MAIN FACTORS DRIVING CONTAMINATION MOBILIZATION DURING DREDGING OF HARBOR SEDIMENT

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ABSTRACT

In general framework of harbor dredging, the determination and study of main factors which could drive contaminant mobilization, represents an important issue to avoid site pollution increase or taking pollution away from harbor. Indeed, sediments constitute an important source of inorganic and organic contaminants of marine environment. In the aim of ECODREDGE project, concerning dredging of Mediterranean Port-Camargue harbor in south of France, sediment granular fraction exceeding 80 µm has been reused and fraction inferior to this value has been re-deposited on harbor floor. Before, during and after this project, an exhaustive morpho-granular, physicochemical and chemical characterization of sediments collected was realized to improve marine sediment characterization, to identify the impact of dredging, and to study concurrently inter-particle or physicochemical phenomena as agglomeration /dispersion or adsorption/desorption of organic pollutant (HAP, PCB). These factors could lead to disperse pollution in water column and/or to be swept away by finest particles in currents. For this purpose, granular aspect and sedimentation behavior of solid matter has been investigated. During experiments, three sediments were chosen in function of different textural properties and their probable organic pollutant concentration. Distribution of organic matter between 4 granular fractions has been determined by TOC. Origin and distribution of PCBs have studied depending particles size and depth. Results have been shown that dredging has had no influence on organic pollution dispersion and granular characteristics.

Keywords: Harbor sediment, Organic mobilization, PCB, Granular characterization, Sedimentation

INTRODUCTION

Harbor dredging could drive contaminant mobilization which can lead to site pollution increase and/or its transfer away from harbor. The processes involved are complex but two main factors can be considered: inter-particle phenomena as agglomeration/dispersion and/or physicochemical as adsorption/desorption of pollutants.

Under ECODREDGE project, concerning dredging of Mediterranean Port-Camargue harbor in south of France, sand fraction of sediment has been reused and finest fraction has been re-deposited on harbor floor.

In this context, an exhaustive morpho-granular and physicochemical characterization of sediments collected was realized to determine some process parameters, to improve marine sediment characterization, to identify the impact of dredging and to study organic (HAP and PCB) or physic pollution mobilization. These works present, before and after dredging, a granular characterization of solid matter investigated by Scanning Electron Microscopy (SEM), laser granulometry, BET specific surface, electrophoresis measurements and study of sedimentation behavior. For this purpose, three sediments were chosen in function of different textural properties and their potential organic pollutant concentration (PCB concentration) depending on the sampling zone in the port. Distribution of organic matter between 4 granular fractions has been determined by TOC. Origin and distribution of organic pollutants have studied based depending particles size and depth.

SITE DESCRIPTION, DREDGING PROCESS AND SAMPLING

Port-Camargue is the largest European Marina localized in south of France in the gulf of Lion, a wide bay of Mediterranean coastline (Fig 1). This site is close to a Natura 2000 zone which is a protected nature reserve.

Three sediment samples (named sample 1, 2 and 3) have been studied and chosen to take into account their different potential pollution, situation in the harbor and granular characteristics.

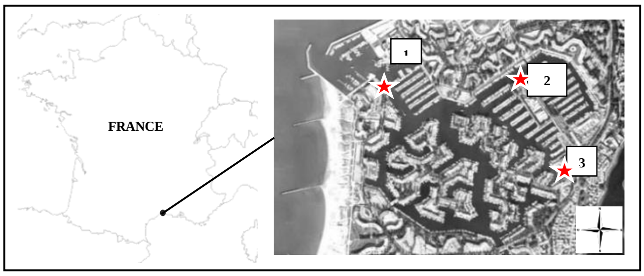

Fig.1 Locations of sampling stations.

A specific dredging process on a floating bridge has been developed in ECODREDGE project which all steps have been realized on water, with a deposit of finest fraction (<80µm) directly on the harbor bottom under a protective skirt, and a reused of sand (>80µm) on site. Only polluted finest fraction located in technic zones have been landfilled.

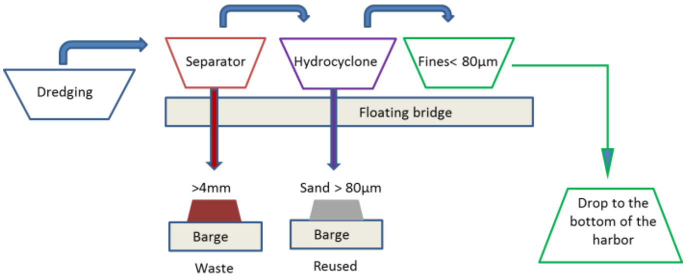

Fig. 2 Specific dredging process on a floating bridge.

MATERIAL AND METHODS

Organic Matter And PCB Analysis

Total Organic Carbon measurements were performed by a Vario TOC-Cube from Elementar Company on the solid fraction of sediments after freeze-drying.

Five grams of dry sediment were introduced into the stainless steel extraction cell (ASE 350 Dionex, France). The ASE extraction was carried out for 15 min with a solvent mixture (hexane/acetone (50/50) at 120°C and 1500 psi of nitrogen. The extract is then kept in contact with copper powder for 48 h in order to remove sulfur interferences. After extraction, the extract was cleaned on a Strata Florisil (FL-PR, 32138). The elution step was carried out by 5 mL Hexane. Purified extracts were analyzed on a GC–MS (Varian 450-GC and Varian 240 MS) working in the electron impact mode at 70 eV. A DB-5ms (Agilent) chromatographic column (30m, 0.25mm ID and 0.25µm of film thickness) was used. The Helium flow rate was fixed at 1 mL min-1. The extract (2µL) was injected on the chromatographic column with a PTV 1079 injector maintained at 300°C.

The initial oven temperature was programmed from 120°C (1 min) to 160°C at 6°C min-1 (holding for 5 min), then the temperature increased to 310°C at 10°C min-1 (holding for 5 min). The MS transfer line 310°C and ion source were kept at 220°C. For PCB analysis, a Selected Ion Storage (SIS) method was employed for indicator PCB detection. The calibration was performed with a mixture composed of PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180 (native and labeled 13C12-PCB).

Granular And Physicochemical Characterizations

Suspensions analyzed were prepared by diluting sediment samples with demineralized water with a volume ratio 1:10 and a mechanical stirring time of 15 min.

Granular characterizations were obtained by an Environnemental Scanning Electron Microscope with energy Dispersive X-Ray spectroscopy (SEM/EDX – Quanta 200 FEG) from FEI Company, a Laser granulometer LS 13320 (optical model chosen: n=1.57+0.3i), a SA3100 BET surface area analyzer from Beckman-Coulter (samples must have dried for 72h at 40°C) at and a Zetasizer Nano-ZS from Malvern Instruments.

To investigate settling behavior, a concentrated dispersion analyzer, a Turbiscan MA2000 (Formulaction) was used.

GRANULAR CHARACTERISTICS TO CUT SIZE DIAMETER DETERMINATION

General Sediment Characteristics

As described in a previous work [1], particle solid phase of studied sediments have similar mineralogical and elementary chemical compositions, mainly composed of silicates, aluminosilicates (lithogenous materials coming from land by erosion) and calcite (biogenous materials derived from hard parts of organisms) [2], and very few organic solid particles, suggesting that organic matter is mainly in the form of dissolved or adsorbed molecules.

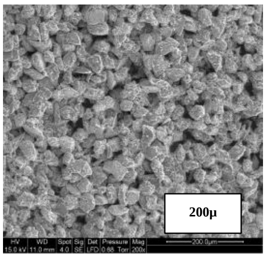

Fig. 3 Example of sediment micrograph.

Based on Zeta potential values, respectively -28.9, -31.9 and -30.3 µm.cm/V.s for samples 1, 2 and 3, all sediments present a weak agglomeration behavior [3]. On an indicative basis, pH, density and water content are respectively 8.3, 2.68 and close to 35% for all sample studied.

Cut Size Diameter Determination And Dredging Impact

Laser granulometric analyses have been performed on sediments before and after dredging (Fig.4). Particles sizes distributions reveal a narrow mode at 200µm corresponding to sand fraction (identical to beach sand near Port Camargue) and a wide supracolloidal mode corresponding to finest fraction (from 0.1 to 80 µm). These results lead to determine cut size diameter value for sand separation by hydrocyclone in the dredging process.

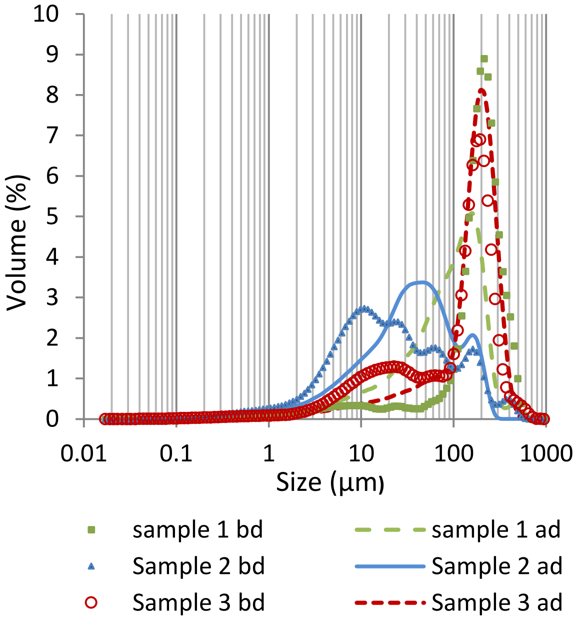

Fig. 4 Particle size distribution of sediments before and after dredging (bd and ad).

We can note that dredging process has no significant effect on particle size distributions: sample 1 before dredging is mainly composed of sand particles (fine/sand volume ratio, estimate from areas under granulometric distributions: 0.2) such as sample 3 that presents slightly more fine fractions inferior to 80 µm (fine/sand ratio: 0.6). Only sample 2 is mainly composed of finest particles (fine/sand volume ratio: 4.5).

ORGANIC MATTER ADSORPTION ABILITY

By comparing Total Organic Carbon (TOC) values and specific surface area BET developed by sediment solid fractions indicated in Table 1, it is interesting to remark that the more sandy sediment (sample 1) has the better organic matter adsorption ability (TOC/BET ratio)

Table 1 BET surface areas and TOC values for the three sediments studied and granular fractions of sample 3.

(Samples)	BET(m2/g)	TOC (%)	TOC/BET
(1)	2.0	2.3	**1.2**
(2)	3.5	3.1	0.9
(3)	3.0	2.5	0.8
>80µm(3)	0.7	0.4	0.6
80-40µm(3)	2.8	3	**1.1**
40-20µm(3)	2.3	2.4	**1.0**
<20µm(3)	7.9	2.8	0.4

Sample 3 which presents finest and sand fractions, has been wet sieved in four fractions according to Renard series (NF X11-504; 1975). The results indicate that better organic matter adsorption ability is obtained, and in comparable value to sandy sample 1, for intermediate granular fractions (20 to 80 µm) and not for the finest fraction inferior to 20 µm, as might be expected.
As organic matter may and organic pollutants as HAP or PCB could be present in the sediments, PCB have been analyzed in this work, in order to determine for all samples the level of pollution.

PCB ANALYSIS

PCBs are well-known as chlorinated highly persistent pollutants in marine environments and are listed as toxic and bioaccumulate contaminants. Due to their high hydrophobicity, PCBs are sorbed on suspended matter and subsequently deposited into sediments. The assessment of sediments contamination is based on six priority PCB congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180).

Sample 3 Results

The distribution of PCBs congener is similar to Alaclor 1254 (PCB commercial mixture use as dielectric fluids in transformer), (Fig. 5).

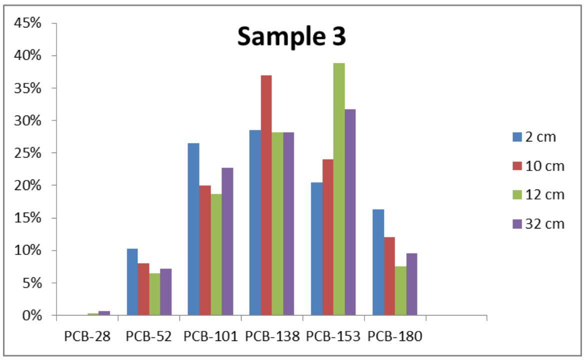

Fig. 5 Distribution of PBs congeners (sample 3).

The total concentration of the six PCB congeners reaches 2164 ng/g which corresponds to a high level of pollution [4], [5]. The maximum concentration is observed for sample 3 at around 22 cm (Fig. 6). According the sedimentation rate of 1cm/year in the harbor, the observed maximum corresponds to 1990s period which is more or less the period when PCBs were prohibited in France (1987).

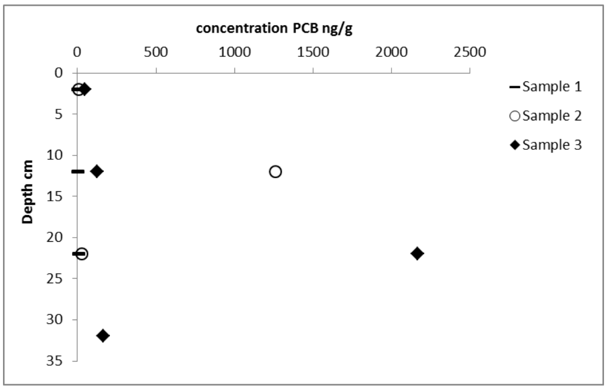

Fig. 6 Variation of PCBs concentration (ng/g) depending on the depth (cm).

The distribution of PCBs concentration according to particle size is presented (Fig. 6). Once a more the maxima is observed at 22 cm for particles range of 80-63 µm in agreement with previous TOC/BET results. PCBs concentration reaches 911 ng/g which corresponds, in this case, to a moderate contamination.

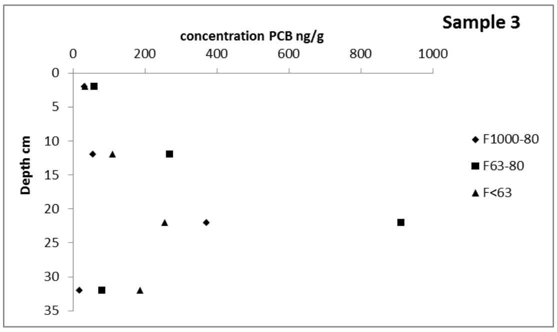

Fig. 7 Distribution of PCBs concentration (ng/g) depending on particles size (sample 3).

Moreover, during the dredging process, water has been sampled near the suction system (mid-channel) and closed to edge of the channel. No PCBs have been detected whatever the sampling point. This result demonstrates that no transfer of pollutant from sediment to water column occurs during the process.

Sample 2 Results

Higher PCBs concentration is observed at 12 cm whatever particles size. The maximum concentration 108 ng/g is observed for the particles size < 63 µm (Fig. 7) which however corresponds to a low level of contamination. This result could be explain by the construction of the northern channel which started from site where sample 2 station. This sample station was supposed to be located near technical zone.

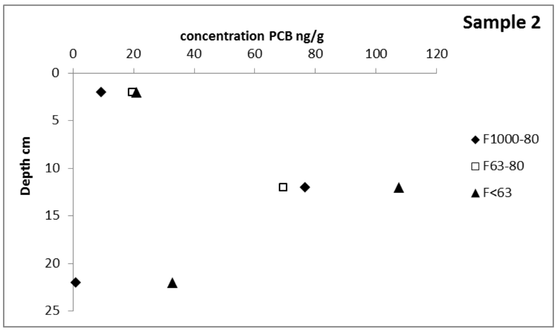

Fig. 8 Distribution of PCBs concentration (ng/g) depending on particles size (sample 2)

SETTLING AND PARTICLE MOBILIZATION

As finest part of dredging sediment must be re-deposit on the harbor bottom, settling behavior has been investigated in order to have a better knowledge of particle dispersion in water column.

This dispersion could participate to pollution mobilization and contaminant transport.
Studied suspensions mainly settle under an agglomerate settling regime which leads to a turbid supernatant. While sample 2 (navigation channel zone) settles under hindered settling regime leading to a clear supernatant (T_{Sup}: 80.9% at a settling time of 30 min) and a sharp interface between water and settling particles.

Table 2 Sedimentation behavior and dredging impact.

Samples	T_{Sup}(%)	V_{sed}(mm/min)	Delay(min)
1-bd	6.2	4.3	0
1-ad	11.8	3.6	0
1-ad(2)	13.9	3.8	0
2-bd	**80.9**	**0.4**	**4**
2-ad	**60.6**	**1.6**	**1**
3-bd	7.9	3.2	0
3-ad	7	3.8	0

Table 2 indicates values of transmission percentage of supernatant at a sedimentation time of 30 min (T_{Sup}), kinetics of sedimentation front (V_{sed}) during the first 6 minutes and possible delay observed before sedimentation front evolution.
For sample 2 presenting a hindered regime, the important volume fraction of particles inferior to 80µm (Fig.4) are trapped in sedimentation column (clear supernatant observed) involving larger volume of deposit (relative height of 80% and around 35-45% for the others samples). At the same time, the sedimentation kinetic of sample 2 is lower (inferior to 1.6mm/min) than the other samples which are more significant (3.2 to 4.3 mm/min). Moreover, they show turbid supernatants (6.2 to 13.9 %T) and could lead to disperse pollution in water column and/or to be swept away in currents.

CONCLUSIONS

This complementary experimental approach using granular and chemical characterizations has highlighted granular fractions that can be re-used, those that can be re-deposit on the bottom of harbor. Moreover, the cut size diameter value has been fixed at 80µm. Even if the sediment contains an important rate of finest fraction (sample 2), sedimentation regime of particles can avoid the pollution mobilization by particle dispersion in water column.
Organic matter and PCB are more concentrated in intermediate granular fractions between 20 to 80 µm and not as expected in fine clay and silt inferior to 20 µm.
PCBs concentrations of the six priority congeners are relevant indictors to identify previous contamination when dielectric fluid has been used in transformer. The compounds are persistent and the contamination is trapped in the sediments for a long time.
Finally, all observations show that dredging process had no significant impact on the sediment characteristics and pollutant mobilization by the two factors identified: dispersion of fine particles in currents or molecular desorption from solid fraction to water column.

ACKNOWLEDGEMENTS

This work was carried out under ECODREDGE project, financed by FUI (Fonds Unique Interministériel) from France. The authors would like to thank the Port-Camargue Master's Office for management of this project and their assistance during sampling. We are also grateful to Kevin Roque (C2MA-Ecole des Mines d'Alès- France) for sampling and granular characterizations.

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