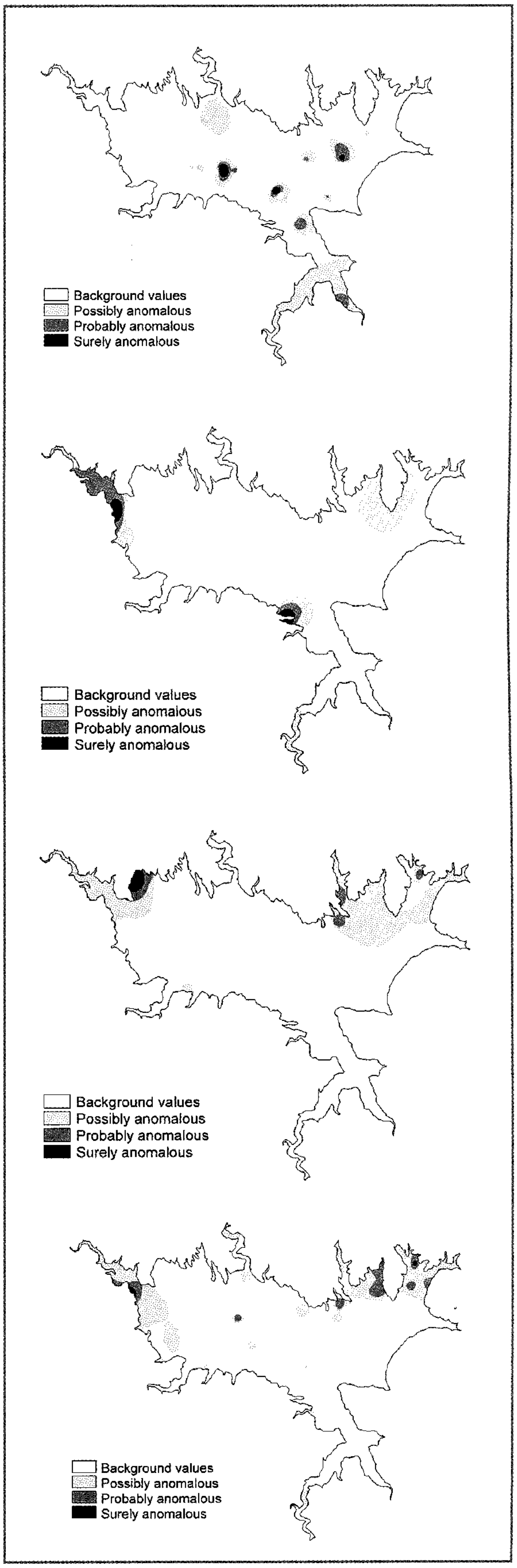

Figure 5. Distribution of W according to the anomaly thresholds given in table 1: a) inner ring; b) intermediate ring; c) outer ring; d) total population.

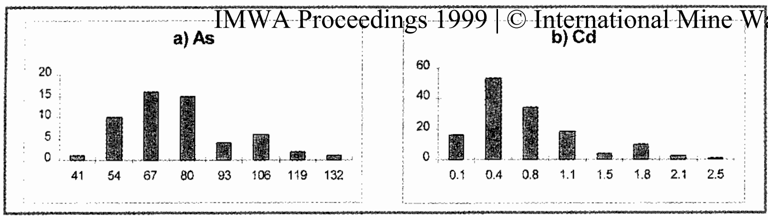

Figure 6. Histograms of the total populations for: a) As; b) Cd

The present study is only concerned with samples of layers not thicker than 20 cm, i.e. the whole sample collected in most sampling stations, situated not very far from the lake shore and prone to cyclical erosion during the flood phases. By contrasting the incisions of the major streams and as one proceeds inward and towards the deeper part of the lake the sediments become increasingly thicker. All this implies that the marginal, thinner sediments consist mostly of newly deposited material, and only grains of heavy and stable minerals are likely to survive alteration, during the dry seasons, and removal, during floods, and by contrast the layers deposited in the central part of the lake and near the dam are continuously covered by fresh material on each flood event.

The above observations explain the relative enrichment in stable heavy minerals, as shown for W, but also true e.g. of Sn, through residual concentration, but does not account for relative enrichment in more mobile metals in the top layer of the deeper sediments. The latter probably only receive the finest fractions of sulphide particles, while larger grains settle in more proximal sediments. Actually, the lesser stability of sulphides is the key to solving this problem.

In the middle, thick sediments of Lake Flumendosa emerged during a recent exceptional lowering of the water level, due to maintenance works at the dam, Fadda et al. (1998) observed an on-going sulphide oxidation, but, when the metal-enriched water squeezed from the sediment reached the higher-pH (about 8) water of the river flowing in its old bed, Fe hydroxide immediately precipitated . The same authors also noticed that the water level variations of the lake were marked on the rocky walls by thin carbonate coatings, so they inferred that buffering of the acid solutions, produced by sulphide oxidation, by the high-pH river water, induced both adsorption of heavy metals on the newly formed Fe hydroxide (Stumm and Morgan, 1970) and reprecipitation of the surviving metallic ions as carbonates. Thus, admitting that similar phenomena also occur in the thinner border sediments, prone each year to oxidation conditions, and not only in Lake Flumendosa but also in Lake Mulargia, whose water, coming mostly from Lake Flumendosa, also has high pH, the following situation emerges.

The sulphide grains deposited in proximal sediments undergo oxidation during the dry season; the smallest grains are totally destroyed and the largest ones dramatically reduced in size; the following flood carries away the rests of sulphide grains along with metal ions, which in turn are reprecipitated as carbonates or adsorbed on Fe hydroxide as soon as, pH reaches a sufficiently high value in the inner part of the lake. In this way, mobile metals -Zn has been indicated, but also Pb, Cu and others, As and Cd included, appear to behave in the same manner- settle mostly in the inner sediments. It is also possible, provided that reducing conditions are reached at least in the deepest part of the thick sediments, that sulphides form from the Fe-hydroxide flocks and the metallic ions adsorbed thereon.

As to the source of the metals, they originate mostly from the Palaeozoic crystalline basement, where both a high geochemical background for several metals (Cd, As, W, and other less important ones) and mineralised concentrations exist. Quaternary basalts also contribute with elements, such as Cr, Ni, and Co, often associated with mafic rocks. For instance, the cited sampling on the Palaeozoic rocks surrounding the lake yelded an arithmetic mean for As of some 260 ppm, which must be considered simply indicative, and surely overestimated, possibly influenced by ore mineral dissemination occurring quite near the lake shore. These disseminations should account for the unevenly distributed concentrations observed in the treatment of the outer ring (Figures 3c and 5c). Treatment of the total populations confirm that these concentrations are sometimes true anomalies (figs. 3d and 5d). The high values observed for W (Figures 4, 5b-c-d) and As, near the stream outlets at the north-western corner, are possibly related with research and exploitation workings, about 1 km upstream, in the W-Sb-As-Au-bearing ore bodies of the disused Genna Ureu mine.

CONCLUSIONS

The distribution patterns discussed, along with those of other elements not shown here, indicate that the cyclic fluctuations in the level of Lake Mulargia have a marked effect on metal distribution in its sediments. As a matter of fact, the rather high heavy metals contents in the lake sediments on first sight would appear to be cause for concern, inasmuch as most of them originate from readily weatherable minerals such as sulphides and the water coming from this lake system is used for drinking water supplies. However the concentrations of heavy metals in the water reaching the treatment plants are normally below the permissible limits for domestic use. Apart from the obvious dilution effect, the cyclic mobilisation-reprecipitation processes suggested by the present study are certainly effective in keeping the soluble metal contents sufficiently low.

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