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Applicability of H14 Protocol for Sediments in Order to Consider their Valorization: Limits and Benefits

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Community and national regulations impose to do not discharge harbor sediments into the sea without first measured the level of pollution and assessed the risk of impacts on the marine environment by the use of ecotoxicity tests on marine species. If the immersion is impossible, sediment has to be directed to inland areas where they have the status of waste. Then, it must identify whether the waste is hazardous or not.
The H14 "ecotoxic" property of the EU Waste Directive, which is conventionally used for the characterization of hazardous waste in case of multiple contaminations, can be applied to sediments. In case of strong positive response to ecotoxicity tests on terrestrial species, the sediment must be managed as a hazardous waste and it must be oriented to regulated waste storage sites. For sediments that do not have a significant toxicity, two alternatives are available for the decision makers: the deposit of sediment in landfills or the valorization of sediments as secondary raw materials (SRM).
The SEDIVALD project aimed to test the application of H14 protocol on a set of marine, lake and river sediments where the main regularly pollutants were dosed. The results of these tests showed first a large variability in levels of sediment pollution, which was fairly predictable because of the types of activities for the concerned ports and watersheds.
In numerous cases, the H14 protocol was effective for characterizing the level of hazard of sediment and seemed correlated with the levels of pollutants measured. In contrast, other sediments were identified as ecotoxic by the H14 protocol without that the dosed pollution left it supposed. According to classical chemical analyzes, sediments appeared not to be polluted and logically should not have to meet H14 protocol. The origin of the pollution (pesticides or other) must be sought because these hazardous wastes could be used in beach nourishment.
The SEDIVALD project has demonstrated the applicability of the H14 protocol to characterize the hazard level of sediments from the ecotoxicological point of view, but it also showed the importance of further investigations to detect contaminants that are not usually taken into account. This is particularly important because the sediments managed in land should be treated by physicochemical and biological processes to enable their valorization as SRM.

1. Context and scope of SEDIVALD project

1.1 Context

Sedimentation of mineral and organic particles from soil and rocks, fauna and flora, human activities or movement of sediment on the bottom, is a natural and continuous phenomenon in freshwaters as marine waters. Accumulation of sediments in quiet areas (lakes, canals, ports ...) requires periodic cleaning to keep the activities. Most dredged material in ports and channels are rich in fine sediments. They often have a high content of organic matter and contain a significant amount of sulphides and are often anoxic. These conditions facilitate the accumulation of many contaminants when the sediment is not subject to the action of waves and currents that can suspend them.
Some marine and inland sediments contain many anthropogenic substances, some of which have a toxic character: heavy metals, tributyltin (TBT), polycyclic aromatic hydrocarbons (PAHs), polychlorinated

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biphenyls (PCBs), pesticides and biocides whose effects on health are multiple (carcinogenic, mutagenic, toxic for reproduction).

In the case of dredging operations there are two categories of sediment:

- Sediments called submersible (or on-site management for river sediment). They are very slightly contaminated sediments, whose environmental quality is close to the observed geochemical background, due to the absence of anthropogenic pressure, the frequency of dredging or their natural granulometry;
- Sediments called non-submersible because too contaminated for dispersion in the aquatic environment that is a particularly sensitive and fragile environment. These sediments must be directed to the land where they take the waste status: this implies an increase of cost for the companies and ports in addition of the dredging operations. Solutions to depollute and valorise the sediments as secondary raw materials (SRM) must be developed, according to their geotechnical nature and their pollution levels.

The issue of dangerousness assessment covers all waste. It applies to non submersible sediments for which inland management must be organized and they take in this case the status of waste. The assessment of dangerousness of waste is carried out by 15 hazardous properties of Directive 2008/98/EC (November 2008). Once a waste meets one of the 15 properties, it is considered as dangerous. The definition of hazardous waste from the previous question is to guide the possible management methods for the Project Owner.

The status of sediment defines the technical, administrative and financial organization of terrestrial supply chains that are possible to implement for the reuse of sediment. According to the very high levels of contamination that can be encountered on very specific areas in marine ports or rivers (fairing areas, fuelling areas, industrial releases…), it is possible that a proportion of this sediment contains one of the 15 regulatory properties which classify this waste in hazardous waste, especially for the H14 "ecotoxic" property which can be applied to sediments.

1.2 Scope

The SEDIVALD project focuses on the characterization of sediments before dredging in connection with maritime and inland management strategies. Particularly in the context of an orientation to the inland management of sediments, the project examines the hazardous or non-hazardous waste status through H14 and H15 properties of Annex III of the waste Directive 2008/98/EC (Garbolino et al., 2013). The study of the H14 property aims to assess the dangerousness of "waste-sediment" by a "Ecotoxic" approach.

The SEDIVALD project contributes to a national consultation of the French Ministry of Ecology through a national test of H14 "sediment" protocol. The project provides all the Mediterranean samples managed by the General Direction of Risk Prevention (DGPR).

The SEDIVALD project gave the first elements of reflection on the possible effects of laboratory protocol and on possible adjustments to the protocol for continental sediments. The SEDIVALD project also aimed to generate data on environmental and geotechnical characterization. Environmental characterization data consist of physicochemical analyzes on raw sediments, leaching tests, percolation tests and analyzes of the supernatant water during the sampling. Geotechnical characterization data are derived from particle size testing, blue testing and dosing of organic matter. The production of these additional data analysis has led to progress on the reflections according the terrestrial scenarios like storage or valorization and improving knowledge about the sediments of Rhone Mediterranean Corsica basin.

2. Methodology

In relation to H14 property and environmental analyzes, the project began with a campaign of underwater sediment sampling on all ports and river sites selected for the project according to suspected levels of contamination. Each sample has been homogenized on site before separation to be sent to different laboratories for environmental, ecotoxic or geotechnical analyzes. After the realization of laboratory tests, the project focused on their interpretation.

2.1 The H14 protocol applied to sediments

H14 protocol (Figure 1) has been the subject of a national test conducted by BRGM (Bureau of Geologic and Mining Resources). The protocol includes a step of centrifugation prior to remove the chlorides that may mask toxic effects of real contaminants. This centrifugation step is necessary because the terrestrial species always react to the presence of chlorides, which imped measuring the effects of the toxic cocktail due to multiple contaminants like heavy metals, PAHs, TBT and other unmeasured pollutants such as pesticides. The non-consideration of chlorides means that this issue should be treated at the beginning of inland management scenario.

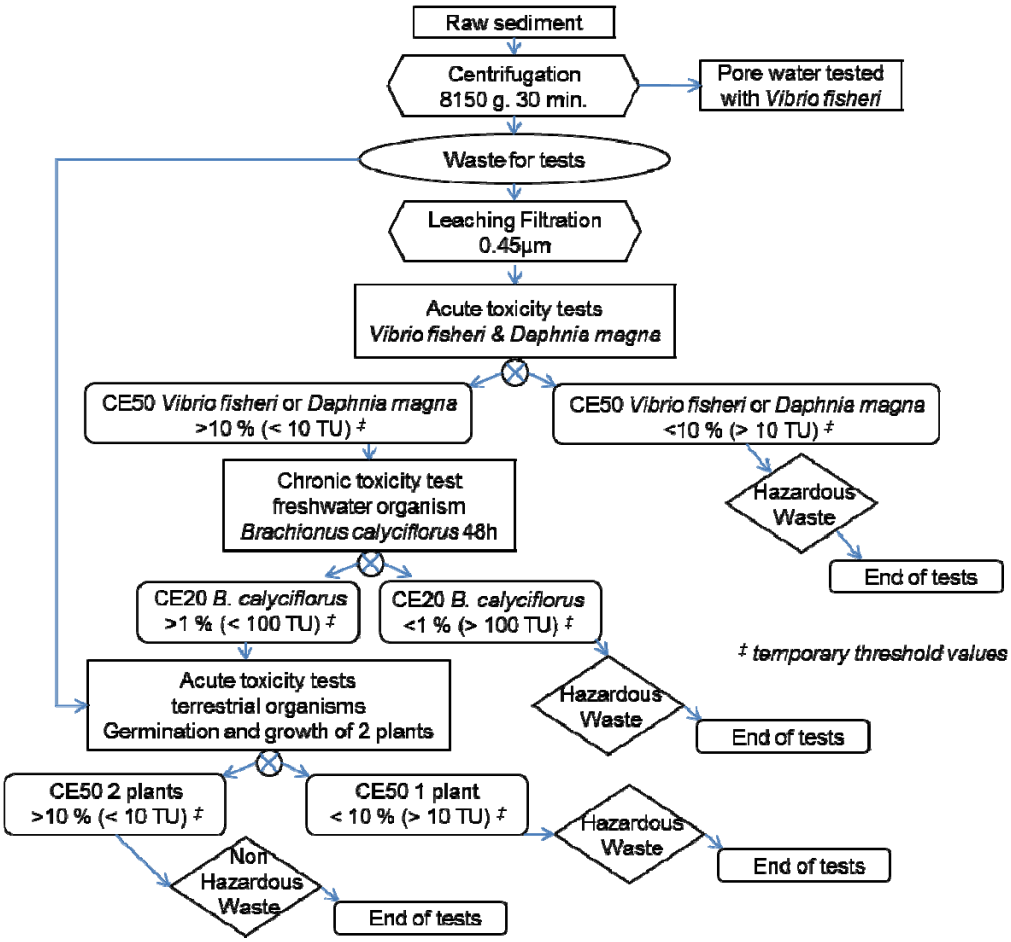

Figure 1: H14 protocol applied to sediments (Mouvet et al., 2009)

The protocol provides the implementation of successive acute and chronic tests from the eluates and then acute tests on terrestrial organisms on sediment matrix. No response at all stages is required to be declared as non-ecotoxic and to not be classified as hazardous waste. H14 protocol base solution or modified solution (without centrifugation for river sediments) was implemented 17 times. The results of tests were interpreted in reference with usual dilution thresholds, although not regulatory, set at 1 % for chronic tests and 10 % for acute tests.

2.2 Toxical analysis of sediments

The content of the environmental analyzes, carried out specifically under SEDIVALD, is enounced in the following points:

- 17 physicochemical analyzes for MTEs – Metal Trace Elements; les PCBs – PolyChlorinated Biphenyl; les PAHs – Polycyclic Aromatic Hydrocarbon; les TBTs – TriButylTin), et les Heavy Metals ;
- 8 leaching tests;
- 4 percolation tests;
- 7 geotechnical characterization.

2.3 Sampling

17 sediment samples were collected from four geographical areas of the Rhône-Mediterranean-Corsica Basin (Figure 2):

- Région Provence Alpes Côte d'Azur – Département of Var : 11 points in Toulon harbor;
- Région Provence Alpes Côte d'Azur – Département of Alpes Maritimes : 1 point ;
- Région Languedoc Roussillon – Département of Hérault : 4 points with 3 points in marinas and/or fishing ports and 1 river point on the reach south of Narbonne;
- Région Rhône Alpes : 1 lake point.

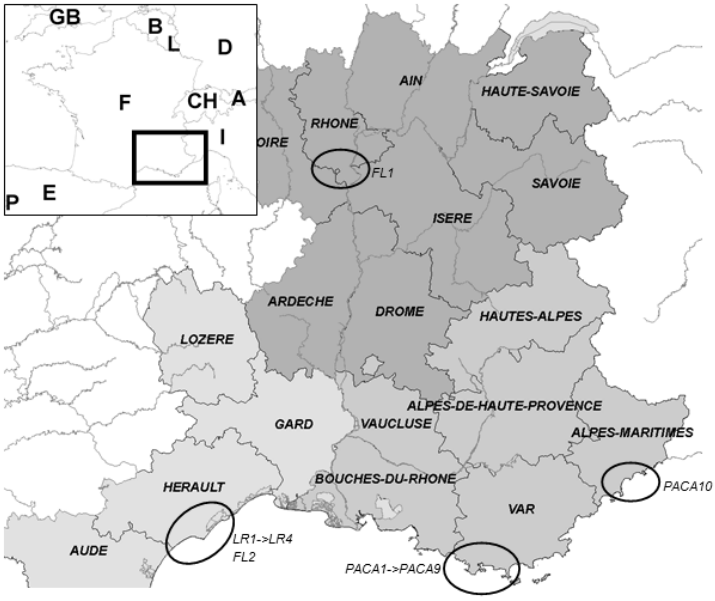

Figure 2: Location of the sampled sites

Points were selected based on high levels or suspected contamination and taken from surface sediment matrix. Environmental analyzes correspond to highly contaminated areas, not necessarily requiring dredging but representative of extreme cases of pollution in order to test the H14 protocol.

3. Results and discussion

Concerning the possibility of positioning sediments according to the dangerous or not-dangerous status through the H14 property, the results confirmed the interest of the tested protocol. The protocol allowed the identification of "dangerous waste" sediment and, in some cases, unexpected toxic response for sediments supposed uncontaminated according to to substances conventionally dosed in France with the "Geode" series. During the SEDIVALD project, the number of "dangerous waste" sediments appeared much lower than the number of non-hazardous sediments. These results are consistent with the conclusion of the BRGM study at national level but with a percentage of dangerous waste higher for the Mediterranean panel than for the national panel. Through these results (table 1), SEDIVALD shows interest in cross characterizations essentially based on physicochemical analyzes of total content, with toxic evaluation because the project has highlighted ecotoxicological sediments qualified as hazardous waste, free from usually dosed contaminants.

It is therefore necessary to consider the need to broaden the nature of the pollutants to be analyzed before dredging in the case of an inland management.

The results show that the three sediments of Languedoc Roussillon LR2, LR3 and LR4 are toxic to be classified as "hazardous waste" (LR2 and LR4) or very close to the limit of toxicity of a hazardous waste (LR 3). Analyses of these sites were made by two different laboratories, and sites that are separated by more than 100 km. These results raise questions because the sediments of the LR series seemed “uncontaminated” according to substances measured under the "Geode" series. The question of the origin of pollutants is asked (pesticides, drugs...). The valorization of such sediments for beach nourishment is therefore excluded.

Table 1: Results and comparison of H14, GEODE and PEC-Q analysis. A=authorized; NA=Not Authorized; LA=Limit to be Authorized. H=Hazardous; NH=Not Hazardous; LH=Limit to be hazardous

	PACA1	PACA2a	PACA2b	PACA3	PACA4	PACA5	PACA6	PACA7	PACA8
H14	NH	LH	NH	NH	-	NH	NH	-	-
GEODE	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mean PEC-Q	0.29	1.56	1.31	1.74	2.12	0.93	6.12	5.51	2.63
	PACA9	PACA10	LR1	LR2	LR3	LR4	FL1	FL2	
H14	NH	NH	-	H	LH	H	NH	NH	
GEODE	NA	NA	NA	NA	LA	LA	NA	NA	
Mean PEC-Q	2.17	0.67	0.65	0.29	0.29	0.21	0.49	0.45	

Mean PEC-Q (Probable Effect Concentration Quotient, see Wenning et al., 2000 for the calculation procedure) provides a sediment assessment tool that distills data from a mixture of contaminants (metals, PCB, PAHs) and provides a way to compare sediment quality over time and space (Long et al., 2006). As mentioned by (Crane et al., 2000) the incidence of toxicity increases as the mean PEC-Q ranges increased. Mean PEC-Q is usually decomposed into five classes (≤0.10; >0.10 to ≤0.50; >0.50 to ≤1.0; >1.0 to ≤5.0 and >5.0) and in this classification, values superior to 0.3 mean that the sediment can be considered as toxic (Wenning and Ingersoll, 2002).

In addition, the SEDIVALD project showed, in order to identify the hazardous nature of the sediments, that it is important to detect the different forms or traces of metals in sediments. In particular, three metal forms (lead (Pb), zinc (Zn) and copper (Cu)) are significantly present and, depending on their speciation, they might generate overruns of values limits that make the sediment as hazardous waste despite any toxicity test.

4. Conclusion and perspectives

SEDIVALD project showed the relevance of the application of H14 protocol to determine the dangerousness of sediments. The results presented are instructive because they show a lack of simple correlation between the presence of pollutants in the "Geode" tests and the results of ecotoxicological tests: sediment initially identified as uncontaminated may then appear hazardous with the H14 protocol. Thus, there are two types of sediments that can be considered as hazardous waste:

- High contaminated sediments and identified through the analysis of the “Geode” tests for which a toxic response is clearly expected. They are located in the most contaminated areas according to the ports activities. They are particular sites with a story of heavy pollution, high levels of anthropogenic activities (military fairing areas, shipyards, industrial ports, etc.). These areas require a special vigilance during dredging activities because they correspond to the most probable cases that may include sediments classified as "hazardous waste". However, it is noted that on the whole panel, the majority of the sediments should not be regarded as hazardous waste, but as a not-inert and non-hazardous waste. This consideration confirms that the largest volume of sediments will not respond to H14 protocol and therefore they shouldn’t be considered as hazardous waste.
- Ecotoxicological sediments but whose toxicity has not been demonstrated because of unidentified substances not assayed in the "Geode" series of regulatory substances like sediments from the Languedoc Roussillon.

These results can also be integrated into the modelling of process and activities that participate to valorize the sediments (Hardy and Guarnieri, 2011).

In conclusion, the results of the SEDIVALD project concerning the "H14" protocol are consistent with the results of the national survey conducted by BRGM and show that the protocol is a relevant operational tool for identifying sediments considered as "waste-dangerous" to other sediments. Its application can therefore be considered with some modifications to simplify the procedure and to detect more quickly ecotoxicological sediments. This simplification may be adopted to test dilutions from 1 %, then 10 % in order to reduce the time and costs. In this context, the application of the systematic use of H14 protocol for all dredging will be regarded in addition to toxicity tests that, for the moment, show that only 20 % of the sediments analyzed in the most contaminated French sites are dangerous.

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