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Chemical and Ecotoxicological Characterization of Averno Lake

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The scope of present paper is to carry out a model study on the lake Averno, a nearly water closed basin polluted by waste waters of nearby communities and by agricultural activities. Lake Averno is a natural basin in the Phlegrean Fields region about 15 km west of Naples (Italy). This lake was formed as a consequence of the collapsing of a large volcano, named Archiflegreo, which was active until historic times. The area around Phlegrean Fields presents signs of thermo-mineral spring streams (at Bagnoli, Pozzuoli and Lucrino) and natural (at Averno and Fusaro) spring streams (Martini et al. 1991; Celico et al. 1992). The water flows into Lake Averno at an average rate of 42 dm^3/s during the rainy seasons and almost zero in the summer months. The water basin is nearly elliptic (1000 m long and 700 m wide), covering a 0.54 km^2 surface, and is 34 m deep at the center, with a total water volume of roughly 6×10^6 m^3. A canal which is almost 1 km long links the lake to the sea, carrying both spring and rain waters to the Lucrino coast in the Gulf of Pozzuoli (Cortini and Scandone 1987). Discharge into the sea through this canal or sedimentation onto the floor are the sole fates of lake pollutants. Lake Averno is heavily polluted by the urban waste waters from overflows of the collector that carries residual waters into the Cuma Plant.

The concentration of toxic metals, polycyclic aromatic hydrocarbons (PAHs), and polychlorobiphenyls (PCBs) were determined in water and sediments in the preliminary stadium in November. The data were analyzed to determine the *total concentration* of inorganic and organic material in order to evaluate the capacity and possibly the mechanism (if there is one) of self purification of the lake.

Here we present the type and quantities of polluting materials introduced in the lake Averno, as well as its state of health. This represents the first stage of deeper study on the lake's natural rate of purification. A further goal may concern restoration measures to restore the lake to its natural conditions.

MATERIALS AND METHODS

The sampling of waters and sediments was initiated in November 1998 at 11 stations (fig. 1), using a Petersen grab for the sediments and a *home made* device for sampling water at different depths. Two different organisms were collected to study the bioaccumulation of pollutants present in the lake water: *Mugil cephalus* (grey mullet), and *Sicyonia sculpta*, a prawn living in the discharge canal.

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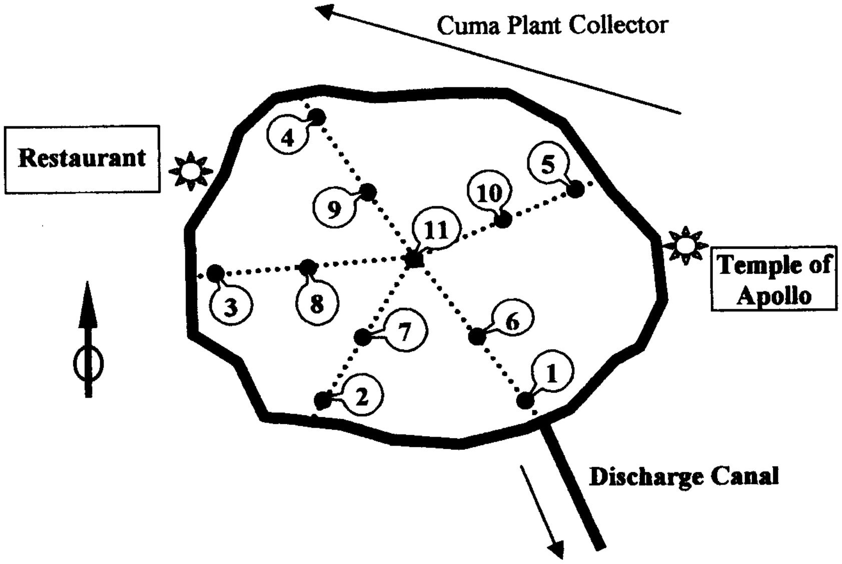

Figure 1. Lake Averno (a map) showing the sampling stations which are defined by angular coordinates with respect to reference points on the coast.

Water parameters were determined following the classical and instrumental techniques used in analytical chemistry. In all water samples, pH and temperature were measured *in loco*. Chlorides, ammonia and phosphates were determined following the Standard Methods for the examination of water and wastewater (APHA, AWWA, WPCF 1998). The water samples were acidified with HNO_3 1.0% (v/v) and filtered through 0.46 μm membrane filter before the instrumental analysis.

Sediments were dried at air temperature and then separated with a 870 μm sieve, so that the gravel is removed, but not the finer-grained fractions. The organic material content was determined on dried sediments by thermography by evaluating the percent loss of weight.

Two different methods were used to dissolve weakly bound metals present in the sediments: one by means of 1 M (Solomons and Förstner 1995) ammonium acetate that removes only the most weakly bound metals (bioavailable fraction) by complexation through acetate ions at neutral pH; a second by 0,1 M HCl (Nolting Rob F and v Hoogstraten 1991) that extracts the metal fraction of "anthropogenic" origin.

About 0.4 g of dry sediment were stirred for 24 hr at room temperature in 100 mL of 1 M suprapure ammonium acetate and 200 mL of suprapure 0.1 M HCl respectively. The solutions thus obtained were filtered and brought to 100 and 250 mL respectively using the same solvents. These solutions were used to determine the concentrations of metals.

The biological material (organs and tissues of *Mugil cephalus* and the entire *Sicyonia sculpta*) were dried at 105 °C, to obtain the dry weight, and then they were heated at 520 °C. The ashes were then dissolved in 5 M suprapure HCl and brought to 100 mL with twice-distilled water to measure the concentrations of toxic metals (Van Loon 1985).

Zinc, copper, cadmium and lead total concentrations in the samples obtained from sediments, tissues and water were determined by means of Metrohm polarograph (746 VA Trace Analyser with a 747 VA Stand) using the anodic stripping method, for the highest sensibility (high sensibility is necessary to detect the small amounts involved). The following parameters were used: reduction potential -1.2 V vs. a 3M KCl/AgCl/Ag reference electrode; electrolysis time 90 sec. Iron, chromium, manganese and magnesium determinations were performed by FA/AAS with a VARIAN mod. SpectrAA 220 Atomic Absorption Spectrometer equipped with a deuterium background corrector, using acetylene and air as fuel and oxidant respectively. All glassware and plastic bottles used for sample treatment and storage were rinsed with 10% (v/v) HNO_3 and twice-distilled water before use.

Analyses of organic compounds extracted from sediments were performed following standard methods. Dry sediments were extracted with organic solvents using a slightly modified EPA method (US-EPA (a) 1997). The Kumagawa extractor was employed in which the solid is continuously extracted at the solvent boiling temperature. The hexane-acetone solvent mixture gives better performances when recovering analytes and proves environment friendly. This solvent in fact has lower disposal costs and lower toxicity with respect to organochlorides and other solvents (US-EPA (b) 1997). In addition, the use of hexane-acetone generally decreases the amount of interfering products extracted and improves the signal-to-noise ratio, compared to methylene chloride-acetone mixture (US-EPA (b) 1997). All glassware was accurately rinsed following EPA recommendations to avoid sample contamination. No plastic materials was used avowing to pollution from phthalic esters (US-EPA (c) 1997; IRSA-CNR 1994; APHA, AWWA, WPCF 1998).

Usually 3-5 g of sediment were extracted overnight (at more than one reflux per minute) with 200 mL of acetone-hexane mixture. The solution was reduced to a few mL volume under vacuum on a Rotavapor-EL, Büchi, and then purified from sulfur and ester contents by passing over a Florisil septum (US-EPA (a) 1997; US-EPA (b) 1997; US-EPA (c) 1997; IRSA-CNR 1994) and analyzed by GC. Extracts were stored at –20°C in the dark and analyzed within three days from the extraction.

The PAHs were analyzed with HPLC using a HP chromatograph equipped with a C-18 column and a mixture of water-acetonitrile as eluent solution. A standard mixture of the most diffuse PAHs was used for calibration. Polychlorinated biphenyls were analyzed alternatively at a Carlo Erba and a Varian GC with a ZB5 column (30 m; 0,32 mm ID; 0,25 μm thin layer film thickness) equipped with an

ECD detector. The oven temperature ranged between 120-300°C (10 min at 120°C; 12°C/min up to 300°C; 15 min at 300°C). Gas flux: 3 mL/min.

The mixture of PCB standards, furnished by Labservice-Italy, consisted of components of different chloride contents in order to obtain a chromatographic window representative of the main mixtures used in Europe.
All the reagents used to check the organic micropollutants were "pesticide grade". Standard solutions of cadmium, copper, lead, manganese, chromium, iron and zinc were prepared by dissolving 1.000 g of each pure metal in a minimum volume of solving concentrated suprapure acid and diluting to 1 L to give 1,000 mg/L concentration of metallic ions. These standard solutions were then employed to prepare reference solutions at varying concentrations. All the dilutions were performed using twice-distilled water whose conductivity was lower than 0.1 μS and had been prepared in our laboratory by means of a Continental Equipment bidistillator, Mod. Still 3/B.

Five samples of sediment and five of biological specimens, chosen randomly among those withdrawn from the lake, were spiked with a mixture of metal soluble salts and with standard mixtures of PAH and PCB, in such quantities to nearly double the original concentration of metals in the samples and the concentration sum of PAH and PCB in all stations. A procedure of extraction for sediments and mineralization for biological specimens was then performed both on the spiked and the original samples in order to carry out the quality control by recovery measurements.

The quality control procedures have shown an average recovery ranging from a minimum of 84% for Cd in biological specimens to a maximum of 97% for Cu and of 85% for PAH and PCB in five samples of sediments, suggesting that the procedures adopted are adequate and the results obtained are reliable.

RESULTS AND DISCUSSION

Table 1. Surface water parameters ± SD.

Temperature (°C)	20.0±0.3
pH at 20°C	8.11±0.01
Conductivity (μS cm^{-1})	2,635±10
Residue at 180°C (g/L)	1.975±0.006
Alkalinity (mg/L HCO_3^-)	372±6
Hardness (°F)	11.7±0.5
Ammonia (mg/L)	0.25±0.02
Phosphate (mg/L P)	1.75±0.55
Chloride (mg/L Cl^-)	580±6
O_2 (mg/L)	7.6±0.4

Table 1 reports the values of the main parameters of surface water samples. The values are averaged on the data collected in 11 different stations. They appear homogeneous in all the stations and show an alkaline pH, the presence of ammonia and minor quantities of chloride, which is indicative of a probable mixing of spring waters with sea waters. Moreover, a high concentration of phosphate was found, indicating an hyper-eutrophication in the lake (OECD 1982).

Table 2. Values of the main parameters of waters sampled at stations 9 and 11 at different depths.

Station	Depth (m)	pH at 20°C	Conductivity (μS cm^{-1})	Alkalinity (mg/L HCO_3^-)	Hardness (°F)	Chloride (mg/L Cl^-)	O_2 (mg/L)
9	0	8.10	2,625	378	11.6	568	7.8
	10	8.04	2,270	372	12.0	564	2.5
	28	7.07	2,960	618	18.8	794	0.0
	34	7.20	3,192	725	21.4	856	0.0
11	0	8.10	2,630	378	11.8	579	7.7
	10	8.02	2,200	348	11.6	540	2.3
	28	7.05	2,934	616	18.7	788	0.0
	34	7.34	3,174	720	21.3	848	0.0

Table 2 reports the values of the same parameters (except for ammonia and phosphate) found in samples of water in stations 9 and 11 at different depths. A careful inspection of these data clearly indicate that a change occurs in the composition of lake water between the depths of 10 m and 28 m.

In fact, the pH values decrease by nearly 1 unit, the conductivity increases by more than 1/3, alkalinity, hardness and chloride almost double. A similar trend was observed at the other stations. Taking into account the conic shape of the lake basin with the steep slope of coast and a very limited communication channel with the sea, these results point to water stratification in the lake, with a slow renewal of lake waters on the surface and lower bottom stagnation where a possible contribution from underground marine infiltration could be present (Celico et al 1991).

The lower pH found on the lake bottom suggests the probable presence of acidic gases (CO_2 and SO_2) caused by emissions of volcanic origin.

Heavy metal concentrations in surface waters are very low in relation to the higher values in deep waters (table 3). This is not surprising given the higher pH value in surface water and the presence of sediments and gaseous emissions of volcanic origin in the bottom of lake.

Table 3. Concentrations values of toxic metals in surface and deep waters (μg/L).

	Zn	Cu	Cd	Pb
Surface waters	5.1	0.1	0.1	0.1
Deep waters	30.1	4.9	1.0	120.0

Table 4. Heavy metal concentrations of sediments lixiviated with 0.1 M HCl or 0.1 M ammonium acetate (mg/kg).

	Station	2	3	4	5	6	7	8	9	10	11	Mean±SD
Zn	HCl	325	284	441	405	61.8	61.2	41.1	93.1	70.0	330	211±160
	Acetate	9.0	19.8	15.0	7.8	5.4	10.0	13.4	11.7	12.2	12.8	11.7±4.0
Cu	HCl	64.7	103	123	131	75.9	65.8	65.0	63.9	48.9	73.9	81.5±27.7
	Acetate	1.2	0.8	2.3	4.8	1.6	1.0	1.8	0.2	1.9	2.1	1.8±1.2
Pb	HCl	25.2	75.6	50.7	68.2	65.9	69.5	72.7	66.4	58.8	54.4	60.7±14.8
	Acetate	9.1	11.6	9.4	9.3	6.8	16.4	12.7	13.4	13.1	13.7	11.5±2.9
Cr	HCl	19.3	25.0	26.2	58.1	53.2	64.1	62.6	83.2	89.9	95.7	57.7±27.4
	Acetate	4.1	7.4	6.3	5.2	7.6	7.4	8.0	8.0	7.8	8.7	7.1±1.4
Mn	HCl	312	422	401	255	713	677	638	743	645	733	554±186
	Acetate	5.1	5.2	6.6	3.4	6.8	6.4	4.4	6.8	9.0	7.0	6.1±1.6
Cd	HCl	0.08	0.34	0.29	0.34	0.32	0.40	0.33	0.34	0.40	0.35	0.32±0.09
	Acetate	0.09	0.10	0.13	0.17	0.16	0.17	0.17	0.14	0.22	0.24	0.16±0.05
Fe	HCl	1,001	3,430	2,835	2,445	2,073	1,896	2,058	2,051	2,243	1,886	2,192±638
	Acetate	121	254	138	132	169	182	200	83.1	n.d.	154	159±50
Mg	HCl	4,175	8,668	5,404	5,320	6,250	6,567	6,495	6,758	6,440	9,136	6,521±1,482
	Acetate	1,230	1,601	1,185	746	1,264	1,245	1,281	1,415	2,407	1,333	1,371±423

The organic material content in dry sediments is definitely large, ranging from 19.3% to 28.3% (w/w). These values suggest organic pollution linked to the overspill of waste waters from the collector of the Cuma Plant and in a lower measure to the illegal disposal of waste water from the buildings around the lake. On the other hand, the anoxic conditions (0.0 mg/L of O_2) in the bottom of lake prevent a fast oxidation of organic substances with accumulation with the time.

Table 4 shows the metal concentrations in sediments as extracted with 0.1 M CH_3COONH_4 and with 0.1 M HCl. In this and other tables data from Station 1 are not reported since at this site, where water is shallower and is characterized by a higher flow, there is no sediment but only stones.

An increase in cadmium, lead and chromium concentrations in the extracts with 0.1 M CH_3COONH_4 is evident when moving from the coast towards the center of lake. A similar trend is observed for chromium and manganese, but not for other metals extracted from sediments with 0.1 M HCl. On the contrary, higher concentrations of zinc and copper are measured using 0.1 M HCl as extractant in stations 2, 3, 4 and 5. A possible explanation of the different metal distribution can be attributed to a different source for them, namely the atmospheric fall-out and the contribution of waste waters for all the metals. For Zn and Cu, in particular, there is a further contribution due to the run-off of agricultural terraces located near stations 4 and 5 in which fungicides as $CuSO_4$ and $ZnCl_2$ were largely used.

It is important to consider that the concentrations of metal ions extracted from the sediments, are nearly equal (Cd) or even larger (Pb, Zn) than those found in solid sediments of non-contaminated sites (Cd 0.3-4 mg/Kg, Pb 20-56 mg/Kg, Zn 66-160 mg/kg) (Bona et al. 1997).
These data, representing only a fraction of metals present in the sediments, indicate that the lake sediments are severely polluted by human activities with a non-negligible risk to release, under particular conditions, in the aquatic system , toxic metals at concentration levels which are comparable to those defined toxic in the sediments of fresh waters.

Table 5. PAH concentrations in sediments from different stations (mg/kg).

Station	*N*	*F*	*AN*	*P*	*A*	*Fluo*	*Pyr*	*BaP*	*DahA*
2	<0.01	0.17	0.33	0.19	0.01	0.37	0.20	0.35	0.55
3	<0.01	0.16	0.47	0.12	0.01	0.21	0.06	0.41	<0.01
4	<0.01	0.15	0.40	0.12	<0.01	0.27	<0.01	0.42	<0.01
5	<0.01	0.15	0.24	0.07	<0.01	<0.01	1.73	0.07	<0.01
6	<0.01	0.25	0.30	0.11	<0.01	0.30	0.26	0	<0.01
7	<0.01	0.24	0.37	0.16	<0.01	0.15	0.19	0.70	<0.01
8	<0.01	0.22	0.35	0.23	<0.01	<0.01	<0.01	0.66	<0.01
9	<0.01	0.40	0.34	0.23	<0.01	0.31	0.20	0.88	<0.01
10	<0.01	0.14	0.31	0.13	<0.01	0.31	0.20	0.71	<0.01
11	<0.01	0.18	0.35	0.13	<0.01	0.31	0.41	0.79	<0.01

(Naphthalene = N; Fluorene = F; Acenaphthene = AN; Phenanthrene = P; Anthracene = A; Fluoranthene = Fluo; Pyrene = Pyr; Benzo(a)pyrene = BaP; Dibenzo(a,h)anthracene = DahA)

Table 6. PCB concentrations in sediments from the various stations (mg/kg).

	Sites									
PCB	2	3	4	5	6	7	8	9	10	11
2,4,4'	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2,2',5,5'	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.24	0.24	<0.01	<0.01
2,2',4,5,5'	0.22	0.08	0.20	0.12	<0.01	0.18	0.24	0.14	0.14	0.18
2,2',3,4,4'5'	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.16	0.15	<0.01	0.05
2,2',4,4',5,5'	<0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2,2',3,4,4',5,5'	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

The PAH and PCB concentrations in the various stations are reported in table 5 and 6.

PAH and PCB are very toxic substances produced by anthropogenic activities, their concentration in sediments gives an important indication on the site health.

In general, the sum of the concentrations of all the PAHs is always higher than 1 mg/kg, which is the limiting concentration imposed by the Italian legislation for the use of dredging sludge in building works (Departmental Order of Environment Ministry 1998). The main PAHs are acenaphthene and benzo(a)pyrene, two major carcinogenic pollutants whose presence must be considered highly dangerous.

Similar results were obtained for PCB: the sum of PCB concentrations in all the stations (with the exclusion of station 6) is always higher than 10 times the limit established by the Italian legislation (0.01mg/kg) for the utilization of dredging sludge in building works.

Table 7. Bioconcentration factors of heavy metals with respect to lake waters.

Metals→ *Organisms↓*	*Cu*	*Cd*	*Pb*
Mullet liver	3.2×10^{6}	1.2×10^{4}	9.1×10^{3}
Mullet, other organs	$1,5\div7,4\times10^{5}$	$4\div14\times10^{3}$	$1\div20\times10^{3}$
Sicyonia sculpta	2.9×10^{6}	0.5×10^{3}	5.1×10^{4}

On the basis of heavy metal concentrations found in surface lake waters (Table 3) the bioconcentration factors (organism/water concentrations ratio) for the two examined organisms were calculated (table 7).

The toxic metals cadmium and lead are accumulated differently by mullets and prawns, with a higher bioaccumulation of cadmium in the former and of lead in the latter. The high value of copper bioconcentration factor found in *Sicyonia sculpta* may be a consequence of the presence in this organism of hemocianine as a respiratory pigment.

The results obtained from Lake Averno indicate serious organic and severe toxic metal pollution. The origin of this type of pollution can be traced back to the water run-off from the adjacent agricultural fields, to the particles present in exhaust gases from cars travelling on the roads nearby and particularly to the overspilling of waste waters and to illegal disposal of various material in the lake. Only a negligible part of the toxic metal pollution is due to the scarce volcanic activities present on the bottom of lake. As a consequence of its morphology and the poor water supply the lake is characterized by a very scarce dilution and turnover. The current situation is creating serious concern because of the irreversibility of the pollution process.

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