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EVALUATION OF METALS CONCENTRATIONS IN WHITE BEACHES AND DISCHARGE OF THE "SODA AND CALCIUM CHLORIDE" PRODUCTION PLANT (SP4)

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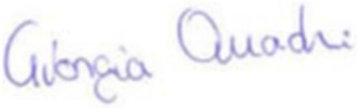
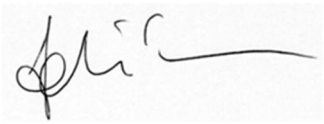
Checked by:	
Approved by:	

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1. INTRODUCTION AND PURPOSE OF THE WORK

The purpose of this document is twofold:

1) to evaluate the concentrations of metals in the *"White Beaches"* near the discharge of Solvay's Rosignano industrial site*"* (Chapter 2);

2) to evaluate the concentrations of metals at the discharge of the *"Soda and Calcium Chloride"* production plant, first, in terms of compliance with the concentrations laid down in the current IPPC permit (Chapter 3) and, secondly, in terms of the possibility to pose a risk in the marine environment.

The conclusions are set out in Chapter 4.

2. EVALUATION OF THE METALS CONCENTRATIONS FOUND IN THE WHITE BEACHES OF ROSIGNANO

2.1 Definition of Reference Values for various stretches of the Italian coast

To date, there is no consolidated protocol for sampling sediments from the coast, and there are no specific values against which to evaluate the collected samples.[1] Therefore, in this document, the first step was to define Reference Values (R.V.) against which to compare the concentrations found in the samples collected along the Rosignano beach. These Reference Values were defined considering the data reported in studies conducted by the control bodies and the Regional Agencies (see the References section). In particular, for each set of data reported in each document, and for each metal, Reference Values were defined by calculating the 95th percentile of the concentrations found. This approach allowed to include in the calculation those sites that did not present the concentrations for the single sampling points. Furthermore, where the surveys concerned different stratigraphic horizons, the data were analysed separately, and the Reference Value was defined as the lowest value. The same approach was applied to the concentrations of metals found in the *"White Beaches"* of Rosignano sampled in April 2016 by the IAMC-CNR study of 2017. Finally, a range of Reference Values was defined and used to evaluate the concentrations found along the Rosignano beach (IAMC-CNR study).

2.1.1 Veneto

In 2019 ARPA Veneto published the results of a study aimed at defining the background values of metals and metalloids in soil. This study entitled *"Metals and metalloids in the soils of Veneto - Definition of background values"*, also envisaged the characterization of portions of the coast by identifying homogeneous depositional units in consideration of the prevailing lithology and the pedogenetic processes that characterize them, and then defining the background values for each unit.

In this paper, the *"North-eastern coast"* and *"Southern Coast"* units were considered (Figure 1).

[1] *"At the national level, in the absence of contamination threshold values for sediments and a specific procedure for assessing the risk for human health and exposed ecosystems, the practice requires the use, as a reference, of the CSCs (contamination threshold concentrations) for soils, defined in Legislative Decree 152/06 "* - Quality standards for river and lake sediments. Criteria and proposal, ISPRA, 2011.

As can be seen from the figures, although reference is made to the coastal area, the samples were not only taken along the coasts. However, in both units the "soils" are classified as sediments "*of marine origin with fluvial reorganization*".

Figure 1: Location of the units for which the Reference Values were calculated, on the left "*North-eastern coast "* and on the right "*Southern Coast "(*Source: ARPAV, *"Metals and metalloids in the soils of Veneto - Definition of background values",* 2019*).*

In the ARPAV study, the Background Values were defined considering the 95th percentile, that is the value greater than or equal (≥) to 95% of the concentration values, defined considering the complete dataset. The study envisaged that the concentration values referring to two different depths were collected and treated separately: for the "*natural-anthropic*" content, the horizon between 0 cm and 40-50 cm in depth was considered; for the "*pedo-geochemical* content" the horizon between 40-50 cm and 70 cm was considered; the Background Values reported in Out of Text Tables 1 and 2 were defined considering the highest value of those found, in accordance with regional legislation (DGRV 464 of 2/3/2010).

In this discussion, the 95th percentiles were calculated for each metal found in the stratigraphic horizons analysed and the Reference Value was conservatively set to the lowest value. The *"Reference Values for Veneto* are reported in Table 1. Adopting the same approach, the table shows the Minimum Value by selecting the lowest value in the *"Lower quartile".*

Table 1: Reference Values for Veneto

	R.V.	Minimum v.
	mg/kg dw	
Sb	0.48	0.1
As	9.3	3.9
Be	0.28	0.25
Cd	0.25	0.25
Co	5	1.2
Cr	20	2.5
Hg	0.06	0.03
Ni	15	3
Pb	11	2.5
Cu	15	2.5
Se	0.1	0.1

	R.V.	Minimum v.
Sn	1.1	0.15
V	22	11
Zn	46	10

2.1.2 Friuli Venezia Giulia

In 2018, ARPA Friuli-Venezia Giulia carried out a study on the sediments along the Isonzo plain; this study also included the characterization of stretches of coast. The results are reported in the document "*Background values in the region outside the SNI* [Site of National Interest] *areas - Transition plan for the mercury parameter in the soils of the Isonzo plain "*.

The sampling points were chosen for the most part in semi-natural areas (e.g., protected areas), avoiding contaminated areas or areas close to possible sources of contamination.

The available data refer to both the surface horizon (samples taken at a depth of between 5 and 40 cm) and the deep horizon (samples taken at a depth of more than 70 cm).

In this paper, the statistical parameters were calculated considering the values of the metal concentrations found in the samples taken from the shores, in particular near the Gulf of Trieste. Figure 2 shows the position of the sampling points on the beaches.

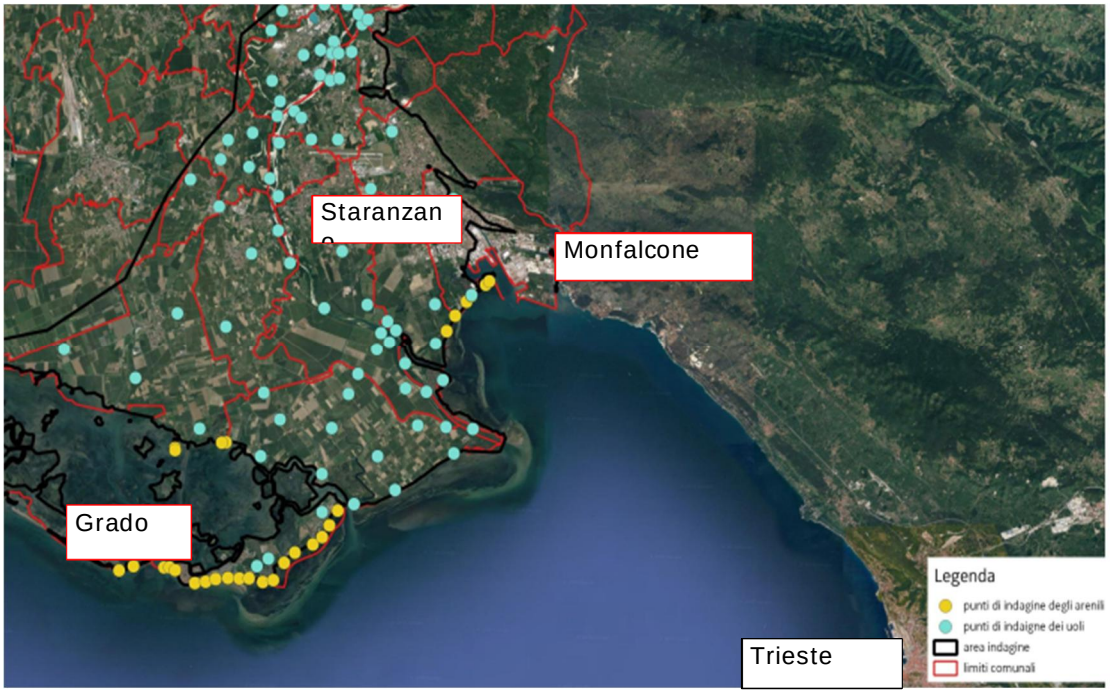


Figure 2: Location of the survey points on the beaches, in yellow (Source: *ARPAFVG, Background values in the region outside the SNI areas – Transition plan for the mercury parameter in the soils of the Isonzo plain*).

Table 2 Table 2 shows the statistical parameters and the *"Reference Values for Friuli-Venezia Giulia".*

Out of Text Tables 3 and 4 show the data taken from the ARPAFVG study used to define the Reference Values referred to in Table 2.

Table 2: Reference Values for Friuli-Venezia Giulia

				Surface horizon				Deep horizon			
	R.V.	Min. value	Max. value	95th p.	Average	Median	Std. Dev.	95th p.	Average	Median	Std. Dev.
	mg/kg dw										
Sb	4.99	<0.1	6.35	4.99	4.99	4.99	0	6.06	3.43	3.43	4.14
As	6.41	1.36	10	6.41	4.61	5.04	1.63	8.37	5.59	5.07	1.73
Be	0.27	0.1	0.7	0.27	0.2	0.2	0.05	0.58	0.31	0.3	0.17
Cd	0.2	0.1	0.2	0.2	0.19	0.2	0.03	0.2	0.2	0.2	0
Co	3.8	<2	6.9	3.8	2.98	2.85	0.68	6.44	4.41	4.64	1.48
Cr	10.1	3.83	24	10.1	6.19	5.68	2.38	23.58	10.05	6.56	7.34
Hg	4.08	<0.06	19	11.58	2.15	0.74	4.45	4.08	1.03	0.54	1.69
Ni	8.03	1.36	27	8.03	4.82	4.11	2.15	22.45	8.36	5.62	7.5
Pb	20.09	2.05	62.2	21.56	7.39	3.47	14.69	20.09	7.03	3.74	9.66
Cu	7.8	<0.1	12	7.8	2.81	1.6	3.02	9.65	4.28	2.3	3.57
Se	<0.5	<0.5	0.6	<0.5	<0.5	<0.5	0	0.6	0.6	0.6	0
Sn	5.32	<0.1	32.4	27.66	8.68	0.8	15.82	5.32	1.72	0.5	2.67
Ti	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	0	0.2	0.2	0.2	0
V	10.35	3.1	27	10.35	6.74	6	2.58	24.2	10.02	7.5	7.13
Zn	25.33	7.53	34.5	25.33	14.18	13.2	6.37	29.18	16.71	13.6	8.11
Al	4075	1100	11000	4075	2757	2350	1095	7430	3386	2200	2604
Fe	5090	1100	11000	5090	3720	3865	1177	7815	4006	2980	2380
Mn	582	144	615	582	398	409	153	600	424	466	143

2.1.3 Tuscany

In 2017 ARPA Toscana carried out a study on sediments sampled along the entire Tuscan coast (see Figure 3). The study considered a total of 23 beaches in 15 Municipalities (in the figure below, for a graphics issue, the Municipalities investigated on the Island of Elba are not specified). The results are published in the document *"Study for the determination of the natural background values in sediments and sea water of the coasts of Tuscany".*

Figure 3: Municipalities on whose beaches sampling was carried out (Google Earth image).

The samples were taken considering the surface horizon 0-10, 0-15 cm.

In the study, ARPAT divided the coast into homogeneous *"Areas"* based on the *geochemical and petrographic provinces of marine sediments and shores.* Finally, for each *"area"*, ARPAT calculated the Natural Background values considering both samples collected from the coast and samples collected from the seabed; therefore, the Natural Background Values defined by ARPAT are not relevant for the purpose of the present document and therefor, specific "*Reference Values for Tuscany"* had to be defined. These values are reported in Table 3 (values defined starting from the data reported in Table 5 extracts from the ARPAT study).

Table 3: Reference Values for Tuscany

	R.V.	Minimum v.	Maximum v.	Average	Median	Dev. Std.
	mg/kg dw					
As	36.6	3.9	98	19.24	16	19.66
Cd	0.5	0.1	1.1	0.28	0.2	0.22
Cr	537.8	12	650	116.35	34	177.67
Hg	<0.1	<0.1	<0.1	<0.1	<0.1	
Ni	224.6	6.9	319	63.02	29	79.53
Pb	13.7	3.6	18	7.72	6.6	3.23

2.1.4 Sardinia

In 2005, as part of the MONIQUA Project "*Ordinary and extraordinary operation and maintenance service of the instrumentation controlled by the automatic monitoring network of the quality of coastal and internal surface sea water in the province of Sassari*", sampling activities were carried out on sediments in Minciaredda, within the remediation site of national interest in Porto Torres.

Of particular interest for this report are the sediment samples carried out along the shores to the east and west of Minciaredda. In these beaches 10 cores were extracted and 30 samples were taken from each core so as to have analytical determinations for the surface (up to 20 cm deep), intermediate (between 30 and 50 cm) and deep (between 50 cm and 70 cm) sands.

Table 4 shows the *"Reference Values for Sardinia"* defined starting from the data taken from the MONIQUA study, reported in Table 6 together with the calculated statistical parameters.

Table 4: Reference Values for Sardinia

	R.V.	Minimum v.	Maximum v.
	mg/kg dw		
Cd	0.02	0.01	0.15
Cr	5.27	0.46	44.91
Fe	2606.65	395.8	17437
Ni	5.45	1.48	41.27
Cu	1.7	1.7	6.12
V	9.96	0	41.07
Zn	9.95	4.07	85.9
Pb	3.89	0.6	9.68

2.2 Reference Values for the *"White Beaches"* of Rosignano

In the period November 2015 - August 2017, in compliance with the requirement no. 3 of the IPPC permit of 7 August 2015 for the operation of the chemical plant of Solvay Chimica Italia SpA (SCI) and Inovyn Italia s.r.l. situated in the municipality of Rosignano Marittimo (Livorno), the Institute for the Coastal Marine Environment (*Istituto per l'ambiente Marino Costiero* - IAMC) of the CNR (*Consiglio Nazionale delle Ricerche*) was commissioned by SCI to carry out an environmental study in the marine - coastal area overlooking Solvay's Rosignano plant; this study, in April 2016, also involved the sediments of the *"White Beaches"* up to a distance of about 1 km from the production plant discharge. The results of this survey are reported in Chapter 7, Section II of the report "*Environmental analysis of the marine-coastal area in front of the Solvay-Rosignano industrial plant with reference to EIA requirement no. 0000177 (point 3) of 7 August 2015 "*, August 2017.

Figure 4 shows the 10 sampling points in the beaches (S0 - S9; the red star indicates the outlet to the sea of the Fosso Bianco). The sediments were subjected to chemical, granulometric and mineralogical characterization.

Table 5 shows the *"Reference Values"* calculated for the *"White Beaches"* of Rosignano defined using the data found in the IAMC - CNR study (reported in Out of text Table 7).

Figure 4: Location of samples taken in April 2016 from the *"White Beaches"*.

Table 5: Reference Values for the *"White Beaches"* of Rosignano

	R.V.	Minimum v.	Maximum v.	Average	Median	Dev. Std.
	mg/kg dw					
Hg	0.01	0.01	0.01	0.01	0.01	0
As	19.55	3.37	20	15.4	16	3.37
Pb	20.1	3.69	21	15.6	16.5	3.69
Ni	7.49	0.5	7.8	3.53	3.05	2.6
Cr	48.1	6.5	49	24.55	17	15.99
Cd	0.36	0.09	0.4	0.23	0.21	0.09
Cu	9.52	0.6	11	4.8	4.65	2.94
V	10.29	2.5	12	6.02	5.65	2.93
Zn	30.55	7.3	31	16.32	14	9.25
Mn	217.5	32.35	222	159.3	150.5	32.35
Al	5200	1400	6100	2600	2200	1400
Fe	9100	1000	10000	4400	3500	3000

2.3 Evaluation of the metals concentrations found in the "White Beaches" of Rosignano

In this Chapter, the Reference Values determined for the *"White Beaches"* of Rosignano (referred to in Chapter 3) will be compared with the Reference Values determined for some Italian regions (referred to in Chapter 2).

Mercury

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 0.06 - <0.1 mg/kg. This range did not include the "*Reference Value for Friuli-Venezia Giulia*", as the high concentrations found in the study taken as a reference, indicate the existence of particular site specific situations for the area studied. The concentration of Mercury found in the *"White Beaches"* of Rosignano, equal to 0.01 mg/kg is significantly lower than the range defined; this concentration is also lower than the lowest absolute value found in the studies analysed (0.03 mg/kg in the Veneto Region). This evidence allows us to conclude that the concentrations of Mercury found by the IAMC - CNR in the *"White Beaches"* of Rosignano are significantly lower than the range concentrations found by other studies carried out on different stretches of the Italian coast.

Arsenic

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 6.41-36.60 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia and Tuscany).

The Reference Value defined for Arsenic in the *"White Beaches"* of Rosignano, equal to 19.95 mg/kg is therefore included in the defined range. Therefore, also for Arsenic, the concentrations found in 2016 by the IAMC - CNR in the "*White Beaches "* of Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Lead

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 3.89 - 20.06 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia, Tuscany and Sardinia).

The Reference Value defined for Lead in the *"White Beaches"* of Rosignano, equal to 20.15 mg/kg is in line with the upper value of the defined range. Therefore, also for Lead, the concentrations found in 2016 by the IAMC - CNR in the "*White Beaches "* of Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Nickel

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 5.45 - 224.60 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia, Tuscany and Sardinia).

The Reference Value defined for Nickel in the *"White Beaches"* of Rosignano, equal to 7.49 mg/kg is close to the lower limit of this range. Therefore, also for Nickel the concentrations found by the IAMC - CNR in the *"White Beaches"* di Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Chromium

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 5.27 - 537.80 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia, Tuscany and Sardinia).

The Reference Value defined for Chromium in the *"White Beaches"* of Rosignano, equal to 48.82 mg/kg is therefore included in this range. Therefore, also for Chromium, the concentrations

found by the IAMC - CNR in the *"White Beaches"* of Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Cadmium

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 0.02-0.50 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia, Tuscany and Sardinia).

The Reference Value defined for Cadmium in the *"White Beaches"* of Rosignano, equal to 0.36 mg/kg is therefore included in this range. Therefore, also for Cadmium, the concentrations found by the IAMC - CNR in the *"White Beaches"* of Rosignano show no anomalies compared to the concentrations found by other studies carried out in different stretches of the Italian coast.

Copper

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 1.70-15 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia and Sardinia).

The Reference Value defined for Copper in the *"White Beaches"* of Rosignano, equal to 9.52 mg/kg is therefore included in this range. Therefore, also for Copper, the concentrations found by the IAMC - CNR in the *"White Beaches"* of Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Vanadium

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 9.96-22 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia and Sardinia).

The Reference Value defined for Vanadium in the *"White Beaches"* of Rosignano, equal to 10.29 mg/kg was found to be in the lower part of this range. Therefore, also for Vanadium, the concentrations found by the IAMC - CNR in the "*White Beaches* " of Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Zinc

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 9.95-46 mg/kg (range defined considering the data found in Veneto, Friuli-Venezia Giulia and Sardinia).

The Reference Value defined for Nickel in the *"White Beaches"* of Rosignano, equal to 30.55 mg/kg is included in this range. Therefore, also for Zinc the concentrations found by the IAMC - CNR in the *"White Beaches"* of Rosignano show no particular anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

Manganese

The test for this element was only carried out in the Friuli-Venezia Giulia study. The most representative parameters found and their comparison with the parameters calculated for Rosignano are set out below:

- Friuli Venezia Giulia: 1) Minimum value - 144 mg/kg; 2) Reference Value - 582 mg/kg;
- Rosignano: 1) Minimum value - 32.35 mg/kg; 2) Reference Value - 217.50 mg/kg.

The parameters referring to the *"White Beaches"* of Rosignano have lower values in both cases. Therefore, also for Manganese, the concentrations found by the IAMC - CNR in the "*White Beaches* " of Rosignano show no anomalies compared to the concentrations found by the study indicated above carried out on different stretches of the Italian coast. Furthermore, it is important to underline that Manganese is typically considered to be of natural origin and its testing is not required in accordance with Table 1 Annex 5, Part IV of Legislative Decree 152/06 (Environmental Code), normative reference typically used also for the characterization of coastal sediments.

Aluminium

Testing for this analyte was performed in the studies carried out for Friuli-Venezia Giulia: the Reference Value, equal to 4075 mg/kg is in line with the value found in the *"White Beaches"* of Rosignano by the IAMC - CNR Study, equal to 5200 mg/kg. Furthermore, it is important to underline that Aluminium is typically considered to be of natural origin and its testing is not required in accordance with Table 1 Annex 5, Part IV of the Environmental Code, a regulatory reference typically used also for the characterization of coastal sediments; in this specific case, the Aluminium concentrations found in the sediments of *"White Beaches"* are attributable to the presence of the nearby mineral deposits. Therefore, also for Aluminium, the concentrations found by the IAMC - CNR in the *"White Beaches"* of Rosignano show no anomalies compared to the concentrations found by the study indicated above carried out on different stretches of the Italian coast.

Iron

The concentration range defined for this analyte in consideration of the Reference Values reported in Tables 1-5 is 2606.65-5090 mg/kg (defined considering the concentrations found in Friuli-Venezia Giulia and Sardinia). The Iron Reference Value defined for the *"White Beaches"* of Rosignano, equal to 9100 mg/kg, is slightly higher than the range defined; this value does not indicate any significant anomaly since, like Aluminium, Iron is attributable to the presence of nearby mineral deposits; Iron is also a metal typically of natural origin and its testing is not required in accordance with Table 1 Annex 5, Part IV of the Environmental Code, the normative reference typically also used for the characterization of coastal sediments. Therefore, also for Iron, the concentrations found by the IAMC - CNR in the *"White Beaches"* of Rosignano show no anomalies compared to the concentrations found by other studies carried out on different stretches of the Italian coast.

The evaluation carried out above allows us to conclude that the values of metals found *in the "White Beaches"* do not show any anomalies with respect to the values found in various studies carried out by the control bodies in different stretches of the Italian coast.

As reported in Chapter 1, to date, *"at the national level, no contamination threshold values have been defined for sediments and the practice requires CSCs to be used as a reference (contamination threshold concentrations) for soils, defined in Legislative Decree 152/06"* – "*Quality standards for river and lake sediments. Criteria and proposal, ISPRA, 2011 "*).

From the comparison of the Reference Values calculated for the *"White Beaches*" of Rosignano with the CSCs defined for public, private and residential Green Sites by Legislative Decree 152/06, it can be observed that these threshold concentrations are always respected.

Table 6: Comparison between the reference values for the *"White Beaches"* and the CSCs (column A, Table 1, Annex 5, Legislative Decree 152-06

	R.V. "White Beaches"	CSC Column A
	mg/kg dw	
Hg	0.01	1
As	19.55	20
Pb	20.1	100
Ni	7.49	120
Cr	48.1	150
Cd	0.36	2
Cu	9.52	120
V	10.29	90
Zn	30.55	150
Al	5200	-
Fe	9100	-
Mn	217.5	-

3. EVALUATION OF THE METALS CONCENTRATIONS AT DISCHARGE SP4

On March 31, 2022, staff from the SGS Laboratory, together with staff from the Solvay plant in Rosignano, took samples from the discharge of the *"Soda and Calcium Chloride"* production plant, (SP4) where an autosampler is installed, see Figure 5 and the document in Annex 1 - (Sampling Report). The objective of this survey was to evaluate the concentrations of metals at the SP4 discharge in consideration of the requirements of the IPPC permit of 20 January 2022. The sampling was supervised by Ramboll personnel.

Figure 5: Sampling by the SGS operator of the autosampler of discharge SP4 (highlighted in the blue box).

Pursuant to requirement 21 of the IPPC permit of 20 January 2022, this point (SP4) represents the official sampling point of the "*Soda and Calcium Chloride"* production plant and, as per the IPPC permit Monitoring and Control Plan, it is sampled quarterly.

Sampling was carried out according to the method APAT CNR IRSA 1030 Manual 29/2003 with automatic sampler, in order to obtain a composite average sample of the 3 hours (the partial fractions sampled at 10-minute intervals). The collection started at 11.00 and ended at 14.00. At the end of the sampling, the collected volume (9 L) was inserted in a plastic container and subjected to mixing, in order to obtain a homogeneous sample of the discharge, from which the necessary sub-aliquots were formed for the execution of the analyses.

The analyses concerned:

- the sample as-is (liquid phase + solid phase);
- the filtered sample: this analysis was carried out on the sample filtered in the field by SGS personnel and on the sample filtered in the laboratory by Solvay personnel (internal method);
- the solid phase (collected on a filter).

The test certificates of these analyses are given in Annex 2.

Tables 7 and 8 show the results obtained for metals. In particular:

- in Table 7 the concentrations of metals, as per Table 5, Annex 5, Part III of Legislative Decree 152/2006, found in the filtered samples are compared with: a) the limits set by the current IPPC permit (Table 3, Annex 5 to Part III of Legislative Decree 152/2006 and b) with the Environmental Quality Standards (EQS) established by Legislative Decree 172/2015 (law implementing Directive 2013/39/EU, which amends the Water Framework Directive 2000/60/EC) for the water column of surface water bodies;
- In Table 8 the concentrations of Chromium, Hexavalent Chromium, Nickel, Arsenic, Cadmium, Lead and Mercury, found in the solid phase are compared: a) with the background values defined by ARPAT in 2017 (*"Study for the determination of natural background values in sediments and coastal marine waters of Tuscany"*) and b) with the Environmental Quality Standards (EQS) established by Legislative Decree 172/2015 for the sediment of surface water bodies.

It should be noted that, pursuant to art. 74 of Legislative Decree 152/06, the EQS are defined as:

"The concentration of a particular pollutant or group of pollutants in water, sediments and biota that must not be exceeded in order to protect human health and the environment".

These values were identified within the scope of the Water Framework Directive (WFD) - Directive 2000/60/EC and aim to bring water bodies back to "Good Chemical Status" (target initially set in December 2015 and subsequently moved to 2021 and, then to 2027). The EQS were derived by conservatively applying the ecological risk analysis methods for the (*worst-case scenario*), i.e., by specifically evaluating the chronic and acute toxicity of individual substances towards different ecological receptors (such as, for example, pelagic community, benthic community and predatory fish) and applying (*Safety Factor*) in order to determine protective thresholds. Each substance identified by the WFD, and by the daughter Directives (2008/105 and 2013/39) is associated with a specific file (*Environmental Quality Standards (EQS) Substance Data Sheet*), which describes how their EQS were defined and lists the studies considered and indicates the safety factors adopted.

Therefore, in order to assess the potential risk for the marine environment associated with the solid and liquid fractions of the wastewater of the *"Soda and Calcium Chloride"* production plant, the first step of the assessment should be a comparison with the EQS defined by Legislative Decree 172-2015.

Table 7: Metals concentrations with a prescriptive limit in the IPPC-permit in the filtered sample

	Filtered in field	Filtered using Solvay internal method	Limit value as per IPPC permit	EQS - AA* in waters Legislative Decree 172-2015	EQS – MAC∞ in water of Legislative Decree 172-2015
	mg/l				
Chromium	0.0117 ± 0.0014	0.0099 ± 0.0012	2		
Hexavalent Chromium	<0.010	-	0.2		
Nickel	<0.0050	<0.0050	2	0.0086	
Copper	<0.0010	0.00119 ± 0.00014	0.1		
Zinc	<0.0050	<0.0050	0.5		
Arsenic	0.00111 ± 0.00012	0.00159 ± 0.00017	0.5	0.005	
Selenium	<0.010	<0.010	0.03		
Cadmium	<0.0010	<0.0010	0.02	0.0002	
Lead	0.00184 ± 0.00024	0.00161 ± 0.00021	0.2	0.0013	0.014
Mercury	<0.0010	<0.0010	0.005		0.00007

* *This parameter represents the EQS expressed as an annual average value (EQS-AA);*

∞*This parameter represents the environmental quality standard expressed as the maximum allowable concentration (EQS-MAC).*

Table 8: the concentrations of Chromium, Hexavalent Chromium, Nickel, Arsenic, Cadmium, Lead and Mercury found in the solid phase

	Solid Phase (Collected on filter)	Background values of ARPAT 2017 - Rosignano	EQS – AA in sediments Legislative Decree 172-2015
	mg/kg		
Chromium	<1.0	138	50
Hexavalent Chromium	<1.0	Testing not performed	2
Nickel	<1.0	145	30
Arsenic	<1.0	34	12
Cadmium	0.137 ± 0.034	0.6	0.3
Lead	4.78 ± 0.94	30	30
Mercury	<0.1	0.5	0.3

The concentrations reported in Table 7 and Table B reveal that:

I. metals are present mainly in the solid phase;

II. the metal concentrations found in the sample filtered in the field are very similar to those found in the filtered sample at the Solvay laboratory, indicating that the two methods are comparable;

III. the concentrations of metals found in the filtered sample are lower than the limits laid down in the current IPPC permit (in compliance with Table 3, Annex 5 to Part III of the Environmental Code);

IV. the concentrations found in the filtered sample for Nickel, Arsenic, Cadmium and Lead are lower than the relevant Environmental Quality Standard; this assessment is not possible for Mercury, since the detection limit of the analysis laid down in the IPPC Monitoring and Control Plan (PMC) (aimed at verifying compliance with the limits of Table 3 Annex 5 to Part III of Legislative decree 152/2006 - discharge limits) is higher than the Environmental Quality Standard defined for Mercury; in any case, the concentrations found in the liquid phase comply with the limit defined for drinking water (<0.001 mg/l); (for other metals of Table 7 the legislation does not define EQS);

V. the concentrations of Chromium, Nickel, Arsenic, Cadmium, Lead and Mercury found in the solid phase are lower than the Background Values defined by ARPAT in 2017 for the Rosignano station (testing for Hexavalent Chromium was not performed by ARPAT);

VI. the concentrations of Chromium, Hexavalent Chromium, Nickel, Arsenic, Cadmium, Lead and Mercury found in the solid phase are lower than the corresponding EQS.

The evidence that, at discharge SP4, that is, before the discharge reaches the stretch of the Tyrrhenian Sea overlooking the coast of Rosignano, metal concentration values are lower than the concentration limits laid down in the Environmental Code for discharges and are lower than the reference EQS allow us to conclude that the concentrations of metals brought by the SP4 discharge, both as dissolved and as a solid phase, are protective of human health and the marine environment.

This evaluation can also be extended to Mercury, although, the limit of detection of the method of analysis adopted for the analysis of the filtered sample, while ensuring that mercury in the liquid phase of the effluent is lower than the limit applicable to drinkable water, does not allow us to verify compliance with the Quality Standard established for the waters of surface water bodies. In fact, the recent surveys (2018) carried out by the *'Institute for the Study of Anthropic Impacts and Sustainability in the Marine Environment* (CNR - IAS), in the sea waters facing the Solvay plant, verified compliance with the Quality Standard defined for Mercury in the waters; this condition was also found for the other parameters analysed: Mercury, Cadmium, Nickel and Lead. The results of this survey are reported in the document: *"Monitoring of the state of health of the marine environment in the area in front of the Solvay plant in Rosignano M.Mo (Li) - CNR IAS",* November 2020. Compliance with the EQS for the parameters Mercury, Cadmium, Nickel and Lead in the sea waters in front of the plant was subsequently confirmed by the survey carried out by ARPAT in 2019, see the document: *"Monitoring of sea water of the coasts of Tuscany, monitoring activities in 2019",* ARPAT 2020.

4. CONCLUSIONS

In this document, the following were assessed:

1) the concentrations of metals found in the "White Beaches" near the Solvay discharge;
2) the concentrations of metals in the discharge of the *"Soda and Calcium Chloride"* production plant; in particular, these concentrations were first assessed, in terms of compliance with the concentrations prescribed by the current IPPC permit IEA and, and, secondly, in terms of the possibility to pose a risk in the marine environment.

The assessment referred to in point 1, was carried out considering the concentrations found in various studies carried out by the control bodies and by the Regional Agencies on different stretches of the Italian coast. In particular, for each study considered, Reference Values (RV) were defined with respect to which to compare the concentrations found in the samples collected along the Rosignano beach as part of the sampling carried out by the IAMC-CNR in April 2016. On the basis of this comparison, it can be concluded that the concentrations of Mercury, Arsenic, Lead, Nickel, Chromium, Cadmium, Copper, Vanadium, Zinc, Aluminium, Iron and Manganese found in the *"White Beaches"* of Rosignano, as part of the sampling carried out by the IAMC-CNR in 2016, did not reveal any anomalies (compared to the values found in various studies carried out by the control bodies on different stretches of the Italian coast) and are lower than the Contamination Threshold Concentrations (C.S.C.) defined for use as protected public, private and residential areas in Legislative decree 152/06; this normative reference, in the absence of specific values, is normally used for the evaluation of contaminated sediments (in terms of potential contamination).

The assessment referred to in point 2, was made by comparing the concentrations of metals found in the discharge, for the filtered phase , with the concentration limits laid down in the IPPC permit pursuant to the Environmental Code, and, for the filtered phase and the solid phase, respectively, with the Environmental Quality Standards (EQS) defined for water and for the sediment of surface water bodies. From this comparison it emerged that, already at the SP4 discharge, and therefore before the discharge reaches the stretch of the Tyrrhenian Sea facing the Plant, the metals are lower than concentration limits established by the IPPC permit, in compliance with the Environmental Code, and the values were found to be lower than the reference EQS. This result allows us to conclude that the concentrations of metals brought by the SP4 discharge, both as dissolved and as in the solid phase, are protective of human health and the marine environment and therefore do not create any risk. This evaluation can also be extended to Mercury, although, the limit of detection of the method of analysis adopted for the analysis of the filtered sample, while ensuring that mercury in the liquid phase of the effluent is lower than the limit applicable to drinkable water, does not allow us to verify compliance with the Quality Standard established for the waters of surface water bodies. In fact, the recent surveys (2018) carried out by the *'Institute for the Study of Anthropic Impacts and Sustainability in the Marine Environment* (CNR - IAS), in the sea waters facing the Solvay plant, verified compliance with the Quality Standard defined for Mercury in the waters; this condition was also found for the other parameters analysed: Mercury, Cadmium, Nickel and Lead. The results of this survey are reported in the document: *"Monitoring of the state of health of the marine environment in the area in front of the Solvay plant in Rosignano M.Mo (Li) - CNR IAS",* November 2020. Compliance with the EQS for the parameters Mercury, Cadmium, Nickel and Lead in the sea waters in front of the plant was subsequently confirmed by the survey carried out by ARPAT in 2019, see the document: *"Monitoring of sea water of the coasts of Tuscany, monitoring activities in 2019",* ARPAT 2020.

5. REFERENCES

ARPA Friuli-Venezia Giulia: *"Background values in the region outside the SNI areas – Transition plan for the mercury parameter in the soils of the Isonzo plain"*, 2018.

ARPA Tuscany: "*Study for the determination of natural background values in sediments and sea water of the coasts of Tuscany - Updated final report*", May 2017.

ARPA Tuscany: *"Monitoring of sea water of the coasts of Tuscany, monitoring activities in 2019"*, ARPAT 2020.

ARPA Veneto: "*Metals and metalloids in the soils of Veneto - Definition of background values*", January 2019.

ISPRA: *"Quality standards for river and lake sediments. Criteria and proposal ",* 2011.

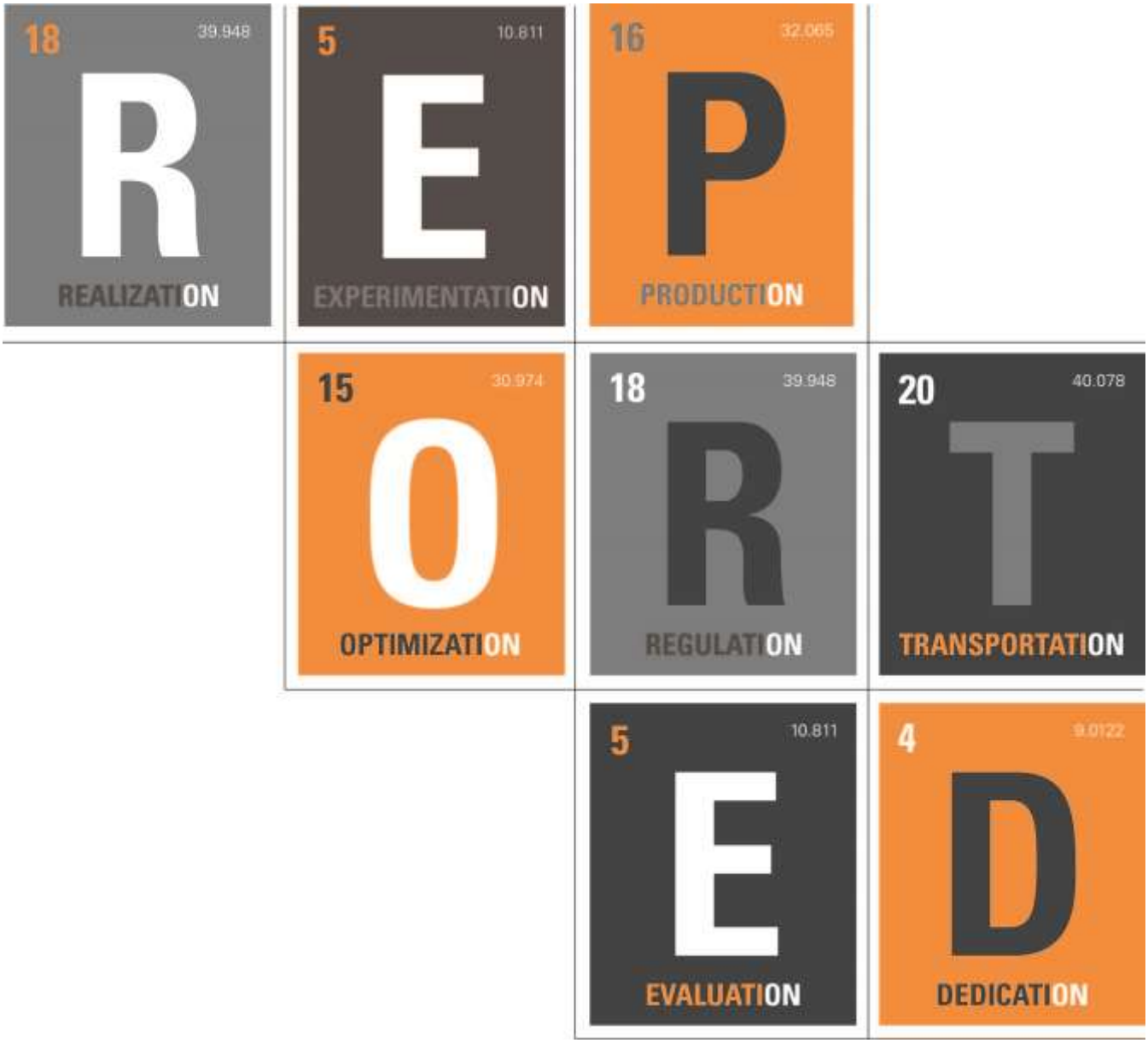
Institute for the Coastal Marine Environment (IAMC) of the CNR: "*Environmental analysis of the marine-coastal area in front of the Solvay-Rosignano industrial plant with reference to EIA requirement no. 0000177 (point 3) of 7 August 2015*", August 2017.

Institute for the Study of Anthropic Impacts and Sustainability in the Marine Environment (IAS) of the CNR: *"Monitoring of the state of health of the marine environment in the area in front of the Solvay plant in Rosignano M.Mo (Li) - CNR IAS"*, November 2020.

MONIQUA Project - Interegg III Community Program - Measure 2.1: *"Ordinary and extraordinary operation and maintenance service of the instrumentation controlled by the automatic monitoring network of the quality of coastal and internal surface sea water in the province of Sassari-Execution of an oceanographic analysis campaign (September 2005) -Final Report*".

ANNEX 1: SAMPLING REPORT

SGS



CAMPIONAMENTO ACQUE REFLUE
PRESSO SOLVAY - ROSIGNANO

ESEGUITO PER:

RAMBOLL

*SGS is the world's leading inspection, verification, testing and certification company. Recognised as the global benchmark for quality and integrity, We provide **innovative** services and **solutions** for every part of the environmental industry. Our global network of offices and laboratories, alongside our dedicated team, allows us to respond to your needs, when and where they occur.*

CAMPIONAMENTO ACQUE REFLUE PRESSO SOLVAY - ROSIGNANO

RT 1608 - 2022

2 MAGGIO 2022

Preparato da

SGS ITALIA S.P.A.

ENVIRONMENTAL SERVICES

VIA CAMPODORO, 25

35010 VILLAFRANCA PADOVANA – PD

Eseguito per

RAMBOLL

Preparato da	Firmata da
Ing Filippi Martina	Dr. Alessandro Loi Head of Laboratory Ordine Interprovinciale dei Chimici di Cagliari

In data 31 marzo 2022, il tecnico di SGS Italia Spa, Alessandro Lorenzoni, si è recato presso il sito di Solvay a Rosignano per eseguire il campionamento di acque reflue allo scarico SP4 – Fosso Bianco.

Il campionamento è stato eseguito secondo le modalità previste dal metodo APAT CNR IRSA 1030 Manuale 29/2003 con campionatore automatico, al fine di ottenere un campione medio composito delle 3 ore.
Il prelievo è iniziato alle ore 11.00 ed è terminale alle ore 14.00 e si sono prelevati più incrementi ad intervalli di 10 min.

Al termine del prelievo, la quantità di acqua prelevata (9 L) è stata introdotta in un contenitore di plastica ed è stata miscelata in modo da ottenere un campione omogeneo dello scarico, da cui sono state formate le sub-aliquote necessarie per l'esecuzione dell'analisi.

Al fine di mantenere inalterate le caratteristiche fisiche, chimiche fino al momento dell'analisi e per evitare modificazioni delle componenti e caratteristiche da valutare, i campioni sono stati raccolti e conservati secondo la tabella sotto riportata.

Aliquote prelevate tal quali senza filtrazione

Parametro	Tipo di contenitori	Conservazione
pH (eseguito in campo)	-	-
Metalli: boro, alluminio, cromo, manganese, ferro, nichel, rame, zinco, arsenico, selenio, cadmio, stagno, bario, piombo, mercurio	Polietilene	Aggiunta di HNO3 fino a pH<2, refrigerazione
cromo VI	Polietilene	Refrigerazione
fenoli	Vetro scuro	Aggiunta di H2SO4 fino a pH< 2 e refrigerazione
Azoto ammoniacale		
fosforo totale		
Solidi sospesi	Vetro scuro	Refrigerazione
Tensioattivi anionici	Polietilene	Refrigerazione, Aggiunta di 1% (v/v) di formaldeide al 37%

Aliquote prelevate con filtrazione in campo

Parametro	Tipo di contenitori	Conservazione
pH (eseguito in campo)	-	-
Metalli: boro, alluminio, cromo, manganese, ferro, nichel, rame, zinco, arsenico, selenio, cadmio, stagno, bario, piombo, mercurio	Polietilene	Filtrazione su filtri da 0,45 µm; aggiunta di HNO3 fino a pH, refrigerazione
cromo VI	Polietilene	Filtrazione su filtri da 0,45 µm, refrigerazione

Al termine del campionamento, le aliquote, dopo idonea etichettatura, sono state raccolte in frighi portatili refrigerati e portati al laboratorio di SGS Italia SpA a Villafranca Padovana.

ANNEX 2: TEST CERTIFICATES

Rapporto di Prova PD22-01126_0

LAB N° 0080 L

Prima pagina

CLIENTE		LABORATORIO	
Cliente	RAMBOLL ITALY SRL	Head of Laboratory	Alessandro Loi
		Laboratorio	SGS Italia S.p.A.
Indirizzo	VIA MENTORE MAGGINI, 50 ROMA RM 00143	Indirizzo	Via Campodoro, 25 Villafranca Padovana (PD) 35010
Contatto		Telefono	+39 049 9050013
Telefono		Fax	+39 049 9050065
Fax		Email	sgs.eco@sgs.com
Email		Accettazione n°	PD22-01126
		Pervenuto il	31/03/2022
Progetto	-	Data inizio analisi.	31/03/2022
Ordine n°	211_2022_C1_PD Rev1	Data fine analisi.	15/04/2022
Matrice	ACQUA(3) DEFAULT(1)		
		Data emissione	28/04/2022
		Rapporto di Prova n°	PD22-01126_0

RIFERIMENTI

Martina Filippi	Alessandro Loi
Project Leader	Head of Laboratory

COMMENTI

Incertezza estesa di misura stimata al 95% di livello di confidenza e fattore di copertura k=2

Documento informatico firmato digitalmente ai sensi del DLgs 82/05 s.m.i e norme collegate, sostituisce documento cartaceo. Firmato da Dr. Alessandro Loi Ordine interprovinciale dei chimici e dei fisici di Cagliari,Nuoro e Oristano.

LAB N° 0080 L

INDICE

LAB N° 0080 L

COMMENTI OPERATIVI

Campione medio di 3 h (11.00-14.00)

LAB N° 0080 L

RISULTATI

	Campione n°	PD22-01126.001	PD22-01126.002	PD22-01126.004
	Sigla campione	Scarico SP4 FBOO Tal quale	Scarico SP4 FBOO filtrato in campo	Scarico SP4 - Filtrato procedura Solvay
	Proveniente da	Solvay Rosignano	Solvay Rosignano	Solvay Rosignano
	Tipo campione	ACQUA	ACQUA	ACQUA
	Campionato da	Ns. personale - Lorenzoni	Ns. personale - Lorenzoni	Ns. personale - Lorenzoni
	Campionato il	31/03/2022	31/03/2022	31/03/2022
Parametro	**U.M.**	**RL**	**Risultato**	**Risultato**	**Risultato**
pH [Analisi eseguita al prelievo + APAT CNR IRSA 2060 Man 29 2003]					
*A pH	Unità di pH	0,1	7,6 ± 0,1	7,6 ± 0,1	-
Metalli [Su campione tal quale + EPA 3010A 1992 + EPA 6020B 2014]					
A Boro	mg/L	0,1	4,10 ± 0,51	3,76 ± 0,47	3,72 ± 0,46
A Alluminio	mg/L	0,01	4,58 ± 0,92	0,0138 ± 0,0028	0,063 ± 0,013
A Cromo	mg/L	0,005	0,0331 ± 0,0040	0,0117 ± 0,0014	0,0099 ± 0,0012
A Manganese	mg/L	0,001	1,98 ± 0,24	0,092 ± 0,011	0,0598 ± 0,0072
A Ferro	mg/L	0,01	4,86 ± 0,63	0,0144 ± 0,0019	0,0200 ± 0,0026
A Nichel	mg/L	0,005	0,0171 ± 0,0026	<0,0050	<0,0050
A Rame	mg/L	0,001	0,0236 ± 0,0028	<0,0010	0,00119 ± 0,00014
A Zinco	mg/L	0,005	0,147 ± 0,017	<0,0050	<0,0050
A Arsenico	mg/L	0,001	0,0205 ± 0,0023	0,00111 ± 0,00012	0,00159 ± 0,00017
A Selenio	mg/L	0,01	<0,010	<0,010	<0,010
A Cadmio	mg/L	0,001	0,00313 ± 0,00038	<0,0010	<0,0010
A Stagno	mg/L	0,005	<0,0050	<0,0050	0,00561 ± 0,00095
A Bario	mg/L	0,01	0,098 ± 0,018	0,056 ± 0,010	0,0533 ± 0,0096
A Piombo	mg/L	0,001	0,113 ± 0,015	0,00184 ± 0,00024	0,00161 ± 0,00021
*A Mercurio	mg/L	0,001	0,00209 ± 0,00029	<0,0010	<0,0010
Cromo esavalente [Su campione tal quale + APAT CNR IRSA 3150 C Man 29 2003]					
*A Cromo esavalente (come Cr)	mg/L	0,01	0,0107 ± 0,0012	<0,010	-
Fenoli (come C6H5OH) [Su campione tal quale + APAT CNR IRSA 5070 A2 Man 29 2003]					
A Fenoli	mg/L	0,1	<0,10	-	-
Tensioattivi anionici (come MBAS) [Su campione tal quale + APAT CNR IRSA 5170 Man 29 2003]					
A Tensioattivi anionici (MBAS)	mg/L	0,05	<0,050	-	-
Azoto ammoniacale [Su campione tal quale + APAT CNR IRSA 4030 A1 Man 29 2003]					
*A Azoto ammoniacale	mg/L NH4	0,05	0,406 ± 0,073	-	-

LAB N° 0080 L

RISULTATI

	Campione n°		PD22-01126.001	PD22-01126.002	PD22-01126.004
	Sigla campione		Scarico SP4 FBOO Tal quale	Scarico SP4 FBOO filtrato in campo	Scarico SP4 - Filtrato procedura Solvay
	Proveniente da		Solvay Rosignano	Solvay Rosignano	Solvay Rosignano
	Tipo campione		ACQUA	ACQUA	ACQUA
	Campionato da		Ns. personale - Lorenzoni	Ns. personale - Lorenzoni	Ns. personale - Lorenzoni
	Campionato il		31/03/2022	31/03/2022	31/03/2022
Parametro	**U.M.**	**RL**	**Risultato**	**Risultato**	**Risultato**
Fosforo totale (come P) [Su campione tal quale + APAT CNR IRSA 4110 A2 Man 29 2003]					
*A Fosforo totale	mg/L P	0,01	0,0145 ± 0,0037	-	-
*A Fosforo totale	ug/L P	10	14,5 ± 3,7	-	-
Solidi sospesi totali [Su campione tal quale + APAT CNR IRSA 2090 B Man 29 2003]					
A Solidi sospesi totali	mg/L	5	3860 ± 460	-	-

LAB N° 0080 L

RISULTATI

Campione n°	PD22-01126.003
Sigla campione	Scarico SP4 -SST raccolti su filtro
Proveniente da	Solvay Rosignano
Tipo campione	DEFAULT
Campionato da	Ns. personale - Lorenzoni
Campionato il	31/03/2022

Metalli [EPA 3050B 1996 + EPA 6020B 2014]

	Parametro	U.M.	RL	Risultato
*A	Boro	mg/kg	50	<50
A	Alluminio	mg/kg	10	219 ± 34
A	Cromo	mg/kg	1	<1,0
A	Manganese	mg/kg	1	85 ± 13
A	Ferro	mg/kg	10	225 ± 40
A	Nichel	mg/kg	1	<1,0
A	Rame	mg/kg	1	1,12 ± 0,93
A	Zinco	mg/kg	5	6,8 ± 1,2
A	Arsenico	mg/kg	1	<1,0
A	Selenio	mg/kg	1	<1,0
A	Cadmio	mg/kg	0,1	0,137 ± 0,034
A	Stagno	mg/kg	0,5	<0,50
A	Bario	mg/kg	1	1,70 ± 0,74
A	Piombo	mg/kg	1	4,78 ± 0,94
A	Mercurio	mg/kg	0,1	<0,10

Cromo esavalente (come Cr) [EPA 3060A 1996 + EPA 7196A 1992]

	Parametro	U.M.	RL	Risultato
A	Cromo VI	mg/kg	1	<1,0

LAB N° 0080 L

LEGENDA

NOTE

^	Eseguito presso laboratorio SGS esterno.	IS	Campione insufficiente per l'analisi.
^^	Eseguito presso laborotorio esterno.	LNR	Campione elencato ma non ricevuto.
RL	Limite di Rapportaggio	NA	Campione non analizzato per questo parametro
↑	Limite di rapportaggio innalzato	TBA	Parametro non ancora analizzato
↓	Limite di rapportaggio diminuito	†	Tempo massimo di conservazione superato
ND	Parametro non determinato		

NOTE RELATIVE ALL'ACCREDITAMENTO

*	Prova non accreditata ACCREDIA.

Il presente Rapporto è emesso dalla Società in accordo con le Condizioni Generali SGS per i servizi di ispezione e controllo (copia disponibile su richiesta). Il rilascio di questo Rapporto non esonera le parti negoziali dall'esercitare i diritti e dall'adempiere alle obbligazioni derivanti dal negozio tra loro stipulato. Ogni patto contrario non è alla Società opponibile. La responsabilità della Società in base a questo Rapporto è limitata al caso di provata colpa grave ed in ogni caso ad un ammontare non superiore a dieci volte i diritti e le commissioni dovute. Eccetto accordi particolari, gli eventuali campioni, se presi, non saranno trattenuti dalla Società per più di un mese. I risultati contenuti nel seguente Rapporto si riferiscono esclusivamente al campione provato e così come pervenuto se campionato dal cliente.
Il Laboratorio declina ogni responsabilità sui dati forniti dal cliente che possono influenzare la validità dei risultati. Il presente Rapporto o copia dello stesso verrà conservato dalla Società per un periodo pari a 10 anni.

Il recupero ove previsto, è da intendersi compreso all'interno dei limiti di accettabilità specifici (70-130% per microinquinanti ORGANICI, 75-125% per microinquinanti INORGANICI). Se non diversamente indicato il risultato è da intendersi non corretto per il recupero ottenuto.
Se non diversamente specificato, valori di concentrazione rilevati inferiori ai Limiti di Rapportaggio (RL) concorrono all'espressione delle somme e/o medie nella misura di 1/2 del Limite di Rapportaggio (criterio "medium bound").

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Eventuali risultati superiori al limite sono segnalati con una cella ARANCIONE.

A=Prova eseguita presso la sede di SGS Italia SpA Via Campodoro 25 – 35010 Villafranca Padovana (PD) – ITALIA
B=Prova eseguita presso la sede di SGS Italia SpA Via Campodoro 23 – 35010 Villafranca Padovana (PD) – ITALIA
C=Prova eseguita presso la sede di SGS Italia SpA Quarta Strada Z.I. Macchiareddu - 09032 Assemini (CA) – ITALIA
D=Prova eseguita presso la sede di SGS Italia SpA C.da Spalla Città Giardino - 96010 Melilli (SR) – ITALIA

--- Fine del Rapporto di Prova ---

OUT OF TEXT TABLES

Table 1: Statistical parameters in the North-Eastern Coastal Unit of Veneto

Horizon		Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
		mg / kg ds													
Surface	no. data	19	22	19	24	24	24	21	24	24	24	19	18	19	24
	Average	0.33	7.03	0.34	0.25	2.66	12.3	0.12	7.34	14	16.1	0.15	0.82	20.8	38.5
	Dev. St.	0.17	2.72	0.16	0.01	1.66	9.77	0.14	6.08	13.2	14.3	0.09	0.61	12.7	19.2
	Median	0.34	7.1	0.25	0.25	2	7.8	0.09	3.9	11	13	0.1	0.51	15	36
	Lower quantile	0.23	4.4	0.25	0.25	1.6	6	0.03	3.1	2.5	5.6	0.1	0.38	12	23
	Upper quantile	0.47	8.6	0.38	0.25	3.3	13	0.15	10	17	21	0.16	1.4	28	52
	95th percentile	0.56	11	0.64	0.25	5.7	32	0.37	19	38	45	0.32	2	43	70
	99th percentile	0.61	13	0.66	0.28	5.9	37	0.51	20	50	49	0.33	2.1	46	70
Deep	no. data	24	24	19	24	24	24	24	24	24	24	19	19	19	24
	Average	0.22	5.79	0.27	0.25	1.98	6.18	0.05	4.91	4.39	4.92	0.1	0.42	13.6	16.4
	Dev. St.	0.14	2.52	0.07	0	1.28	5.89	0.1	4.14	4.12	5.61	0	0.37	5.96	12
	Median	0.18	5.6	0.25	0.25	1.8	3.8	0.03	3.7	2.5	2.5	0.1	0.27	12	10
	Lower quantile	0.1	3.9	0.25	0.25	1.2	2.5	0.03	3	2.5	2.5	0.1	0.15	11	10
	Upper quantile	0.31	7.6	0.25	0.25	2.1	6.8	0.03	4.4	2.8	3.4	0.1	0.61	15	19

Horizon		Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
	95th percentile	0.48	9.3	0.28	0.25	5	20	0.1	15	11	15	0.1	1.1	22	46
	99th percentile	0.57	11	1	0	5.5	23	0.41	18	17	24	0.1	1.3	32	48

Table 2: Statistical parameters in the Veneto Southern Coastal unit

Horizon		Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
Unit of measure		mg / kg ds													
Surface	no. data	48	49	47	55	55	55	48	55	54	54	46	45	47	55
	Average	0.45	10.8	0.46	0.26	9.45	68	0.05	44	17.5	20.6	0.27	1.94	36.5	69.7
	Dev. St.	0.29	5.91	0.34	0.05	4.15	38.3	0.04	28.2	12.9	14.8	0.21	1.13	17.6	42.2
	Median	0.42	8.7	0.25	0.25	8.2	59	0.03	38	14	16	0.22	1.7	32	58
	Lower quantile	0.25	6	0.25	0.25	6.5	31	0.03	20	9.4	8.7	0.1	1.2	22	42
	Upper quantile	0.62	14	0.71	0.25	13	89	0.05	64	21	29	0.41	2.4	48	83
	95th percentile	1	23	1	0.26	16	144	0.13	96	42	48	0.68	4.7	70	158
	99th percentile	1.2	24	1.5	0.5	17	155	0.21	113	61	59	0.82	5.5	85	201
Deep	no. data	48	48	46	49	49	49	48	49	47	49	42	45	46	49
	Average	0.35	8.85	0.39	0.25	8.64	68.2	0.04	44.3	9.83	12.3	0.17	1.55	29.2	44.5
	Dev. St.	0.28	5.81	0.28	0	4.08	45.9	0.06	28.7	5.36	13.4	0.13	1.38	14.8	21
	Median	0.28	7.1	0.25	0.25	7	58	0.03	41	10	5.4	0.1	1.2	25	39
	Lower quantile	0.1	5.9	0.25	0.25	5.4	33	0.03	20	4.4	2.5	0.1	0.87	20	29
	Upper quantile	0.41	10	0.25	0.25	12	85	0.03	58	14	18	0.1	1.7	34	55

Horizon		Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
	95th percentile	0.88	20	1.1	0.25	16	166	0.06	105	18	35	0.46	3	56	84
	99th percentile	1.3	30	1.2	0.25	18	186	0.29	110	21	54	0.49	7	78	97

Table 3: Concentrations in the surface horizon of the beaches of the Isonzo plain

Municipality	Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	Ti	V	Zn	Al	Fe	Mn
	mg / kg ds																	
Grado							0.08											
Grado	<0.10	5.05	<0.10	0.2	<2	3.16	0.07	1.99	2.27	<0.1	<0.5	<0.5	<0.1	2.6	8.66	960	2000	512
Grado	<0.10	7.67	<0.2	0.2	<2	3.92	0.3	2.71	2.39	<0.1	<0.5	<0.5	<0.1	6.6	5.9	1500	2600	550
Grado							0.12											
Grado	<1	5.66	<0.2	0.2	<2	5.24	0.46	3.79	5.01	1.6	<0.5	0.8	<0.1	4.7	13.6	2200	3010	514
Grado							0.76											
Grado	<0.1	5.99	0.2	0.2	2.23	6.12	1.8	4.34	3.04	0.5	<0.5	<0.5	<0.1	5.2	12.6	2300	3540	481
Grado	<0.1	5.03	0.1	0.2	<2	10.7	3.5	4.67	2.29	1.4	<0.5	<0.5	<0.1	9.4	10.4	2400	3130	576
Grado	<0.1	5.31	<0.2	0.1	<2	4.33	0.24	3.06	2.76	<1	<0.5	<0.5	<0.1	4.2	9.54	1800	2720	541
Grado							0.83											
Grado	<1	5.77	0.3	0.2	3.72	7.9	1.9	6.51	3.01	1.1	<0.5	<0.5	<0.1	7.9	13.6	4300	4710	555
Grado							1											
Grado	<0.1	5.2	0.2	0.2	3.1	9.9	19	7.6	2.7	2.4	<0.5	<0.5	<0.1	12	14	3700	4700	600
Grado							1.2											
Grado	<1	2.12	<0.1	0.2	<2	4.15	0.76	3.45	3.83	1.3	<0.5	0.7	<0.1	3.1	9.35	1800	2260	313
Grado							3.3											
Grado	<1	4.52	<0.2	<0.2	<2	4.54	0.15	3.49	3.15	1.3	<0.5	0.8	<0.1	4.4	7.53	2000	2450	272
Grado							0.57											
Grado	<1	4.88	0.2	0.2	3.82	8.92	13	9.32	4.15	3.5	<0.5	<0.1	<0.1	8	13.1	3800	5270	435
Grado							1											
Staranzano	<0.1	1.36	<0.1	0.2	<2	3.98	<0.06	2.33	5.4	1.1	<0.5	<0.1	<0.1	5.1	13.3	1300	1670	181
Monfalcone	<1	2.16	0.2	0.2	<2	8.49	0.71	6.23	8.01	5	<0.5	<0.1	<0.1	9.8	22.9	4000	4710	219
Monfalcone							<0.06											
Monfalcone	4.99	5.5	<0.1	<0.2	<2	4.11	0.26	3.87	62.2	12	<0.5	32.4	<0.1	5.3	32.6	1300	5030	144
Monfalcone							<0.06											
Grado	<1	3.64	0.2	0.2	2.6	6.75	<0.06	7.36	4.25	2.6	<0.5	<0.1	<0.1	8.5	13.3	3900	4690	383
Grado	<1	3.86	0.2	0.2	2.39	6.78	0.1	6.41	3.78	2.7	<0.5	<0.5	<0.1	6.7	12.7	3800	4190	367
Grado							0.53											

Table 4: Concentrations in the deep horizon of the beaches of the Isonzo Plain

Municipality	Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	Ti	V	Zn	Al	Fe	Mn
	mg / kg ds																	
Grado							0.08											
Grado	<0.1	7.67	<0.2	0.2	<2	3.92	0.3	2.71	2.39	<0.1	<0.5	<0.5	<0.1	3.6	9.33	1600	2400	502
Grado	0.5	4.32	<0.1	0.2	<2	5.94	0.58	4.144	2.88	1.6	<0.5	<0.5	<0.1	8.2	10.1	2000	2960	531
Grado							0.19											
Grado	<1	5.66	<0.2	0.2	<2	4.57	0.34	3.27	4.61	1.1	<0.5	0.5	<0.1	3.8	23.2	1800	2880	479
Grado							0.71											
Grado	<0.1	5.48	0.1	<0.2	<2	4.3	0.63	2.89	2.79	<1	<0.5	<0.5	<0.1	3.8	10.3	1600	2580	466
Grado	<0.1	5.07	<0.1	0.2	<2	6.56	0.21	1.36	2.05	1.4	<0.5	<0.5	<0.1	10	8.89	2200	2980	594
Grado	<0.1	4.92	<0.2	0.2	<2	5.08	0.17	3.53	2.64	<1	<0.5	<0.5	<0.1	4.5	10.3	2200	2860	527
Grado							1.3											
Grado	<1	4.54	0.2	0.2	2.45	6.92	1.8	5.89	4.14	2.3	<0.5	<0.5	<0.1	6.6	14.4	3300	3860	379
Grado							0.87											
Grado	<0.1	10	0.4	0.2	6.9	24	7.5	27	5.5	9.1	<0.5	<0.5	<0.1	23	25	1100	1100	590
Grado							0.55											
Grado							0.16											
Grado	<1	6.52	0.3	0.2	3.39	8.21	0.52	7.68	3.74	2.5	<0.5	0.5	<0.1	7.5	13.6	3700	4260	384
Grado	<1	5.86	<0.1	0.2	<2	3.83	0.3	2.81	3.22	<1	<0.5	<0.1	<0.1	4.2	10.1	1300	2360	357
Staranzano							0.84											
Staranzano	<0.1	4.91	0.3	0.2	3.42	11.6	0.78	9.89	11.3	5.9	<0.5	0.6	<0.1	13	26.9	4300	4950	208
Monfalcone	<1	3.95	0.3	0.2	4.71	21.2	4.2	12.8	7.04	1.8	<0.5	<0.10	<0.10	13	16	5900	5710	615
Monfalcone	6.35	4.83	0.3	<0.2	4.64	15.5	0.44	15.3	40.6	10	<0.5	6.5	<0.1	15	34.5	5900	6450	190
Grado	<1	2.91	0.2	<0.2	<2	5.78	<0.06	5.62	3.43	2.1	<0.5	<0.1	<0.1	7.1	12.8	2900	3750	327
Grado							<0.06											
Grado	<1	7.23	0.7	0.2	5.35	23.4	0.25	20.5	9.19	9.3	0.6	0.5	0.2	27	25.3	11000	11000	213
Grado							<0.06											

Table 5: Metals concentrations on the coasts of Tuscany

Municipality	Location	As	Cd	Cr	Hg	Ni	Pb
Unit of measure		mg / kg ds					
Carrara	T. Parmignola - Porto M. di Carrara	7	0.3	313	<0.1	85	7
Mass	Porto M. di Carrara - T. Versilia	7	0.2	77	<0.1	70	6.6
San Giuliano T.	Serchio River - Bocca d'Arno	5.3	0.1	68	<0.1	21	5.8
Pisa	Serchio River - Bocca d'Arno	3.9	0.1	18	<0.1	18	4.3
	Marina di Pisa - Tirrenia	6	0.1	25	<0.1	21	6.1
	Calambrone	7.6	0.1	27	<0.1	25	6.8
Rosignano Marittimo	Vada (Pietrabanca - Pier)	4.2	0.3	43	<0.1	6.9	6.8
	Mazzanta (Pier – Fosso Mozzo)	17	0.3	338	<0.1	135	5.9
Cecina	Fosso Mozzo - Cecina River	9.9	0.3	560	<0.1	230	8.1
	M. di Cecina (F. Cecina - T. Cecinella)	20	0.4	650	<0.1	319	9.8
San Vincenzo	S. Vincenzo (Rimigliano)	37	0.2	91	<0.1	59	5.8
Piombino	Gulf of Baratti	33	0.2	34	<0.1	32	14
	Piombino (T. del Sale - Scrub)	11	0.1	12	<0.1	10	10
Follonica	Follonica (Pratoranieri - N. Solmine pier)	18	0.1	12	<0.1	10	10
Castiglione della Pescaia	Fosso Alma - Punta Ala	28	0.3	23	<0.1	23	3.6
	Castiglione p. (Rocchetto - Fosso Tonfone)	26	0.5	36	<0.1	31	7.4
	Castiglione p. (Fosso Tonfone - Harbour)	21	0.4	28	<0.1	29	6.4
Grosseto	Marina di Grosseto	8.7	0.2	30	<0.1	27	5.9
	Marina di Albense (Mouth	11	0.2	30	<0.1	31	6.6

Municipality	Location	As	Cd	Cr	Hg	Ni	Pb
	of the river Ombrone)						
Orbetello	Mouth of the river Albegna	21	0.5	20	<0.1	24	6
Capoliveri	Lacona	16	0.1	13	<0.1	9.6	5.6
Porto Azzurro	Spiaggia Reale	98	1.1	151	<0.1	176	11
Portoferraio	Warehouses	26	0.4	77	<0.1	57	18

Table 6: Metals concentrations in Minciaredda (Porto Torres)

	Cd	Cr	Fe	Ni	Cu	V	Zn	Pb
Unit of measure	mg / kg							
00-20 cm	0.05	1.82	881.46	2.85	1.7	5.13	4.94	2.03
	0.02	3.16	1793.3	5.6	1.7	9.6	11	3.58
	0.02	1.72	1865.22	3.61	1.7	7.62	9.23	2.01
	0.02	3.31	4138.46	4.06	1.93	10.25	11.99	2.13
	0.02	3.23	1167.87	4.37	1.7	4.56	6.27	2.18
	0.02	2.86	1241.6	2.76	1.7	3.94	6.31	1.58
	0.02	3.7	2026.76	4.65	1.7	6.59	7.76	2.52
	0.02	4.17	1534.16	3.54	1.7	6.14	6.89	2.35
	0.02	6.92	2771.93	5.26	1.7	9.55	9.36	3.76
	0.02	4.68	1701.8	3.67	1.7	0	10.25	4
95th percentile	0.04	5.91	3523.52	5.45	1.83	9.96	11.54	3.89
Average	0.02	3.56	1912.26	4.04	1.72	6.34	8.40	2.61
Median	0.02	3.27	1747.55	3.87	1.70	6.37	8.50	2.27
Dev. Std.	0.01	1.50	941.52	0.94	0.07	3.14	3.14	0.95
30-50 cm	0.02	2.33	1945.59	4.7	1.7	7.24	7.83	2.11
	0.02	2.25	1671.65	3.52	1.7	6.16	9.5	5.14
	0.02	2.42	2120.49	2.97	1.7	10.31	10.31	2.22
	0.02	3.1	1014.52	2.62	1.7	6.82	6.82	3.31
	0.02	0.46	395.8	6.33	1.7	0	4.75	2.85
	0.02	3.51	1459.85	3.16	1.7	3.95	6.51	3.55
	0.02	2.16	680.93	2.33	1.7	3.11	4.28	0.88
	0.02	5.76	2695.85	4.8	1.7	9.02	8.06	1.71
	0.02	4.57	1690.59	3.4	1.7	5.67	7.37	1.85
	0.01	4.66	2497.62	5.32	1.7	11.02	8.93	3.97
95th percentile	0.02	5.27	2606.65	5.88	1.70	10.70	9.95	4.61
Average	0.02	3.12	1617.29	3.92	1.70	6.33	7.44	2.76
Median	0.02	2.76	1681.12	3.46	1.70	6.49	7.60	2.54
Dev. Std.	Dev. Std.	0.00	1.54	750.15	1.30	0.00	3.38	1.94
50-70 cm	0.02	2.04	3195.08	4.76	1.7	9.33	7.74	1.41
	0.15	44.91	17436.81	41.27	6.12	41.07	85.9	9.68
	0.02	2.19	3045.59	4.07	1.7	7.93	9.12	2.35
	0.02	1.38	1949.42	2.92	1.7	6.03	7.78	3.31
	0.02	1.33	954.58	1.48	1.7	1.48	5.27	0.99
	0.02	2.44	1240.14	3.01	1.7	4.32	6.58	2.44
	0.02	6.08	7918.77	7.08	1.7	8.66	10.08	1.73
	0.02	3.38	1418.57	3.23	1.7	4.85	6.11	1.02
	0.02	3.85	1632.04	4.16	1.7	6.42	7.56	6.69
	0.01	0.5	576.96	2.71	1.7	0.97	4.07	0.6
95th percentile	0.09	27.44	13154	25.88	4.13	26.79	51.78	8.33
Average	0.03	6.81	3936.80	7.47	2.14	9.11	15.02	3.02

	Cd	Cr	Fe	Ni	Cu	V	Zn	Pb
Median	0.02	2.32	1790.73	3.65	1.70	6.23	7.65	2.04
Dev. Std.	0.04	13.48	5190.89	11.97	1.40	11.57	24.97	2.92

Table 7: Metals concentrations in the *"White Beaches"* of Rosignano

	Distance from discharge	Hg	As	Pb	Ni	Cr	Cd	Cu	V	Zn	Al	Fe	Mn
Unit of measure	m	mg / kg ds											
S0	10	0.01	16	18	4.5	49	0.4	7.7	8.2	31	2000	10000	212
S1	100	0.01	18	19	2.7	13	0.3	4.2	8.1	26	4000	7000	152
S2	200	0.01	20	18	0.5	6.5	0.24	5.4	6.1	15	2000	5000	131
S3	300	0.01	15	17	3.4	42	0.31	5.1	7.1	30	2400	8000	157
S4	400	0.01	19	14	7.8	47	0.17	11	3.1	13	1800	4000	137
S5	500	0.01	11	21	0.6	11	0.13	3.1	3.2	9.2	1400	2000	130
S6	600	0.01	11	10	1.7	14	0.16	1.8	5.2	7.8	2300	1000	140
S7	700	0.01	17	12	5.4	29	0.18	5.1	2.5	8.9	1600	2000	163
S8	800	0.01	11	16	1.6	15	0.16	0.6	4.7	7.3	2300	2000	149
S9	950	0.01	16	11	7.1	19	0.25	4	12	15	6100	3000	222