ENVIRONMENTAL PROBLEMS RELATED TO OLD MINING AND NEW INDUSTRIAL SETTLEMENT

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ABSTRACT

The paper concerns the environmental pollution of the Boi-Cerbus basin (quite a lagoon), near the industrial settlement of Portovesme, situated in the East Coast of Sardinia - Italy, close to old mines and metallurgical plants. As a consequence of industrial and mine tailings contribution (from recent and old plants) from the surrounding regions, a pollution of heavy metals has been revealed (Massoli Novelli and Mocci Demartis, 1989).

Chemical analyses of samples collected in the Boi-Cerbus basin evidence in particular lead, zinc, and cadmium contamination of the sediments. Furthermore, high level of contamination has been detected in the submarine vegetation (micro-algae) implanted around the roots of the lagoon vegetation (reed).

The contamination area has been outlined and a strategy for decontaminating the sediments has been designed.

INTRODUCTION

Since several years, the island of Sardinia - Italy has suffered for exploitation due to mining and metallurgical activity. Nowadays, although less than in the past, Sardinia is characterized by the presence of industrial plants for primary raw material production. In particular the southwest part of the island (the Sulcis-Iglesiente area) is subject to an intense exploitation due to the presence of an important industrial settlement (Portovesme) producing a huge environmental impact in the surroundings.

An example of the environmental impact coming from the Portovesme industrial settlement can be found in the status a small basin (quite a lagoon) included in the naturalistic context of the Sulcis-Iglesiente area, which represents the fatal receptor of the waste waters carrying dangerous substances uttered by the industrial settlement. The pollutant input originates from the principal tributary to the lagoon, the Paringianu Canal, toward which several tailings are conferred coming from industrial activities.

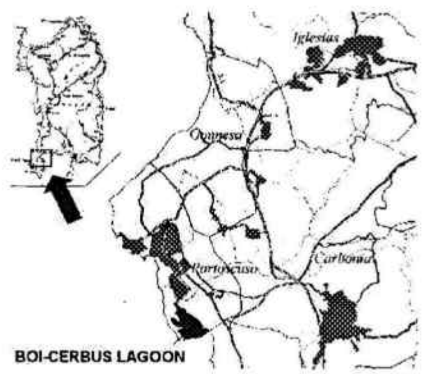

Figure 1 – Boi-Cerbus lagoon

CHARACTERIZATION OF THE BOI-CERBUS LAGOON

The environmental characteristics of the Boi-Cerbus lagoon have been investigated during a surveying work program developed by the University of Rome "La Sapienza" (De Giorgi, 1999), within the *Program for the remediation of the Sulcis Iglesiante area*, coordinated by ENEA. This study has evidenced a prevailing pollution by heavy metals in accordance with Fergusson, 1990.

Samples of sediments, water, lagoon vegetation and algae have been collected in situ and transferred in laboratory, in order to be analyzed and treated (Boulding, 1994). The aim of the study, in fact, has been to suggest a lagoon remediation and a recovery program. All the samples, identified with the codes RP2, RP3, RP4 and RP5, have been collected in the lagoon basin, except the sample with the code RP1 collected in the Paringianu Canal.

In order to appreciate the pollutant distribution in the sediments, a wet screening operation has been performed in order to separate the finest fraction (<38 μm). The results of the chemical analysis on the different size-classes are shown in Table I. A critical concentration of zinc, lead and cadmium have been found, particularly in the finest size-class (<38 μm). Moreover, the mercury concentration shows a not negligible value, higher than the standard established in the List "A" of the Dutch rules concerning soil pollution. The water analysis, on the contrary, has revealed a low contamination by heavy metals: the pollutants are therefore fixed on the sediments (Alloway and Ayres, 1993)

The aerial portion of the vegetation samples (leaves and shoots) has been cut off from the roots to evaluate the heavy metals concentration in each fraction separately. The analyses carried out on the vegetation are reported in Table II. It has to be revealed the presence of high heavy metals concentration (especially for zinc, lead and cadmium, in order of content). The roots, in fact, behave as a filter to prevent contamination of the aerial part of the growth, while the algae, storing the pollutants, represent important indicators as pollutant accumulators.

In particular, high values of heavy metals concentration have been measured in the mucilage, composed by microscopic algae adhering to the vegetation roots (Piacenti et al., 2000).

Table I - Analysis of heavy metals content in sediments coming from the Boi-Cerbus lagoon.

Sample	Size class	Weight	Cd	Pb	Ni	Hg	Cr	Cu	Zn	As
	mm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
RP1	-1 +0.5	1.84	15.27	843.51	51.53	1.50	12.65	75.38	719.02	20.99
	-0.5 +0.038	23.81	7.84	400.78	25.48	1.47	9.59	51.93	545.30	22.54
	-0.038	74.36	10.73	580.48	49.95	1.66	12.49	50.22	718.40	26.45
RP2	-1 +0.5	9.61	1.00	18.98	9.99	0.10	1.60	10.99	73.99	7.99
	-0.5 +0.038	51.50	2.00	38.96	8.99	0.17	6.00	8.99	139.92	6.99
	-0.038	18.83	40.93	393.64	27.59	1.00	19.03	53.44	878.52	25.40
RP3	-1 +0.5	12.65	20.96	61.89	5.99	0.17	4.52	8.98	293.20	9.98
	-0.5 +0.038	68.59	10.98	33.94	5.99	0.11	3.03	6.99	196.83	10.98
	-0.038	18.76	354.82	746.76	38.05	1.86	138.56	46.83	8986.91	211.96
RP4	-1 +0.5	1.37	<1.00	16.98	4.00	0.16	5.14	8.99	33.68	<5.00
	-0.5 +0.038	95.76	1.00	10.99	4.00	0.08	5.92	5.00	38.83	<3.00
	-0.038	2.87	31.91	277.47	39.85	1.23	142.55	35.60	934.65	70.51
RP5	-1 +0.5	1.65	<1	24.96	1.00	0.07	1.58	7.99	39.31	<5.00
	-0.5 +0.038	90.77	2.00	32.95	7.99	0.05	2.00	6.99	73.60	3.00
	-0.038	7.59	44.20	461.55	36.62	1.40	58.55	38.85	1456.92	52.78
Dutch standards (max level)			*0.50*	*57.00*	*12.00*	*0.20*	*54.00*	*19.00*	*63.00*	*18.00*
Italian standards (max level)			*1.00*	*45.00*	*45.00*	*0.50*	*20.00*	*40.00*	*200.00*	*15.00*

Table II - Analysis of heavy metals content in vegetation coming from the Boi-Cerbus lagoon.

Sample	Class	Cd	Pb	Zn	Ni	Hg	Cr	Cu
		ppm	ppm	ppm	ppm	ppm	ppm	ppm
RP1	algae	39	690	3243	27	1.84	6	39
RP2	algae	4	149	290	8	0.83	2	14
	roots	11	181	354	38	0.48	2	50
	aerial portion	2	44	101	5	0.09	2	16
RP3	algae	32	193	643	13	2.02	13	15
	roots	63	310	1277	14	0.62	7	22
	aerial portion	3	52	90	7	0.09	4	17
	mucilage	381	982	4953	23	2.44	10	30
RP4	algae	19	209	482	16	0.98	10	14
	roots	1	33	46	5	0.06	1	20
	aerial portion	1	23	36	2	0.06	0	12
RP5	algae	8	143	229	7	0.34	2	10
Dutch standards (max level)		*0.50*	*57.00*	*63.00*	*12.00*	*0.20*	*54.00*	*19.00*
Italian standards (max level)		*1.00*	*45.00*	*200.00*	*45.00*	*0.50*	*20.00*	*40.00*

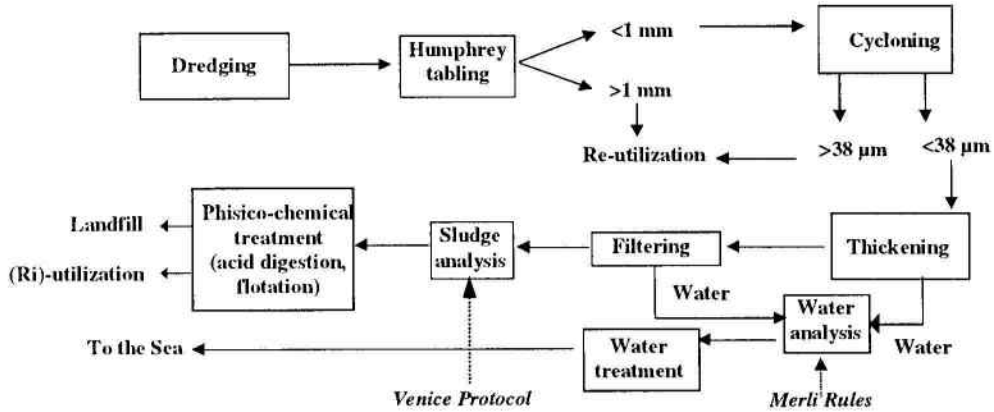

Figure 2 - Sediment treatment flow sheet.

PROCESSING OF SEDIMENTS

Chemical analyses concerning heavy metals content in the sediments of the Boi-Cerbus lagoon show a very high content of lead, zinc and cadmium. Furthermore, the highest concentration is found in the fines (<38 Γm).

A remediation process of sediments is proposed, as presented in Figure 2, including the following steps:

- dredging and transportation;
- coarse and heavy particles separation by Humphrey tabling;
- size classification by cycloning;
- pretreatment by sediment thickening;
- filtering;
- physico-chemical treating (acid digestion, flotation);
- landfill, reutilization.

The prevailing contamination of the fine fraction (<38 µm) requires a size classification, in order to separate the non-contaminated coarse fraction. Such a fraction can be re-utilized without any further treatment, while the fine fraction is forwarded to a proper treatment plant, allowing a significant cost reduction in front to submit to treatment all the sediment (U.S. EPA, 1996; Gentilomo, 1998).

In the case of the sediments coming from the Boi-Cerbus lagoon, the cost of remediation is relevant because of the high percentage in weight of the coarse fraction (>38 µm). The amount of sediments to be treated after size separation is reduced up to 80% in weight.

The separation of coarse materials in sediments can be performed by Humphrey Spiral (particle size >1 mm). Such a device provides a separation by gravity and size. The further separation can be performed by hydro-cycloning (particle size >38 µm).

After size classification, a thickening operation, followed by a filtration, is executed, in order to separate the thickened sludge from the waters. Then, the recovered waters are submitted to a decontamination process before to feed to the nearest sea while the sludge is sent to a specific treatment.

The treatment process of the sludge is based on an acid digestion, to reduce Pb and Zn content and by a flotation process to separate Zn and Cd (U.S. EPA, 1987; 1997).

The dredged sediments can be landfilled or re-utilized, if economically convenient. The re-utilization is practicable if the sediments are compatible, by quality and size distribution, with the final destination. The International Conventions (London Convention-1972-, Oslo and Paris Convention-1992), the European Directives and the Rio Declaration on Environment and Development (1992) encourage the re-utilization of sediments as well as recommend to limit dredging as it is strictly necessary. To this purpose, the Italian legislation established some criteria to assess for the environmental safety in the case of sediment dredged from the Lagoon, the so-called Venice Protocol (1991). Such a Protocol defines different categories for the sediment utilization, excluding the sediments classified as toxic and hazardous according the Italian legislation (D.P.R. 915/82 and addendum).

The treatment process has been applied to a representative sample, obtained after reconstruction from all the collected samples of sediments. In the following, the results, obtained under different processing conditions, are reported.

Leaching treatment

- After leaching pollutants are dissolved and transferred into solution, properly prepared to remove some specific metal from sediments. In particular, the capability to extract Pb and Zn has been investigated, adopting solutions of acetic acid (CH_3COOH 1.0 N), ammonium acetate (CH_3COONH_4 10% in weight) and of ethylene-di-amine-tetra-acetic acid (EDTA 0.1% N). The treatment has been applied to the matrix of the reconstituted size-class <38 Γm, representative of the corresponding size-classes coming from all the collected samples. The tests have been executed under constant-temperature, in three flasks in parallel, submitted to agitation. Each flask contained 6 g of material and 1 ml of the testing solutions, assuring a solid/liquid ratio equal to 1/10 in volume. To verify the effect of the temperature on metal extraction, each test has been performed at 25 °C and at 50 °C. Samples of the leaching solution have been withdrawn at increasing time intervals (1, 2, 5, 10, 20, 40, 80, 160 and 1,440 minutes). The heavy metal concentration in the collected samples has been analyzed. The results, shown Table III, evidenced that Pb and Zn are extracted mainly by EDTA solution; the acetic acid and ammonium acetate solutions being less effective. Furthermore rising of the temperature is essential: the highest heavy metal extraction is achieved.

From the comparison of the results obtained by using different leaching solutions, it is evident that the choice of extracting solution is a critical step. In particular, it is notable the efficiency of EDTA in heavy metals extraction (Figure 3). In fact, EDTA is able to extract 99% of the total content of Pb in 1,440 minutes (24 hours), at 50 °C (50% of the total content of Pb at 25 °C). Instead the Pb extraction, by using CH_3COOH, is only 35% of the total content.

Also in the case of Zn, the maximum efficiency of the leaching process is achieved by using EDTA, but the metal extraction is limited to 45% in 1,440 minutes, at 50 °C.

Table III - Pb and Zn content in the liquors after different leaching conditions.

Time (min)	Pb (%)						Zn (%)					
	EDTA		CH_3COOH		CH_3COONH_4		EDTA		CH_3COOH		CH_3COONH_4	
	t=25°C	t=50°C	t=25°C	t=50°C	t=25°C	t=50°C	t=25°C	t=50°C	t=25°C	t=50°C	t=25°C	t=50°C
0	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
1	14.83	33.28	11.83	16.97	5.52	8.73	6.2	13.1	7.5	10.6	2.7	3.3
2	14.68	30.76	10.87	17.68	4.20	9.59	5.2	12.1	7.2	9.9	1.7	3.5
5	16.11	31.42	9.44	17.89	3.82	8.42	5.2	9.7	5.5	10.1	1.1	2.9
10	18.02	51.58	9.39	16.01	4.12	8.37	4.8	14.0	5.2	8.3	1.0	2.4
20	18.47	53.28	9.90	16.79	2.98	7.63	4.9	14.0	5.1	8.5	1.2	2.2
40	19.82	76.82	10.08	19.64	2.93	10.25	5.1	23.2	5.5	9.9	0.8	7.4
80	21.45	78.78	10.64	30.13	4.02	7.53	6.2	24.3	5.9	18.4	1.1	2.5
160	25.37	88.42	13.49	26.26	5.06	5.65	7.9	29.4	7.4	16.1	1.2	2.2
1440	50.79	99.52	22.75	36.90	6.82	7.10	17.4	43.7	15.3	29.9	2.7	4.3

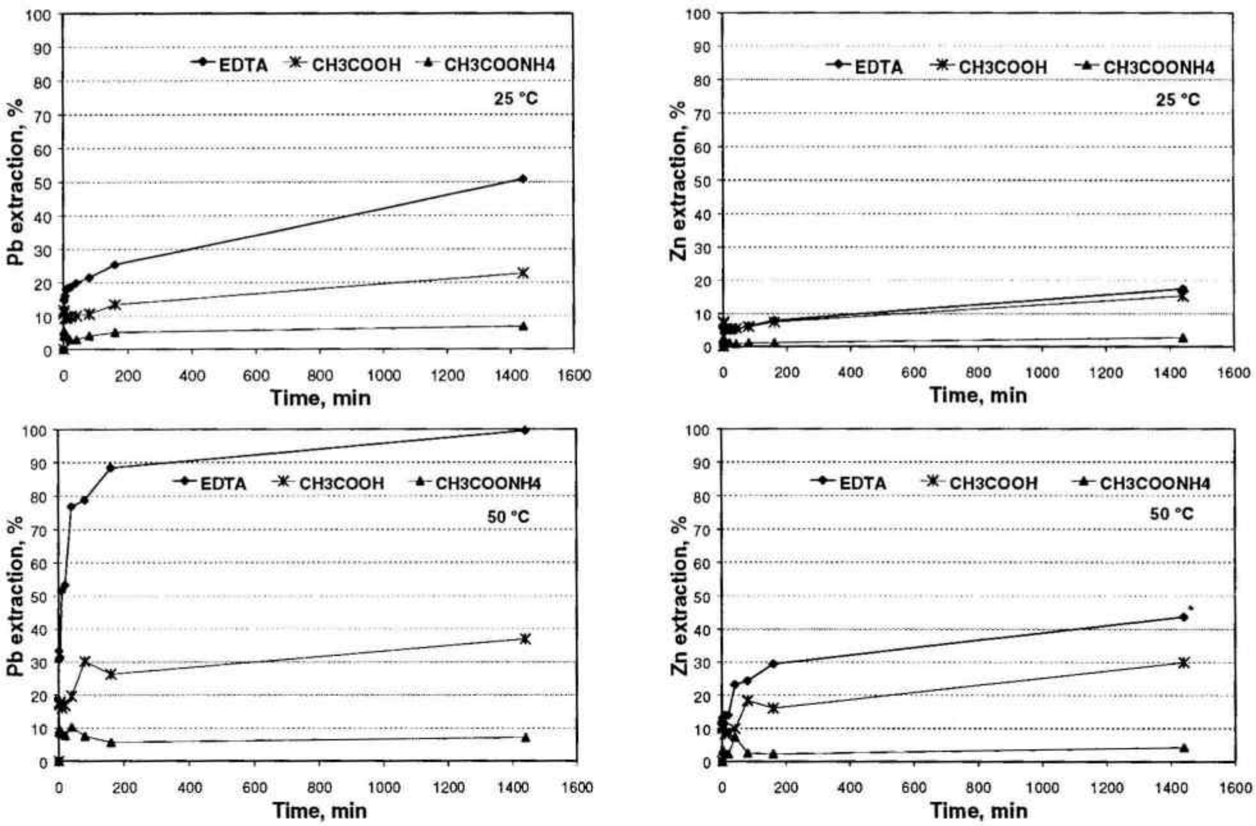

Figure 3 – Pb (left) and Zn (right) extraction after different leaching processes.

It is to be observed that the temperature contributes strongly to improve the process efficiency. In fact, it determines a noticeable increase in extraction, particularly by using EDTA: Pb extraction passed from 45% at 25 °C up to 99% at 50 °C, while Zn extraction passed from 17% at 25° C up to 23% at 50 °C.

Flotation

To remove the mineral species bearing Pb, Zn and Cd, different flotation processes has been pointed out, by recovering the particles including such metallic cations.

The experimental tests have been performed on four representative samples, constituted by blending the intermediate size class –0.5+0.038 mm of the samples RP2, RP3, RP4 and RP5.

The experimental conditions adopted for each test are reported in Table IV. The results of flotation tests (Table V, Figure 4) indicate that the efficiency of the process. Particularly, the II test allows a higher extraction of heavy metals in the floats while the heavy metal content in the tailings is lower than the acceptable level. The tailings of the IV test present a content in heavy metals close to the levels of the actual Dutch list for soil standards.

The modulus of the vector of metals has been calculated taking into consideration the square root of the sum of the squares of all the metal grades related to the number of metals taken into consideration. The calculations, shown in the last column of the Table V, evidenced the selectivity of the flotation tests and the efficacy of the decontamination.

CONCLUSIONS

Observing the results obtained after the different treatment operations performed on samples of sediment collected in the Boi-Cerbus lagoon, it is evident that both leaching and flotation processes allow the removal of metallic cations (Pb, Zn and Cd).

Table IV - Experimental conditions adopted for the different flotation process.

Test	NaOH	Na_2S	Pine oil	Na-silicate	Oleic acid	Na-amylxantate	Cocoamine(*)
	g/t	kg/t	g/t	g/t	kg/t	g/t	g/t
I test	400	2	200	-	-	400	-
II test, I phase	400	2	100	-	-	200	-
II test, II phase	-	2	100	-	-	400	-
III test, I phase	160	-	-	500	1	-	-
III test, II phase	-	-	-	-	1	-	-
IV test, I phase	50	4	-	-	-	40	200
IV test, II phase	-	1	-	-	-	20	100

(*) 1% dodecyl-amine-acetate, 0.25% pine oil, 0.125% kerosene.

Table V - Flotation results. The contribution of all the metals is computed as modulus of the vector of the metal grades.

Test	Product		Pb	Zn	Cd	Cu	Cr	Ni	All metals
		%	ppm	ppm	ppm	ppm	ppm	ppm	modulus
I	Float	1.96	241	324	33	8	59	128	175
	Tail	98.04	13	97	0	2	2	0	40
	Feed	100.00	17	101	0.6	2	3	3	42
II	Float 1	0.50	341	2350	46	57	85	85	971
	Float 2	0.71	280	1223	20	50	87	84	515
	Tail	98.79	14	82	1	2	2	2	34
	Feed	100.00	17	101	1.4	3	3	3	42
III	Float 1	0.31	142	730	16	45	37	38	305
	Float 2	14.00	33	202	2	3	2	2	84
	Tail	85.69	14	82	1	2	3	3	34
	Feed	100.00	17	101	1.2	2	3	3	42
IV	Float 1	12.49	5	264	3	5	6	6	108
	Float 2	1.35	291	863	21	22	64	62	374
	Tail	86.17	15	66	1	1	2	2	28
	Feed	100.00	17	101	1.5	2	3	3	42
Dutch standards (max level)			*57*	*63*	*0.5*	*19*	*54*	*12*	*42*
Italian standards (max level)			*45*	*200*	*1.0*	*40*	*20*	*45*	*88*

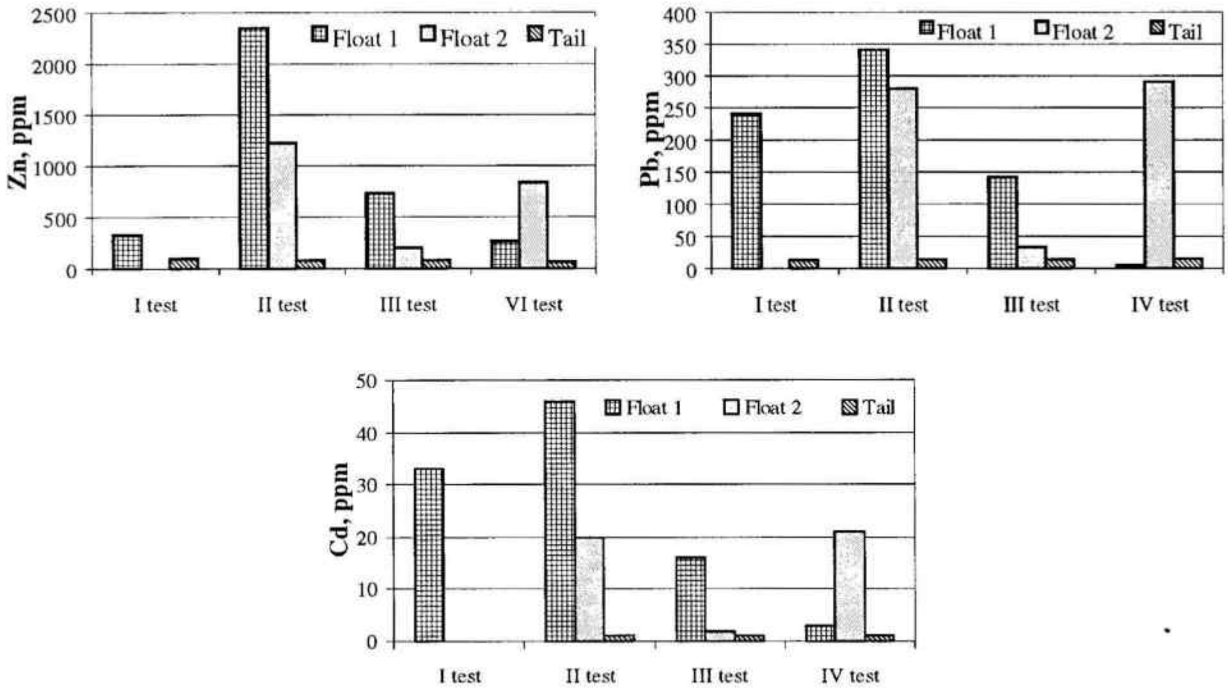

Figure 4 - Extraction of Zn, Pb and Cd mineral species by flotation.

In particular, the best results are achieved after leaching by using EDTA at 50 °C and after flotation by using sodium-amyl-xanthate as collector.

The efficiency of these processes allows to hypothesize their application for the remediation of the lagoon area. Such procedures, in fact, even if expensive and not easily applicable at a real scale, are more convenient than the permanent environmental damage in action into the lagoon area and its surroundings due to the heavy metal pollution. In fact the lagoon environment needs a particular protection for its present destination: professional fishing. Furthermore, in spite of the limited variety of species hosted in the lagoon, most of them are threatened with extinction. Considering, the relevance of the natural habitat, the remediation of the area is really compelling.

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