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Physicochemical Characterizations of Marine and River Sediments in the North of France

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***Abstract*—This work is undertaken to develop a methodology to enhance the management of dredged marine and river sediments in the North of France. The main objective of this study is to determine the main characteristics of these sediments. In this order, physical, mineralogical and chemical properties of both types of sediments are measured. Moreover, their potential impacts on the environment are assessed throughout leaching tests. From the obtained results, the potential of their use in road engineering is discussed.**

***Keywords*—Marine sediments, River sediments, Physicochemical characterizations, Environmental characterizations.**

I. Introduction

DREDGING is a permanent operation to maintain navigation in waterways and access to ports. It produces a considerable quantity of sediments. The traditional solutions such as the immersion and the deposit are likely to redistribute pollutants into the environment. It is thus necessary to find new managing methods which enable to respect the criteria of sustainable development and use reliable processes from economical point of view.

In this context, beneficial use of dredged sediments could enhance the management of natural resources in various fields as in: civil engineering works, manufacture, agriculture or rehabilitation of natural sites [1]-[3]. In France, the civil engineering consumes approximately 400 million tons of granular materials in 2004 [4]. Among various sectors of civil engineering, the road field demands are the largest part (50.7% in France) [5]. Also the performances needed, for used materials in road construction domain, are various depending on the road category, the layer in the road structure, the type and the amount of binders.

Dredged sediments are complex materials including organic matter, metals and pollutants. According to the French decree of 18 Aprils 2002 [6], sediments are classified as a waste. For their beneficial use in road construction field, in addition to the physical and chemical characteristics it is important to classify these materials in the road domain and determine their potential impacts on the environment. In this study, the physical, the mineralogical, and the chemical characteristics of marine and river sediments from the North of France are discussed.

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II. Presentation of Site

In the middle of the triangle formed by Paris-London-Brussels, the port of Dunkirk, France's third port, handles annual cargo traffic of more than 56.65 million tons and receives about 7060 ships a year. Regarding sedimentary activity, approximately 4 million m^3 of mud are dredged each year [7]. The marine sediments were dredged from this port, in the zone called “Réparation Navale”. This zone is considered as polluted, according to a zoning study carried out in the port [8].

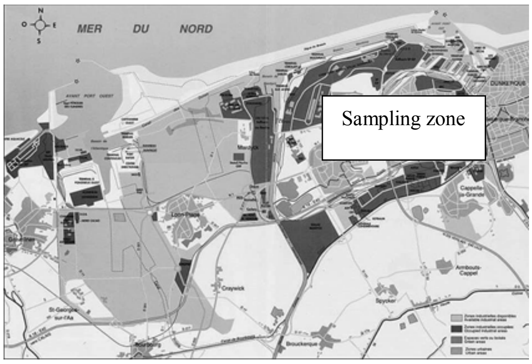

Fig. 1 (a) Sampling zone of marine sediments

Fig. 1 (b) Sampling zone of river sediments

The river sediments were dredged from the canal called the “upper Scarpe” which cross the town of “Brebières” situated about 50 km from the city of Lille (France). The sampling was carried out in the middle of the canal using an excavator, and then the sediments were stored in hermetic plastic barrels.

III. Test Results and Discussion

A. Physicals Analysis

The main physical characteristics determined for both types of sediments are: particles size distribution, quantity and the activity of clay fractions, organic matter contents, Atterberg limits and absolute density. The values obtained have allowed classifying both materials according to the guide in use, in France, for road materials classification (GTR) [9].

The particle size distribution (also called grain size distribution or texture) is one of the most important characteristics of soils. The particle size distribution has an effect on several properties of the material such as the compaction, the permeability, the moisture content, etc.

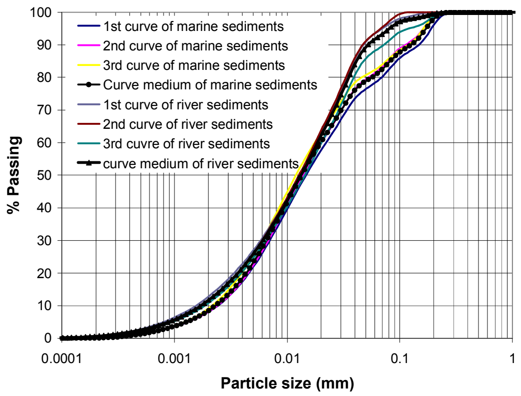

Fig. 2 Particle size distribution of the sediments

The particles size distribution of the sediments was determined by the granulometer laser. The grain size distribution curves for both sediments are shown on Fig. 2 in terms of cumulative weight percent passing versus particles size. Fig. 2 shows that the sediments are composed mainly of fine particles (particles size less than 80μm). The proportion of fine particles is close to 95% for river sediments and close to 85% for marine sediments. In terms of particles size, the river sediments contain more clay proportion (particles size less than 2μm) than the marine sediments. For river sediments, the clay content is close to 12% whereas for marine sediments the clay content is close to 9%.

The activity of clay minerals in the sediments is evaluated by methylene adsorption method, according to test standard NF P 94-068 [10]. The tests results for each type of sediments shown on Table I are the average value of three tests. These results are in correlation with the analysis of particles size distribution which shows a larger proportion of clay in the river sediments than in the marine sediments. According to the blue methylene values (BV), the sediments present a relatively active fraction fine and are classified as a silty soil. In practice, this type of material requires treatment before use in road construction.

The organic matter content (OM), for both sediments, was determined using two methods: By ignition method at 450°C according to test standard XP P 94.047 and by sulfochromic oxidation according to test standard NF ISO 14235 [11], [12]. In the second method, the organic matter content is deduced from the proportion of organic carbon by multiplying the latest quantity by 1.72 [13].

As shown on Table I, test results seem to be consistent for marine sediments where organic matter content of about 8% is estimated with both methods whereas for river sediments the relative difference observed is close to 100%. The difference in the results observed, for river sediments, seems to be due to the presence of a higher amount of Smectite which could induce more weight loss by heating due to the loss of combined water [14].

TABLE I
PHYSICAL CHARACTERISTICS OF DREDGED SEDIMENT

Parameters	Marine sediments	Rivers sediments
% < 2µm (clay)	9%	20%
2µm < % < 63µm (silt)	53%	71%
63µm < % (sand)	38%	9%
Methylene blue value	3.4	4.2
% MO by ignition	8.6	7.2
% MO by oxidation	7.2	3.1
LL (%)	89.4	49.5
PL (%)	35.5	28.0
PI (%)	53.9	21.5
ρ (t/m^3)	2.53	2.56
ρs (t/m^3) heated at 4500C	2.69	2.66

The Atterberg limits are determined according to test standard NF P 94 051 [15]. The liquid limit is measured by using Casagrande apparatus and the plastic limit by rolled thread technique. In terms of the plastic limit both type of sediments exhibit a value around 30 % where as for the liquid limit, the marine sediment exhibits a value almost twice that of river sediments. This result, according to complementary study, is mainly due to the presence of organic matters.

In terms of physical characteristics of marine and river sediments, the main test results are given in Table I. The particles density (ρs) is measured using a helium pycnometer of type Accupyc 1330. For each sediment type, the results presented on Table I are the average value of 240 measurements performed on three samples. For the tested sediments, the measured values are less than the reference value obtained for standard materials (about 2.70 t/m^3). This difference can be explained, by the presence of organic matters which are lighter than mineral particles. To highlight this assumption, particles density of marine sediments, heated at 450 °C during 12h, was measured. The result obtained is comparable with the standard values of inorganic materials.

The studied sediments are classified as moderately organic materials as the organic matter content is higher than 3%. This class of material is indicated as a Class F material. According to particles size distribution, the bleu methylene value and the Atterberg limits, as shown on Fig. 3, the marine sediments are classified as A4F11 type of material. This class gathers clayey soils which are moderately organic. The river sediments are classified as A2F11 material which design silty soils which are moderately organic [9].

B. Mineralogical Analysis

A good knowledge of mineralogical composition of the materials is essential to anticipate the difficulties that could be induced in the process of beneficial use of dredged sediments. In this study, the crystalline phases in the materials are identified by the use of X-rays diffraction technique. The equipment used is of type D500 manufactured by Siemens.

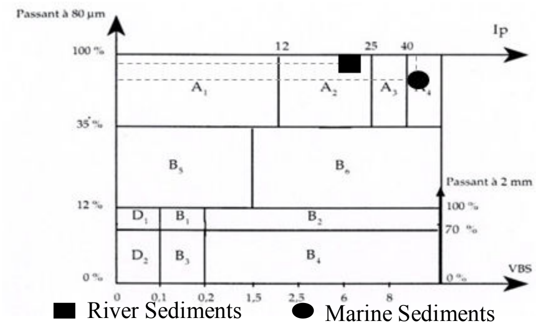

Fig. 3 Classification according to GTR. 1992 [9]

For the studied marine sediments, the three principal crystalline phases detected are: calcite, quartz and halite. For the river sediments, calcite and quartz are the two principal crystalline phases detected (Figs. 4, 5).

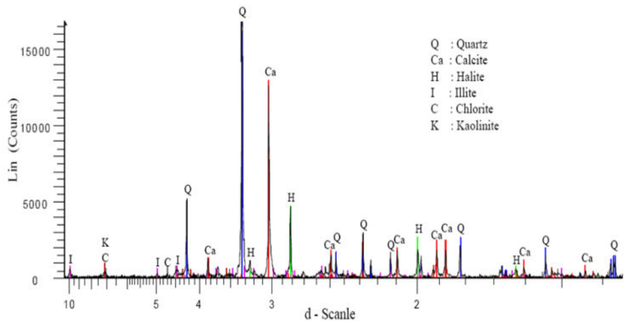

Fig. 4 Crystalline phases detected by the diffraction of X -rays of marine sediments

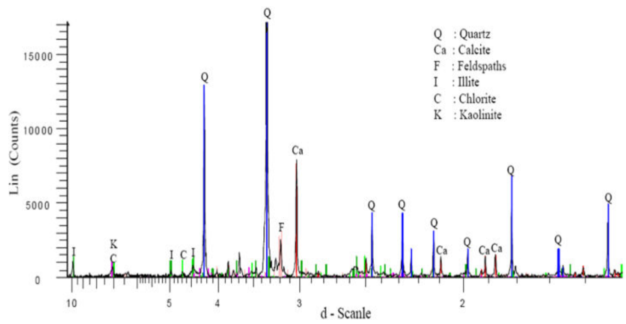

Fig. 5 Crystalline phases detected by the diffraction of X -rays of river sediments

To specify the nature of clay minerals, a specific analysis was carried out on particle sizes lower than 2µm. This analysis consists in characterising the raw material, the heated material at 450°C during two hours in order to characterise the Kaolinite and the saturated material by vapours of ethylene glycol to highlight Smectites (Figs. 6, 7). The results, on Table II, show that the clay phases of marine sediments are composed of Smectites, Illite and Kaolinite in equal proportions. The river sediments are composed mainly of Smectites.

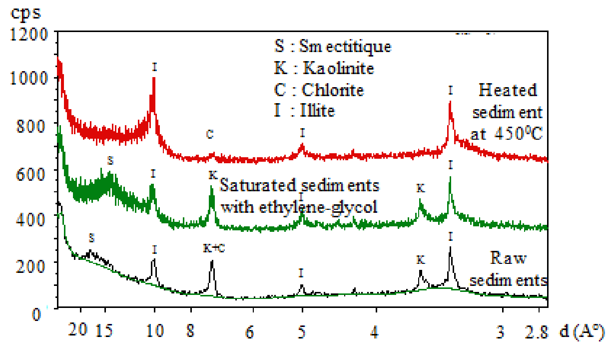

Fig. 6 Clay mineral phase of marine sediments

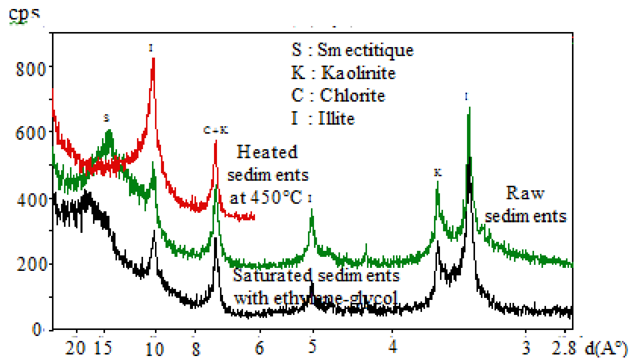

Fig. 7 Clay mineral phase of river sediments

TABLE II
PHYSICAL ANALYSIS OF MARINE AND RIVER SEDIMENTS

Minerals	Smectites	Illite	Kaolinite	Chlorite
Marine sediments	30%	32%	30%	8%
River sediments	55%	20%	15%	10%

C. Environmental Analysis

In this study, to evaluate the environmental impacts of raw dredged sediments, leaching tests are performed according to the European test standard EN 12457-2 [16]. The test consists in adding leaching fluid to the test sample (deionised water with no pH control) as the liquid to solid ratio is 10. The sample with added leaching fluid is agitated in an end-over-end shaker for 24 hours under specified test conditions. The liquid is then separated from the solid by centrifugation and filtration (0.45 µm pore size).

Inorganic parameters such as metals and anions are analysed as the concentration that is leached under tests conditions, leading to an understanding of both the long term and short term leaching behaviour.

Organic parameters, such as total organic carbon (TOC), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), benzene, toluene, ethyl benzene and xylene compounds (BTEX) and mineral oil are determined as 'total' concentrations. The samples are analysis 'as received' rather than first undergoing one of the prescribed leaching tests.

The leachate quality threshold from French decree of 14 June 2001 and the European decision 2003/33/CE are applied to leachates from materials to assess the leachability under mild extraction conditions for material reuse options [17]. It's to note that the used threshold was developed for establishing criteria and procedures for the acceptance of waste at landfills and at present no specific threshold was developed for beneficial use of dredged sediments in road construction.

The results obtained on Tables III and IV according to European decision 2003/33/CE, show that for marine sediments the proportion of chloride, molybdenum and hydrocarbons exceed the limit of inert waste. For river sediments, only the content of PAHs exceeds the limit of inert waste. It's to note that for marine sediments, the tests were performed on sediments at initial water content which was around 200%. Complementary tests, performed on samples at lower water content after a consolidation process, have showed lower amount of chloride in the generated eluates due to departure of salt in excess pore water.

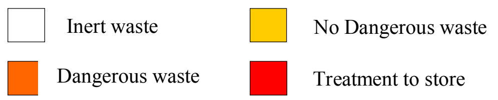

Fig. 8 Color of inert, no dangerous, dangerous waste and treatment to store

TABLE III
RESULTS OF LEACHING TEST ON THE RAW SEDIMENTS

Elements	Unit	Marine sediments	Rivers sediments
pH		8,3	8.0
Conductivity	mS/cm	7.7	0.2
As	mg/kg	<0.5	<0.5
Ba	mg/kg	<0.2	<0.2
Cd	mg/kg	<0.04	<0.04
Cr	mg/kg	<0.5	<0.5
Cu	mg/kg	<0.5	<0.5
Hg	mg/kg	<0.001	<0.001
Mo	mg/kg	4,19	<0.5
Ni	mg/kg	<0.4	<0.4
Pb	mg/kg	<0.5	<0.5
Sb	mg/kg	<0.06	<0.06
Se	mg/kg	<0.1	<0.1
Zn	mg/kg	0.73	<0.5
Fluorides	mg/kg	7.1	2.5
Chlorides	mg/kg	27537	30
Sulphates	mg/kg	3718	310
Phenol index	mg/kg	0.64	<0.10
TOC	mg/kg	479	78

TABLE IV
RESULTS OF THE ANALYSIS ON SOLIDS OF RAW SEDIMENTS

Elements	Unit	Marine sediments	Rivers sediments
TOC	mg/kg	42000	8.0
BTEX	mg/kg	<5	0.2
PCBs	mg/kg	0.28	<0.5
Hydrocarbon	mg/kg	820	<0.2
PAHs	mg/kg	29.1	110

The studied raw sediments exhibit a low bearing ratio, a low strength and a high sensitivity to water. In the field of road construction and in order to keep the proposed beneficial use sustainable and economically viable, the raw sediments performance will be enhanced by modifying its granular distribution by adding natural sand from careers and/or dredged sand (SB an/or SD) in combination with binders at a moderate amount. In this study, the amount of the fine marine and river sediments is fixed to about 33% and 22% in the mix in order to reduce the total amount of organic matters content in the mix and to insure fine particle content less than 12 %. This mixture is then treated by lime and/or cement. The proposed mixes are summarised on Tables V and VI:

TABLE V
COMPOSITIONS OF THE MIX USING MARINE SEDIMENTS

Elements	FM1	FM2	FM3	FM4
%marine sediments	33%	33%	32%	32%
%river sediments	/	/	/	/
% SD	20%	61%	20%	60%
% SB	41%	0%	40%	0%
% cement	6%	6%	6%	6%
% lime	0%	0%	2%	2%

TABLE VI
COMPOSITIONS OF THE MIX USING RIVER SEDIMENTS

Elements	FF1	FF2	FF3	FF4
%marine sediments	/	/	/	/
%river sediments	23%	23%	22%	22%
% SD	24%	71%	24%	70%
% SB	47%	0%	48%	0%
% cement	6%	6%	6%	6%
% lime	0%	0%	2%	2%

TABLE VII
LEACHING TEST ON MONOLITH SAMPLES OF DESIGNED ROAD MATERIAL USING MARINE SEDIMENTS

Test	Monolithic			
Elements(mg/kg)	FM1	FM2	FM3	FM4
pH	11.3	11.3	11.8	11.7
Conductivity(mS/cm)	1.6	1.6	2.2	2.1
As	<0.5	<0.5	<0.5	<0.5
Ba	0.15	0.17	0.21	0.22
Cd	<0.04	<0.04	<0.04	<0.04
Cr	<0.5	<0.5	<0.5	<0.5
Cu	1.96	1.98	1.93	1.77
Hg	<0.001	<0.001	<0.001	<0.001
Mo	<0.5	<0.5	<0.5	<0.5
Ni	<0.4	<0.4	<0.4	<0.4
Pb	<0.5	<0.5	<0.5	<0.5
Sb	<0.06	<0.06	<0.06	<0.06
Se	<0.1	<0.1	<0.1	<0.1
Zn	<0.5	<0.5	<0.5	<0.5
Fluorides	1.3	1.3	1.1	1.3
Chlorides	3627	3632	3477	3476
Sulphates	196	175	145	140
Phenol index	0.19	0.23	0.23	0.24
TOC	120	131	114	140

In this section, we discuss only the environmental behaviours without addressing the mechanical questions. The results are shown on Tables VII-XI.

TABLE VIII
LEACHING TEST CRUSHED SAMPLES OF DESIGNED ROAD MATERIAL USING MARINE SEDIMENTS

Test	Crushed			
Elements (mg/kg)	FM1	FM2	FM3	FM4
pH	12.1	12.2	12.6	12.5
Conductivity (mS/cm)	4.4	4.4	7.9	7.5
As	<0.5	<0.5	<0.5	<0.5
Ba	0.46	0.47	0.91	1.06
Cd	<0.04	<0.04	<0.04	<0.04
Cr	<0.5	<0.5	<0.5	<0.5
Cu	12.8	12.5	9.22	8.94
Hg	<0.001	<0.001	<0.001	<0.001
Mo	2.75	2.70	2.65	2.49
Ni	<0.4	<0.4	<0.4	<0.4
Pb	<0.5	<0.5	<0.5	<0.5
Sb	<0.06	<0.06	<0.06	<0.06
Se	<0.1	<0.1	<0.1	<0.1
Zn	<0.5	<0.5	<0.5	<0.5
Fluorides	5.8	5.7	4.8	4
Chlorides	7009	8004	6681	7099
Sulphates	823	673	401	353
Phenol index	0.54	0.63	0.57	0.69
TOC	530	520	455	466

TABLE IX
LEACHING TEST ON MONOLITH SAMPLES OF DESIGNED ROAD MATERIAL USING RIVER SEDIMENTS

Test	Monolithic			
Elements (mg/kg)	FF1	FF2	FF3	FF4
pH	7.93	8.11	11.38	10.78
Conductivity (mS/cm)	0.7	0.7	1.7	1.5
As	<0.5	<0.5	<0.5	<0.5
Ba	0.2	0.2	0.4	0.3
Cd	<0.04	<0.04	<0.04	<0.04
Cr	<0.5	<0.5	<0.5	<0.5
Cr (VI)	<0.5	<0.5	<0.5	<0.5
Cu	<0.5	<0.5	<0.5	<0.5
Hg	<0.001	<0.001	<0.001	<0.001
Mo	<0.5	<0.5	<0.5	<0.5
Ni	<0.4	<0.4	<0.4	<0.4
Pb	<0.5	<0.5	<0.5	<0.5
Sb	<0.06	<0.06	<0.06	<0.06
Se	<0.1	<0.1	<0.1	<0.1
Zn	<0.5	<0.5	<0.5	<0.5
Fluorides	1.4	1.4	1.6	1.3
Chlorides	36.3	16.5	21.1	48.2
Sulphates	38.1	35.5	30.3	25.4
Phenol index	/	/	/	/
TOC	48	55	54	52

Test results, as expected, on monolithic samples don't indicate particular pollution except moderate content of chlorites. On crushed samples the chlorites content are almost twice those measured on monolithic samples and almost four times lower than those measured on raw sediments. For tests on crushed samples moderate content of copper, molybdenum, chlorites and hydrocarbon are measured in leachate. According to the proportions of these elements, the materials exceed the level of inert waste and locate in the class of non-dangerous waste. For this case, complementary studies are necessary to improve the environmental impact of these materials preserving the mechanical performances without generating expensive costs for the treatment.

The proportion of copper on the studied formulations is higher than that in the analyses on the raw sediments. This phenomenon is imputable by the copper contribution by other components of the formulation. The leaching tests on the components are underway to be realized to verify this hypothesis.

The leaching tests on the designed road materials based on river sediments have not revealed particular problems.

TABLE X
LEACHING TEST ON CRUSHED SAMPLES OF DESIGNED ROAD MATERIAL USING RIVER SEDIMENTS

Test	Crushed			
Elements (mg/kg)	FF1	FF2	FF3	FF4
pH	11.05	12.08	12.55	12.58
Conductivity (mS/cm)	3.2	3.4	7.3	7.1
As	<0.5	<0.5	<0.5	<0.5
Ba	0.9	1.2	2.1	1.9
Cd	<0.04	<0.04	<0.04	<0.04
Cr(VI)	<0.5	<0.5	<0.5	<0.5
Cr	<0.5	<0.5	<0.5	<0.5
Cu	<0.5	<0.5	<0.5	<0.5
Hg	<0.001	<0.001	<0.001	<0.001
Mo	<0.5	<0.5	<0.5	<0.5
Ni	0.5	0.46	<0.4	<0.4
Pb	<0.5	<0.5	<0.5	<0.5
Sb	<0.06	<0.06	<0.06	<0.06
Se	<0.1	<0.1	<0.1	<0.1
Zn	<0.5	<0.5	<0.5	<0.5
Fluorides	6.4	6.5	4.9	5
Chlorides	122.7	59.3	87.4	150.7
Sulphates	122.2	104	25.7	31.1
Phenol index	/	/	/	/
TOC	200	211	179	202

TABLE XI
ANALYSIS ON THE SOLID MATERIALS

Test	Mix of river sediments				Mix of marine sediments			
Elements (mg/kg)	FM1	FM2	FM3	FM4	FM1	FM2	FM3	FM4
TOC	7.93	8.11	11.3	10.7	12.1	12.2	12.6	12.5
PCB	0.7	0.7	1.7	1.5	3.2	3.4	7.3	7.1
Hydrocarbon	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
PAH	0.2	0.2	0.4	0.3	0.9	1.2	2.1	1.9

IV. CONCLUSION

The dredged sediments are regarded as wastes according to Europeans classification. To promote their possible beneficial uses in road construction, it is necessary to enhance the knowledge of their physical, mineralogical, and chemical characteristics as their potential impacts on the environment.

The study of physical characteristics shows that the studied sediments are fine materials, mainly silts, moderately organic and highly plastic. The environmental impact evaluated throughout leaching tests shows a high content of chlorites, molybdenum and hydrocarbons for marine sediments. For river sediments, only the content of PAH is noticeable.

For designed materials, leaching tests performed on monolithic samples have not revealed particular pollution except moderate amount of chlorites for materials using dredged marine sediments. For tests on crushed samples moderate level of copper, molybdenum and hydrocarbon are observed. The leaching tests on the designed road materials based on river sediments have not revealed particular problems. It's to note that the European decision establishing criteria and procedures for the acceptance of waste at landfills was used to evaluate the environmental impact of designed materials and at the present no specific threshold was developed for beneficial reuse of dredged sediments in road construction works.

For better assessment of the environmental impacts as the mechanical behaviour, it seems important at this stage to investigate the behaviour of designed material in the framework of a monitored experimental road.

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