

# Arsenic contamination of natural origin in stream sediments of Lake Mulargia Reservoir, Southern Sardinia

S.Fadda<sup>1</sup>, M.Fiori<sup>1</sup>, S.M.Grillo<sup>2</sup>, C. Matzuzzi<sup>1</sup>, P. Valera<sup>2</sup>

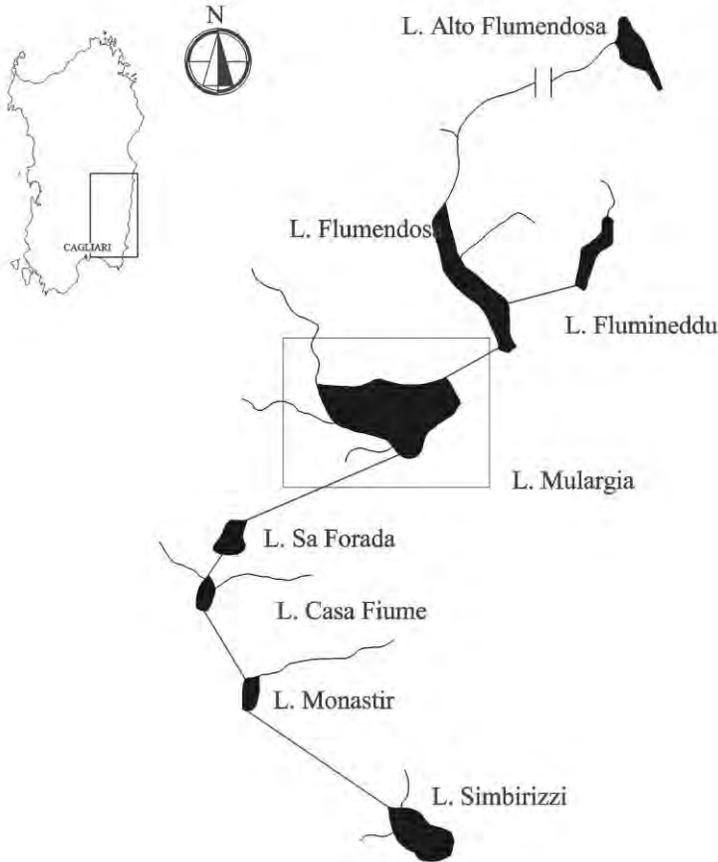
<sup>1</sup>Centro Studi Geominerari e Mineralurgici del CNR - P.za d'Armi, (Ca) Italy

<sup>2</sup>Dipartimento di Geoingegneria e Tecnologie Ambientali -P.za d'Armi, (Ca) Italy

**Abstract.** High As contents have been detected in the stream sediments of Lake Mulargia and in the tributaries draining the basin which carry mineral matter mostly containing Fe, As and Sb sulphides. Systematic sampling has shown the presence of significant amounts of arsenic originating from natural sources alone, as it is supplied by the surrounding mineralised rocks. The seasonal water level fluctuations peculiar of this lake cause oxidation and remobilization of most metals. Arsenic is readily released in the acid waters, but the constantly high-pH of the main body of water causes adsorption and co-precipitation of this element on the abundant newly formed Fe-hydroxides. These trap the As, as the negligible arsenic contents in the lake waters clearly demonstrate.

## Introduction

Lake Mulargia reservoir was completed in 1963. It has a maximum capacity of about 350 Mcu.m, and a roughly triangular shape with a maximum surface area of about 124km<sup>2</sup>. It forms part of the Flumendosa Reservoir system which comprises six interconnected artificial lakes of different size (Fig.1). The entire system supplies almost all of its water to the distribution network located chiefly in the Campidano plain, from the L.Alto Flumendosa to Simbirizzi area (Botti et al.2001). Water levels in the lake are strongly affected by the warm and semiarid climate of the island of Sardinia, characterised by two short rainy periods and a long dry season lasting at least six months, during which extensive lake bottom areas gradually become exposed all along the lake edges.



**Fig. 1.** Sketch maps of the Flumendosa-Campidano reservoir system.

The lake system is over dimensioned because multi annual cycles overlap seasonal wet and dry spells with alternating wet and longer drought periods. As a consequence, water levels in these lakes are prone to wide variations and the bottom sediments are cyclically exposed. As the water stored in the reservoir is used for agricultural and municipal purposes the consequent As release in solution may constitute a public health hazard.

During the exceptional drought of the late eighties (Botti et al.2001, Fig.2), samples were collected in the deepest part of the lake, at its edges and in the now submerged drainage framework which has been reconstructed with the aid of old maps of the area before the artificial basin was inundated. The analytical data from more than 200 samples have been statistically treated and processed with a GIS to create maps showing the As distributions and to highlight those areas of arsenic dispersion and accumulation. Observation of the maps reveals that the terrains containing As-bearing minerals are probably the neighbouring outcropping rocks

where the pyrite-arsenopyrite association is frequently observed in the ore bodies containing prevalently Fe, As and Sb sulphides.

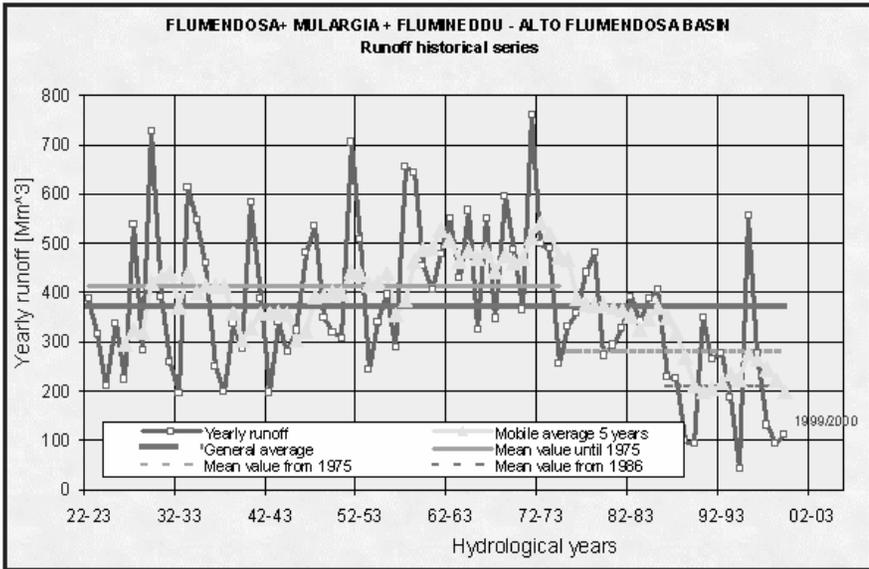
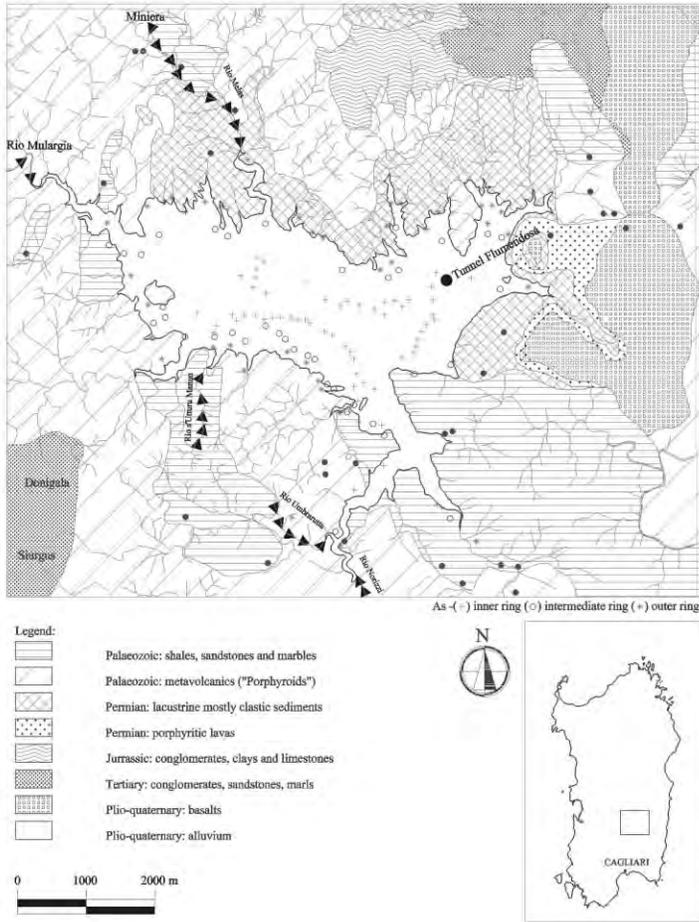


Fig. 2. Runoff historical series starting from 1922. The driest six-years in the last decade.

## Geological context

The geology of the area around Lake Mulargia includes a Palaeozoic crystalline basement overlain by younger sediments and volcanic rocks (Fig.3). The lower to middle Palaeozoic basement (Carmignani 1982) comprises predominantly clastic meta sediments, mostly shales and meta sandstones with marble lenses, and acid meta volcanic rocks, "porphyroids". These are covered by lacustrine sediments of Permian age, mainly conglomerates to siltstones, overlain by porphyritic rocks. The series crops out along the northern and eastern sides of the lake (Marcello 1961). On the northern side rests the transgressive Jurassic series, including a quartzose conglomerate passing to sandstone and clay and finally to carbonate beds. Again on the northern flank of the lake is a new continental phase, represented by Eocene conglomerates. The Miocene transgression is represented by platform limestones and marls (western side), while the last continental phase (Pliocene to present) is represented by alluvium (northern side) and flood basalts (eastern side).

The terrains in the drainage basin include complexes hosting heavy-metal bearing mineralizations, mostly base metal sulphides accompanied by hydrothermal alteration. These sulphides may be the principal arsenic bearing minerals in the source rocks.



**Fig. 3.** Geological sketch map of terrains surrounding the lake Mulargia and schematic maps showing the sampling patterns 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" sample (third or outer ring). Dots represent the sampling sites in the rocks surrounding the lake.

Within the Palaeozoic rocks, the most important supply source is the disused Genna Ureu mine, where Fe, As, Sb and W minerals occur with minor Cu, Au, Ag, Bi, Ni and Co contents. This mine and the surrounding meta volcanic rocks ("porphyroids") are situated in the Rio Mulargia drainage basin, which enters the lake at the western corner. Other small manifestations consist of pyrite lenses and disseminations, occurring all around the lake's perimeter, in particular in the Rio Norizzi basin, with a drainage area of about 15km<sup>2</sup> and drained by minor tributaries flowing into the southern corner of the lake. Besides the mine pits, trenches, galleries, small mining explorations, unexplored mineralized outcrops and numer-

ous mine waste dumps, another anthropogenic factor comes into play: Lake Mulargia receives water from Lake Flumendosa through a tunnel (Fadda 1996), situated near the eastern end on the northern side. The Flumendosa reservoir drains a much wider basin where several mixed-sulphides ore bodies occur, including a disused mine within the lake itself (Fig.3).

### Sampling, analysis and data treatment

A total of 140 points were sampled and more than 200 samples collected. The bottom sediments were collected in 1990 in the deepest part of the lake and in 1991 in the outer parts. Three "rings" were sampled: the first in the central bottom area, following the tributaries draining into the lake based on old maps indicating the submerged drainage pattern. The second concerned the intermediate zone and the third the stream sediments along the lake's edge at its maximum level. Inter-stream, exclusively lacustrine sediments were also collected (Fig.3). In addition to the lake sediments, samples of rock were taken from the main rock facies around the lake in order to ascertain the influence of the surrounding terrains on the sediments' metal content.

Analyses were performed on the upper part (20cm) of all the samples weighing on average around 300 g, dried then split into two. One half was split again and this quarter was sieved to -2mm and prepared for As determination. Chemical analysis were carried out with ICP-MS after solubilization by mixed acid attack performed in a fully automatic microwave oven.

Chemical determinations for As in the sediments were treated using statistical methods so as to detect the existence of any homogeneous populations and then determine their statistical parameters. The results concerning the kind of the studied populations were first verified through the Henry's line test, then the population parameters calculated (Table 1).

**Table 1.** Main statistical parameters for As. Anomaly thresholds are given, for a normal population by: means plus 1,2 and 3 standard deviations. (As limit thresholds of intervention for stream sediments fixed by regulation of Canada: 33 ppm and Holland: 55 ppm).

Element	Mean value m(ppm)	Standard Deviation s(ppm)	Anomaly thresholds		
			possible	probable	sure
As-inner	19.00	9.20	28.20	37.40	46.60
As-intermediate	19.30	1.23	20.53	21.76	22.99
As-outer	73.70	1.23	74.93	76.16	77.39
As-population	67.36	1.30	68.66	69.96	71.26

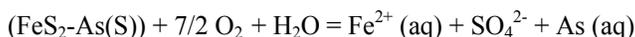
### Discussion and conclusions

The geogenic sources of arsenic can be traced to the geological formations of the drainage basin which have a high natural geochemical background of heavy met-

als and where arsenic bearing ores occur, thus producing sites with considerable contamination potential. Samples of the Palaeozoic rocks cropping out around the lake yielded an arithmetic mean of about 250 ppm for As which is simply indicative and over-estimated as it is affected by the ore mineral disseminations occurring quite near the lake shore. The highest As values along with the major anomalies were in fact observed near the shore and appeared to be related to sulphide occurrences in the vicinity of the lake. The high values observed near the stream inlets in the north-western corner ( Rio Mulargia, Rio Melas) are related with research and mining explorations about 1km upstream in the W-Sb-As-Au bearing ore body of the disused Genna Ureu mine. As values as high as 100 ppm have been detected in the southern corner of the lake at the inlet of the Rio Norizzi where the Rio Umbrarutta and Rio S'Utturu Mannu also drain into the lake (Fiori et al.2001).

In Italy there is no legislation regulating metal concentrations in stream sediments so the limits established for arsenic by Canada (Canadian Council of Ministers of Environment, CCME 1995) and Holland (data from Italian Ministry of the Environment) regulations have been considered here. The background level for an element, obtained from classic statistical techniques, is the mean value plus the coefficient of variation for the normal population and should represent the upper limit for a value that is certainly not anomalous. Thus a comparison of this value with risk parameters should give an idea of the environmental situation in a given area. The As background level of 68 ppm (Table 1) in the near-shore samples (third or outer ring ) is higher than the Canadian and Dutch limits. However, far higher As concentrations have been detected locally, for instance 129 and 192 ppm in the Norizzi basin (S.M.Grillo et al. 2001), and these can be regarded at risk level. Fig.4 shows As anomaly maps constructed using the statistical parameters given in Table 1. The peculiar characteristics of arsenic concentrations can be clearly observed, the highest values, along with the major anomalies, occurring in the outer sampling ring which comprises both the stream inlets and sulphide occurrences fairly near to the edge of the lake at its maximum level. The maps also clearly show that, regarding bottom area and middle lake sampling, large portions of the lake yielded As contents consistently lower than the risk level.

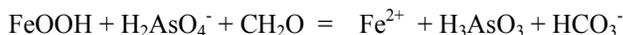
Arsenic minerals in the mineralization and disseminations are represented by mixed sulphides and the pyrite-arsenopyrite ( $\text{FeS}_2\text{-As(S)}$ ) association is frequently observed. These may be considered to be the chief As-carrier minerals in the source rocks while the nature of the As carrier phases in the derived residual soils and stream sediments is under study. When subjected to weathering these sulphides can release soluble arsenic into natural waters



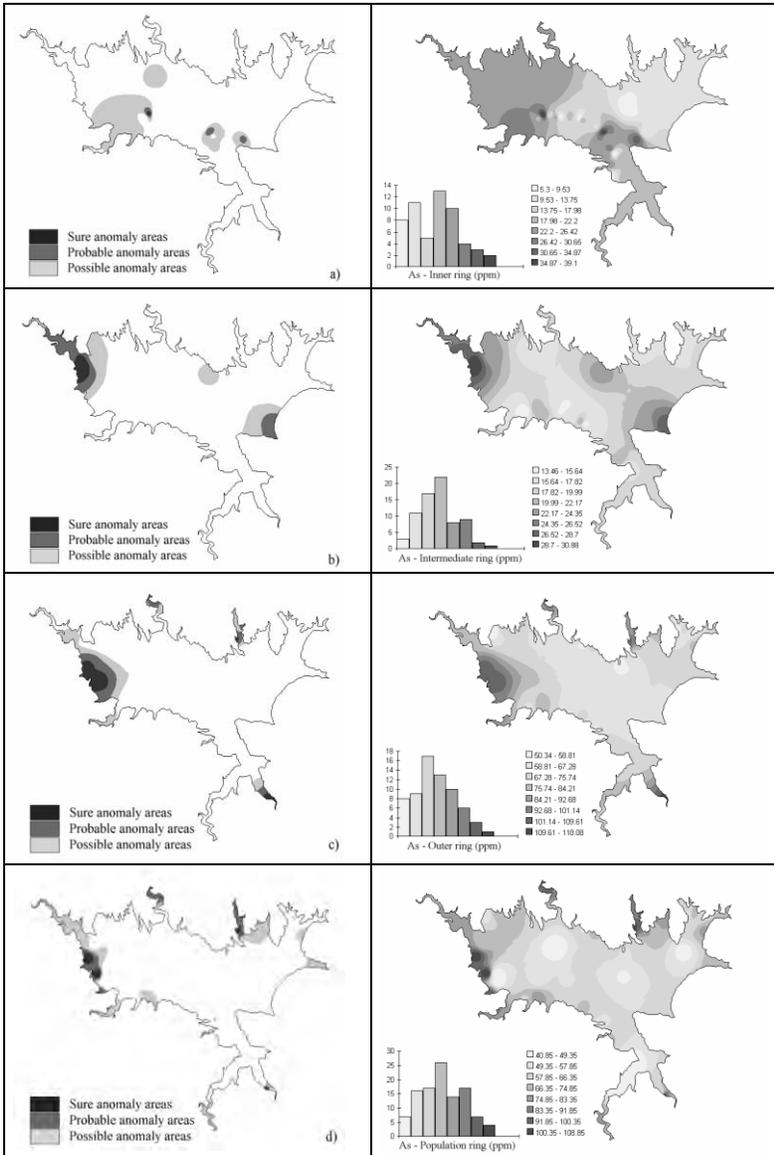
where arsenic forms no single cations but reacts readily to inorganic acids. During transportation the dissolved predominant arsenic species are in the higher (+V) oxidation states and are very effectively adsorbed onto ferric oxide-hydroxide goethite ( $\text{FeOOH}+\text{H}_2\text{AsO}_4^-$ ), manganese oxides or hydroxides as well as onto clay minerals and organic matter. Its behaviour appears to be mainly controlled by

these sorption processes even if a slow release may be possible and can be related to pH increase in the aqueous phase.

It is quite likely that at least a part of the original readily weatherable sulphides still persist in the stream sediments. The grains deposited in proximal sediments may undergo oxidation during the dry season; the smaller grains are totally destroyed and the largest ones reduced in size. Floodwaters carry away the rest of the sulphide grains along with As oxyanions which in turn are adsorbed or co-precipitated onto Fe hydroxide as pH reaches a sufficiently high value settling in the inner sediments. Furthermore, during recurrent drought, when precipitation is not sufficient to completely fill the lake and water deliveries empty it almost entirely, most of the bottom sediments undergo alternate phases of dryness and are reworked by the incipient river flows after the first heavy rains. The supply of new material includes anthropogenic organic matter contained in the largely domestic wastewater discharged by several villages in the main valleys. Another contribution to organic matter derives from the agricultural and pastoral activity in the vicinity of the lake, in the tributary valleys and in those parts of the lake bottom regularly exposed during the dry season. It is possible, provided that reducing conditions are attained in the deepest part of the thick sediments, that sulphides form from the Fe-hydroxide flocks and the metal ions adsorbed thereon. In other words, once deposited the arsenic may undergo reduction by organic carbon in the deeper parts of the bottom sediments with dissolution of arseniferous iron-oxhydroxide, formation of new sulphides and soluble arsenic mainly as neutral  $\text{H}_3\text{AsO}_3$  complex which in turn may undergo exchange processes (Sahu 2001)



Though the cyclic filling-emptying of the lake favours the mobilization of arsenic and other elements into acid solutions, the constantly high pH (always above 8) of the main body of water in the lake prevents the elements remaining in solution (Fiori 1999). Arsenic trapping can be correlated with the rapid precipitation of abundant iron oxyhydroxides and hydroxides-sulphates for which this metalloid has a strong sorptive affinity as is well known in water treatment plants. This leads to the immobilization of most arsenic in sediments settling near the shore lines and the inlets of the tributaries as is also indicated by the decreasing concentration of this contaminant towards the lake bottom. However, small quantities of As may also be released locally under anoxic conditions in the deepest parts of the lake. Apart from the obvious dilution effect, the cyclic mobilisation-precipitation processes are certainly effective in keeping the soluble As sufficiently low as is clearly demonstrated by its negligible contents in the waters of this lake.



**Fig. 4.** On the left distribution of As according to the anomaly thresholds given in table 1. On the right distribution of As according to the frequency classes of his histograms relative to the three samples collection. (a - inner ring; b - intermediate ring; c - outer ring; d - total population).

## Acknowledgements

This study was supported by the Centro Studi Geominerari e Mineralurgici del CNR, Facoltà di Ingegneria, Piazza d'Armi, 09123 Cagliari, Italy

## References

- Botti P., Dessena M.A., Fiori M., Grillo S.M., Marcello A., Matzuzzi C., Pretti S., Vacca S. (2001). "The Medio Flumendosa Reservoir". Field Trip Guide of the "Tenth International Symposium on Water-Rock Interaction": 1-20
- Carmignani L., Cocozza T., Ghezzi C., Pertusati P.C. & Ricci C.A. (1982) "Lineamenti del basamento Sardo. Guida alla Geologia del Paleozoico Sardo". Soc. Geol. It., 11-23
- Fadda S., Fiori M., Grillo S.M., Manca M.G., Marcello A., Matzuzzi C., Pretti S. (1996) "Influenza della vecchia attività mineraria nel bacino del Lago Flumendosa e sui contenuti di metallo nei sedimenti del Lago Mulargia" Atti del Congresso Internazionale per il Centenario dell'Associazione Mineraria Sarda 1896-1996, 137-149
- Fiori M., Grillo S.M., Manca M.G., Marcello A., Matzuzzi C., Pretti S. (1999) "Spatial distribution patterns of heavy metals in lake bottom sediments: an example from the Mulargia reservoir (Italy)" Proceedings of the Mine, Water & Environment, International Congress, 157-162
- Fiori M., Grillo S.M., Marcello A., Pinna D., Pretti S. (2001) "Heavy metal pollution of natural origin in the Rio Norizzi basin (Southwestern Sardinia, Italy). The As aspect". Proceedings of the Tenth International Symposium on Water-Rock Interaction: 1091-1094
- Marcello A. (1961) "Il bacino Permico del Rio Mulargia (medio Flumendosa) e le sue successive modificazioni geologiche". Ph-th, 1-39
- Sahu S.J., Roy S., Jana J., Nath B., Bhattacharya R., Chatterjee D., Dey Dalal S.S. (2001) "Water chemistry and sediment-water interaction responsible for mobilization of arsenic in groundwater in Bengal delta plain ". Proceedings of Tenth International Symposium on Water-Rock Interaction: 1139-1142.