



ENVIRONMENTAL ASSESSMENT OF THE STATE IN FRONT OF THE SITE-ROSIGNANO SOLVAY

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1. ABSTRACT

The research described in this document has as its ultimate aim to respond effectively to the demands of the AIA requirements N.0000177 of 07/08/2015 (point 3), implemented by Solvay SpA of Rosignano and which verbatim reads:

" ...

- 1) the Operator must prepare and submit to the Competent Authority within 12 months of issuing the this AIA provision, an updated environmental study aimed at verifying the health of the marine environment in the area affected by the activities of the establishment; this study must consider all the biotic and abiotic components of the stretch of sea considered ... The study must also contain a comparative analysis with the original state of the places before the effects resulting from the presence of the Solvay plant and an analysis of the present and future;
- 2) The manager must transmit, every two years, the results of the verification carried out on the basis of the monitoring system in point 1 above;
- 3) the Operator must prepare and submit to the Competent Authority a feasibility study aimed at identifying the best design solution for the removal or safety of the mercury deposits lying in the stretch of sea in front of the establishment, taking care to outline the following scenarios for the introduction of suspended solids: a. current status and maximum production capacity; b. reduction (70%, 50%, 30% analysis) of soda production in the plant; d. interruption of operation and zeroing of soda production in the plant " .

An effective response to these requests was obtained by carrying out a complex environmental survey that involved a stretch of sea of about 100 km² in front of the Solvay industrial plant in Rosignano and an analysis of all environmental matrices (sediments, sea water, biota, atmosphere) in order to verify the sources, pathways and fate of mercury, considered a priority contaminant and whose biogeochemical cycle is among the most complex in nature.

First of all (through a complete geophysical survey) a high morphobathymetry was acquired resolution of the survey area and a clear description of the sedimentary substrate. Then, 51 cores of marine sediments were taken from which an important number of sub-samples with



variable resolution between 2 and 10 cm were obtained, analyzed from the point of view of mineralogical, granulometric, chemical composition (Hg, MeHg, and for half the number of cores collected also As, Cd, Pb, Cr, Cu, Ni, V, Zn, Al, Fe and Mn). Six of the sediment cores collected were also analyzed, in terms of the vertical distribution of the radionuclides, useful for a timely dating of the records and to estimate the sedimentation rates in the different survey areas. Flows from sediment to seawater and mercury flows from seawater to the atmosphere were measured. Possible contamination phenomena on the 12 beaches adjacent to the Solvay plant (the famous "white beaches" of Rosignano, a real local tourist attraction) through chemical and ecotoxicological analysis. The values of contaminants on the suspended solids emitted by the Solvay plant were also measured directly on the marine-coastal area in front. The quality status of the water and sediments was assessed.

The concentration levels of Hg, As, Cd, Zn, Ni and Cu were measured on a significant number of samples belonging to a group of fish species of particular commercial interest in order to evaluate the potential transfer of these metals along the food chain. marina.

On the modeling front, numerical simulations have been carried out relating to the dynamics of the currents that persist in the area of interest (supported by appropriate current and measurements hydrographic carried out in various measurement campaigns carried out in the survey area) and to the effects of transport, deposition and erosion of the sediment present at the bottom also as a function of possible reductions to 70, 50, 30 and 0% of the flow of suspended solids by the Solvay industrial plant in Rosignano.

The amount of data is significant and offers a clear image of the sedimentological and chemical-processes physical that persist in the study area, creating, even after comparing the data obtained with the information available in the bibliography and relating to numerous measurement campaigns carried out in the various environmental sectors in the past thirty years, a robust and adequate conceptual matrix to respond to the cognitive and management needs posed by the aforementioned AIA prescription.

2. Conclusions

On the basis of what has been elaborated in this study, it is possible to respond in a timely and adequate manner to the questions posed by point 3 of the AIA prescription No. could have a decrease in the quantities of suspended solids introduced by the Solvay plant.

The significant amount and type of data collected made it possible to understand in depth and in terms of spatial and temporal variability, the processes and dynamics that characterize the area of interest and it is therefore possible to provide clear information on the chemical-physical and biological phenomena that characterize it.



The survey made it possible to verify the progressive and unequivocal improvement of the environmental status of the investigated area (both for the abiotic and biotic sector) compared to the industrial period prior to 1976. Also the comparison with the results recently obtained by ARPAT (Regional Agency for Protection of the Tuscany Environment) from similar environmental investigations supports this evidence.

In particular, a large stretch of sea in front of the famous white beaches of Rosignano appears to be characterized by phenomena of effective burial of the underlying sediment layer. The remaining investigated area (especially the outermost area with respect to the coast) appears to be influenced by a complex sedimentary dynamics which, in some cases, involves the exposure of sediment characterized by Hg contents (mercury) higher than the SQA values. (Quality Standard Environmental). However, of the entire volume of sediment investigated only 0.0177 km³ (about 18% of the total analyzed) are characterized by Hg content > SQA.

On the other hand, there are no contaminations by heavy metals (including Hg) and organic compounds on the beach of Rosignano Solvay (Ref. Tab. 1, All. 5, Part IV, Title V, D, Lgs. 152 of 2006).

Below are reported in greater detail some of the most relevant evidence taken from the study carried out:

- 1) In the area of interest there is, at a depth of up to 40 cm, a layer of sediment, with a thickness varying between 5 and 20 cm, having concentrations of Hg higher than the EQS value (0.3 mg/kg) established by Ministerial Decree 260/2010 and by Legislative Decree 172/2015, for marine sediments; in certain points the concentrations exceed the above limit by an order of magnitude and, in some areas, the layer characterized by Hg > SQA contents is present on the surface, at the interface with sea water. Methylation processes of Hg can be favored by the chemical-physical conditions of the sediment (especially as a function of the low values of Eh- redox potential - measured). The concentrations of MeHg (Methylmercury) are generally proportional and well correlated to the contents of total mercury, even on the surface. The investigated system is substantially characterized by the presence of Hg of natural origin on which contributions of an anthropic nature of historical origin have been added (referring above all to the period prior to the entry into force of the Merli law of 1976) which, due to processes hydrodynamic and sedimentary dynamics, interfere with the current mechanisms of deposition of material characterized by concentrations of Hg < SQA, exposing, at the interface with sea water, sediment with higher Hg contents.



2) Hg fluxes calculated at the atmosphere-sea interface are negligible if compared with measurements carried out in areas characterized by the presence of variable Hg concentrations in sediments. The Hg flux values calculated at the sediment-water interface, with all the limits related to the reduced number of measurements, were 1.6 ± 0.3 and 3.4 ± 0.4 $\mu\text{g}/\text{m}^2 / \text{day}$ for the two points investigated. From this it emerges that the transfer of Hg from the sediment to the water column is in some way active, albeit reduced, as evidenced by the concentration levels of Hg measured in the dissolved phase, always below the SQA-CMA levels (Quality Standards- Maximum Permissible Concentration). The value of the mercury flow from the sediment to the water column is also limited in the station with a Hg \gg SQA content in the most superficial part, which suggests a reduced potential for transfer of the element to the aqueous compartment.

3) The set of sedimentary phenomena investigated suggests a strong variability of the erosive-depositional processes that persist in the area. The 5 different scenarios analyzed on the basis of hydrodynamic modeling, each of which characterized by a different flow rate of the suspended solids calculated at the discharge of the Fosso Bianco della Solvay (corresponding to a relative load of 100%, 70%, 50%, 30% compared to the current value and the total absence of the same), show that: i) the area in question, with the exception of the stretch of coast in front of the Solvay drain and the town of Rosignano, is characterized by the presence of predominant phenomena erosive (especially during the autumn-winter period), as also confirmed by various geological and sedimentological studies relating to the state of erosion of the coasts of the Tuscany region; ii) the thickness of sediment with concentrations of Hg $<$ SQA in the stretch of sea relating to 1-1.5 km of coastline in front of the white beaches of Rosignano is about 40 cm thick and is effective in isolating the underlying sediment; iii) the presence of depositional processes in the area in front of the Solvay discharge and the built-up area of Rosignano is mainly due to the load of sediments leaving the discharge itself; iv) a reduction of the outgoing solid load (already with values of 50% compared to the current one) could have the immediate consequence of a) reducing the thickness of sediments deposited not only in the coastal area in front of the discharge but also in the more external and therefore b) to counter in a less effective way the erosion processes of the seabed sediments. In the event of a complete interruption of the introduction of suspended solids from the drain, the thicknesses of sediments deposited in the area in front of the drain and the built-up area of Rosignano would also be progressively lacking. Therefore, the constant emission of suspended solids from the Solvay industrial plant in Rosignano in quantities similar to those currently



reported, represents a safety element for the marine-coastal environment under examination due to production (especially in the area adjacent to the coast) of an uncontaminated sediment thickness above the range characterized by $Hg > SQA$. An interruption and / or a decrease in this flow of particles, which are followed by the deposition processes, would entail that erosion, resuspension and transport of the most superficial part of the sedimentary layer would risk further reducing its thickness or even exposing it to the water-sediment interface larger areas characterized by relatively higher Hg concentrations.

4) Net of the complex dynamics to which the investigated area is subjected and of the strong variability in the deposition processes in the different sectors of the area itself, it emerges that the sedimentation rate values vary from 0.19 to 1.7 cm year⁻¹. The tendency to a progressive lowering of the Hg concentration values in the superficial sediments, a process which is however complicated by all the post-depositional dynamics linked to the oceanographic and sedimentary dynamics of the area, certainly represents a positive evaluation element.

5) As for most of the water bodies of the Tuscany Region, the concentrations of arsenic (As), cadmium (Cd), total chromium (Cr) and nickel (Ni) measured in the sediments exceed the EQS values in almost all of the intervals sedimentary plants analyzed. Overruns of these limits were also detected for lead (Pb) in the majority of the levels considered. However, it should be noted that the concentrations of As, Ni and Cd are generally lower than the natural background values (VFN; ARPAT, 2015), while the Pb contents are lower or slightly higher than the VFN. Only for Cr is there a significant overcoming of the VFN in most of the levels analyzed; however it is emphasized that the highest concentrations were measured in the pre-industrial sedimentary ranges. At such levels, Cd and Ni concentrations were also higher than those measured at industrial levels. On the other hand, no significant differences were found between pre-industrial and industrial levels for As and Pb. These evidence, together with the inverse correlations measured between Cd, Cr, Ni, Pb and the content of calcite in the sediments, allow us to hypothesize, for these metals, a different source from the Solvay plant. However, it should be emphasized that Cd concentrations higher than the EQS values but always lower than the VFN, were also detected in the suspended solids of the industrial waste. This may have contributed to the overruns recorded in the sediments, overruns presumably related to a natural origin of these elements. With regard to As, which is not significantly correlated with the other metals or with the mineralogical phases present in the sediments, no enrichment was recorded in the different sedimentary intervals identified (superficial, industrial and pre-industrial). On the other hand, the concentrations



of As measured in the suspended solids of the discharge were found to be <EQS, confirming the hypothesis of the existence of a source different from the Solvay plant also for this element.

6) Generally speaking, the mercury levels detected in the marine biotic sector respect the limit imposed by the current legislation on products intended for food consumption (EC Reg. 1881/2006). However, exceedances of the above limit have been observed in some specimens belonging to the species *Mullus* spp., *Scorpaena porcus*, *Diplodus* spp. and *Torpedo marmorata* taken from Rosignano-Vada. The Hg levels found in the mussel pulp are in excess of the EQS value envisaged by Ministerial Decree 260/2010. It should be emphasized that similar, or even greater, excesses were found in specimens taken in fishing areas not affected by the discharge of the Solvay plant.

It should also be emphasized that, with the exception of arsenic, the trend in the concentrations of metals over time in the pulp of the mussels planted in Vada, highlighted a phenomenon of bioaccumulation in the investigated species. These results identify in the historical Hg contamination of the investigated area the primary source in the contaminant transfer processes from the environment to the biotic compartment.

7) The monitoring carried out for the purpose of assessing the chemical status (Ministerial Decree 260/2010; Legislative Decree 172/2015) showed the failure to achieve the "Good" chemical status (NB), both for water and for sediments, in the stretch of sea in front of the plant. The data relating to the sediment matrix confirmed the trend of the previous years (2010-2015), recording an overrun of the limits for Ni, Hg and hexachlorobenzene. With respect to the water matrix, compared to the past, the SQA values for Cd, Ni, Pb have been exceeded and an improvement with respect to the TBT parameters is-tributyltin-recorded (<SQA) and Hg. However, the measured values were found to be below the natural background values reported by ARPAT (2015). If these values were transposed by environmental legislation, according to the directives of Ministerial Decree 260/2010 relating to the Geochemical Regions that have natural background levels higher than the EQS, the assessment of the chemical state of the study area would change to GOOD STATE.

8) In accordance with the provisions of current legislation (DM 260/2010 point A3.6) and downstream of the environmental survey carried out, it is suggested the activation of a "survey monitoring" that allows to deepen the real risk for the environment and the marine ecosystem potentially deriving from the exceeding of the Environmental Quality Standard, in the specific case identified for Hg. It is



therefore advisable to carry out an appropriate risk analysis able to investigate and verify the real effect that this contaminant can have on the marine environment and its ecosystem, also based on the encouraging results obtained in the context of the investigation on the biological sector in the area of interest. Only after this in-depth analysis will it be possible to assess the need for an intervention of possible environmental recovery which, however, would be very complex in light of the specific geological and hydrodynamic characteristics of the area (high bathymetry, high dynamism of the area, etc.). Furthermore, the very limited availability of experimental data on similar intervention cases makes the choice of possible design solutions very complex and leads to extremely prudent assessments regarding the real benefit that the environmental system considered could actually register.
