STATUS OF WATER QUALITY AND IMPACT OF DREDGING ACTIVITIES IN FOUR PORTS OF THE GULF OF AIGUES MORTES (FRANCE)

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Abstract – Coastal hydrosystems, located at the land-sea interface, are both subject to autochthonous sources of pollution but also form a receptacle for terrigenous inputs from upstream areas.

The Gulf of Aigues Mortes (GAM) extends along the western margin of the Rhone delta. The marinas spread over this restricted geographical area present variable management problems depending on their size and location. Due to silting and/or siltation phenomena, the situation is becoming increasingly difficult to manage to maintain the depths of most ports. In these marinas that are not dredged regularly, the quantities of potentially contaminated sediments (organic and metallic micro-pollutants) to be extracted represent from a few thousand to several tens of thousands of m³ of sediments on the scale of each port.

Four ports of the GAM have joined together to set up a mutualized dredging project based on the valorization of dredged sediments.

The objective of this work is to carry out a diagnosis of the chemical and microbiological contamination of the waters of the 4 ports located in the Gulf of Aigues Mortes. Regular water sampling was done before, during and after dredging operations. Water column quality/contamination was characterized by major physicochemical water parameters, trace metallic elements and organotin compounds. In addition to chemical parameters, indicators of faecal contamination were also monitoring.

Dredging operations have induced the resuspension and/or readsorption on suspended matter of trace metal elements and organotin compounds in the water column. A significant increase in the concentrations of As (enrichment factors ranging from 1.2 to 2.15 times the post-dredging values) inducing exceedance of the EQS was observed. The behavior of copper and zinc is different according to the ports studied and during dredging operations. The resuspension of sediments, constituting both a sink and a source for (organo)metallic compounds, generated modifications of physico-chemical conditions and favoured increasing or decreasing of chemical elements concentrations observed in the dissolved fraction of the water column. These resuspensions are themselves related to the nature of the dredged sediments.
1. Introduction

The Mediterranean coastal zone represents an important socio-economic and ecological area under great pressure [1,2]. The ports represent both areas of heavy pollution linked to the density of activity, but also areas of refuge for many biological species [3]. The attractiveness of these environments leads to high population densities, the permanent development of activities and the construction of infrastructures, resulting in the qualitative degradation of coastal aquatic environments. This is particularly true in the case of marinas, which are both places of dense internal activities (yachting, marina, shipyards (careening and maintenance of boats)) but also receptacles of waters from the catchment areas loaded with suspended solids and/or contaminants, to which they are connected.

In order to maintain good seaworthiness conditions, four ports in the Gulf of Aigues-Mortes (GAM) (Palavas, Pérols, Port-Camargue and Carnon) carried out joint dredging as part of the regional dredging scheme in Occitanie based on the recovery of dredged sediments. In France, dredging operations are authorized by prefectural decrees established for each port. The decree of 16/06/2002 defines levels N1 and N2 to guide the choice of the administrative procedure for the examination of dredging files, in accordance with article L.214-1 and following of the environmental code [4]. These are not thresholds aimed at authorizing or prohibiting the dumping of sediments, but rather benchmarks for deciding on the administrative regime of the operation (declaration or authorization), for assessing the impact that the planned operation may have, and for directing the dumping or management of sediments on land. Thus, the N1 and N2 levels have been established according to the concentration of pollutant in the sediments:

- Lower than N1: too little pollutant for any impact, or negligible impact.
- Greater than or equal to N1 but less than N2 (N1<N2): alert level. If N1 is exceeded research can be done on the actual impact of the pollutants. Although the pollutant concentration is still considered "acceptable" and can therefore be discharged or reused as is.
- Greater than or equal to N2: further investigation is necessary because there are significant indications of a potential negative impact of the operation (a specific study on the sensitivity of the environment to the substances concerned, with at least a global ecotoxicity test of the sediments, an assessment of the foreseeable impact on the environment and, if necessary, refinement of the sampling grid in the area concerned.

These authorizations are drafted in relation to the levels of chemical contamination of the sediments to be dredged and for given durations. The monitoring of water quality during dredging operations is also defined in these decrees. In the ports studied, only turbidity or suspended matter concentration monitoring is required during the work.

The objective of this study is to acquire environmental data in these harbors by carrying out a diagnostic of chemical contamination and microbiological waters. The four studied harbors offer us the possibility to work on sites of different sizes with heterogeneous sedimentary materials and levels of contamination, which will allow us to determine the parameters likely to influence the phenomena of sorption/desorption of contaminants during dredging operations. The monitoring of the chemical and microbiological qualities of port waters during these dredging operations aims at determining the impact of these operations on the resuspension of contaminants. Indeed, these operations can lead to a resuspension of pollutants in the water column in the more or less long term. At certain levels, these can harm
2. Materials and Methods

2.1: Study areas

The Gulf of Aigues-Mortes contains the Natura 2000 area, under the Gulf of Lion entity. It is the northernmost part of the Gulf of Lion, between the commune of Villeneuve-lès-Maguelone and the commune of Grau du Roi, at the point of Espiguette. This small gulf borders the territory of the communes of Villeneuve-lès-Maguelone (in its eastern part), Palavas-les-Flots, Mauguio (Cannon) and La Grande-Motte, all four located in the department of Herault, as well as the territory of the municipality of Grau du Roi, (up to the point of Espiguette), located in the Gard (Figure 1).

Figure 1 – Gulf of Aigues Mortes localization.

Figure 2 – Location of the ports studied: (PC) Port-Camargue, (PA) Palavas-les-Flots.
Our study concerns four ports in the Bay of Aigues Mortes (Figures 2 and 3). The size of the marinas varies from 130 to 5000 boat places. The volume of dredged sediments is between 5 000 m³ of sand and 30 000 m³ of mud.

2.2: Methodology

Quality monitoring in harbour waters and sediments prior to dredging was implemented. These are surface water withdrawals filtered (0.22 µm acetate) and acidified with pure HNO₃ (Nitric acid). Measurements of physical-chemical parameters of water (T°C, pH, [O₂], Salinity, Turbidity) are performed by Multiparameter Probes portable HACH® (Hq40d) LDO101, pHC301 and CDC40101. The quantification of trace metals elements (ETM) is carried out by inductively coupled plasma mass spectrometry (ICP-MS) (iCAP-Q, Thermo Fisher Scientific) and a speciation analysis of organotin compounds (OSn) is performed by coupling SPME-GC-ICP-MS (TRACE 1300 GC Thermo Fisher Scientific-ICP-MS X Series II-Thermo Fisher Scientific ®). A particular focus will be made on Copper (Cu) and tributyltin (TBT) used in the compositional anti-fouling paints applied on the hulls of boats. Note that the use of TBT-based paints has been prohibited in Europe since 2008 and are replaced by Cu-based paints.

Surface sediment samples are collected at various ports for further analysis. Sediments were digested using a mixture of HF/ HNO₃ /HCl suprapur acids (Merck Millipore®). Digestion was carried out in a microwave oven (Ultrawave, Milestone ®). Trace element concentrations were measured using ICP-MS-Q, iCAP-Q (Thermo scientific ®) equipped with high matrix interface. The accuracy and the precision of the methods have been tested using certified reference materials (CASS-6 and PACS-2; Canadian National Research Council).

The resulting trace metals and TBT concentrations were compared to the N1 and N2 thresholds reported by the Geode [4] (Table1).
In order to enumerate faecal indicator bacteria (thermotolerant coliforms (TTC) and intestinal enterococci (IE)), the collected water samples were treated according to the reference methods ISO 9308-1:2014 and ISO 7899-2:2000, respectively. Water volumes were filtered on 0.45 µm cellulose nitrate membrane (Sartorius). TTC were quantified on Lactose Triphenyl Tetrazolium Chloride Tergitol-7 agar (Biokar) incubated for 24 h at 44 °C, and IE were enumerated on Slanetz-Bartley agar (Biokar) incubated for 48 h at 37 °C. The results are expressed as Colony Forming Units (CFU) per liter.

**Dredging operations** - The dredging was carried out hydraulically with a stationary suction dredger in Port-Camargue, Pérols and Palavas. The dredging of the port of Carnon has not yet started:

- **Port Camargue** - The work consisted of spot maintenance dredging of the south channel to an average depth of 3.5 meters. A suction dredge was used to pump the dredged sediments to a floating pipe that mixes the water and sediments towards a calibration workshop installed on the bank near the channel. The dredged sediments were screened at 80 µm by hydrocycloning and then separated into two streams: the fine sands above 80µm are used to recharge the beach, the muddy materials below 80µm are drained into geotubes and then reused as reclamation materials. According to the prefectural decree DREAL/DMMC-30-202-001, the turbidity of the water in the channel is measured continuously (turbidimeter) immediately downstream of the discharge of the water from the buffer basin during the entire duration of the discharge.

- **Pérols** - The works consisted in carrying out a punctual maintenance dredging of the access channel to the harbour basin to recover an average depth of -1.4 m NGF. The mixture of water and sediment sucked up by the dredger is discharged into filtering geotextiles for the dehydration of the sediments. The lowering of the dryness of the sediments will allow the acceptance or the elimination in a waste storage channel adapted to the nature of the waste or their valorization. According to the prefectural order DREAL/DMMC-34-2019-003, a physico-chemical monitoring (pH, dissolved oxygen, turbidity and conductivity) at three stations: around the dredge, near the sediment dewatering area and in the channel must be performed daily and every 3 hours before, during and after dredging at the 3 stations.

- **Palavas** - The Prefectural Order PEL-2015-001 authorizes for a period of 10 years the dredging work necessary to maintain the nautical characteristics of the entrance to the port of Palavas and to ensure access by users in good conditions of navigability and safety (-2.50 m NGF). The sediments sucked up by the dredger are discharged directly through pipes for the seasonal recharging of the adjoining beaches for bathing use. Water quality monitoring includes continuous visual monitoring of the intensity and diffusion into the marine environment of the turbidity plume that will be generated by the dredging work, daily monitoring of turbidity levels.

### 3. Results and discussion

#### 3.1: Quality of dredged sediments

The concentration of trace metals and organotin compounds in the sediments of the studied harbors was determined. The concentrations obtained were compared to the Geode N1 and N2 levels (Table 1).
Table 1 – Qualitative assessment of sediments in the four ports relative to threshold levels (Geode, 2018).

<table>
<thead>
<tr>
<th>Port</th>
<th>Threshold levels</th>
<th>Copper concentration in g/kg</th>
<th>TBT concentration in μg(Sn)/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC : Port Camargue</td>
<td>&lt;N1 Except [Cu] = 77 ± 53 mg/kg &gt;N2</td>
<td>&gt;N2</td>
<td></td>
</tr>
<tr>
<td>P: Pérols</td>
<td>&lt;N1 Except [Cu] = 77 ± 7 mg/kg &gt;N1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA: Palavas les Flots</td>
<td>&lt;N1 Except [Cu] = 155 ±25 mg/kg &gt;N2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: Carnon</td>
<td>&lt;N1 Except [Cu] = 126 ±77 mg/kg &gt;N1 or &gt;N2</td>
<td></td>
<td>Except [TBT]= 198 μg(Sn)/kg &gt;N2 careening area</td>
</tr>
</tbody>
</table>

In all 4 harbors, copper concentrations above the N1 level (45 mg·kg⁻¹) or even the N2 level (90 mg · kg⁻¹) were measured. In the port of Carnon, TBT concentrations above the N2 level were also measured in the technical areas (N1 = 41 ng(Sn)·g⁻¹, N2 = 164 ng(Sn)·g⁻¹).

3.2: Water quality before dredging operations

3.2.1: Physico-chemical parameters measured in situ

Physical-chemical measures varied from port to port. This variation can be explained by the geographical location of ports and the effect of current, (table 2).

Table 2 – Physio-chemical parameters in the four ports before dredging operations.

<table>
<thead>
<tr>
<th>Port</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>%O₂</th>
<th>Salinity (PSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camargue</td>
<td>Janv-21 7.7</td>
<td>8.28</td>
<td>11.2</td>
<td>32.6</td>
</tr>
<tr>
<td>Pérols</td>
<td>Nov-20 12.2</td>
<td>8.34</td>
<td>86.1</td>
<td>27.9</td>
</tr>
<tr>
<td>Palavas Flots</td>
<td>Janv-21 14.0</td>
<td>8.28</td>
<td>115.2</td>
<td>32.2</td>
</tr>
<tr>
<td>Carnon</td>
<td>Sept-21 24.8</td>
<td>7.96</td>
<td>7.9</td>
<td>37.1</td>
</tr>
</tbody>
</table>

3.2.2: Trace metals and organotin concentrations

The Arsenic (As) concentration is consistently above the Environmental Quality Standard (EQS) before dredging begins in all 4 ports (Table 3). The concentrations of Copper (Cu) and Zinc (Zn) are below the EQS prior to dredging operations except for Cu in the port of Carnon. All three forms of butyltins (MBT, DBT, and TBT) are detected at all points at spatially and temporally variable concentrations. The presence of contaminated sediments in the dredged areas could be the cause of resuspension in the water column.

The establishment of environmental quality standards (EQS) has been proposed (Directive No. 2008/105/EC) for these substances. The EQS propose values of annual average concentrations (AA) and maximum allowable concentrations (MAC) to ensure the protection of the aquatic environment and human health against long-term and chronic effects and against direct and acute ecotoxic effects respectively. These values are lower than ng(Sn)·L⁻¹ for tributyltin compounds (EQS-MA = 0.082 ng(Sn)·L⁻¹ and EQS-CMA = 0.61 ng(Sn)·L⁻¹). The average TBT concentrations largely exceed the EQS-MA in the four studied ports (Table 3).
Table 3 – Trace metals and organotin dissolved concentrations in the four ports before dredging operations.

<table>
<thead>
<tr>
<th></th>
<th>PORT-CAMARGUE</th>
<th>PÉROLS</th>
<th>PALAVAS</th>
<th>CARNON</th>
<th>EQS</th>
</tr>
</thead>
<tbody>
<tr>
<td>As µg·L⁻¹</td>
<td>1.68±0.21</td>
<td>0.79±0.46</td>
<td>1.37±0.02</td>
<td>1.38±0.23</td>
<td>0.83</td>
</tr>
<tr>
<td>Cu µg·L⁻¹</td>
<td>1.49±0.39</td>
<td>1.49±0.39</td>
<td>0.56±0.13</td>
<td>3.60±2.42</td>
<td>1.6</td>
</tr>
<tr>
<td>Ni µg·L⁻¹</td>
<td>0.37±0.04</td>
<td>1.27±0.05</td>
<td>0.70±0.01</td>
<td>0.45±0.06</td>
<td>4</td>
</tr>
<tr>
<td>Zn µg·L⁻¹</td>
<td>1.39±0.33</td>
<td>2.10±2.81</td>
<td>0.67±0.01</td>
<td>2.41±1.2</td>
<td>3.1</td>
</tr>
<tr>
<td>MBT ng(Sn)/L⁻¹</td>
<td>6.04±0.07</td>
<td>5.26±2.05</td>
<td>8.02±2.19</td>
<td>2.09±0.76</td>
<td>0.082</td>
</tr>
<tr>
<td>DBT ng(Sn)/L⁻¹</td>
<td>0.84±0.07</td>
<td>0.44±0.12</td>
<td>1.20±0.3</td>
<td>0.56±0.08</td>
<td>0.61</td>
</tr>
<tr>
<td>TBT ng(Sn)/L⁻¹</td>
<td>0.28±0.05</td>
<td>0.28±0.10</td>
<td>0.38±0.09</td>
<td>0.14±0.15</td>
<td>0.082</td>
</tr>
</tbody>
</table>

EQS: Environmental Quality Standards; AA: annual average; MAC: maximum allowable concentration

3.2.3: Microbiological quality

Faecal indicator bacteria (thermotolerant coliforms (TTC) and intestinal enterococci (IE)) ranged from 0 to 25 CFU/100mL in the ports studied.

3.3: Impact of dredging activities

3.3.1. Physicochemical parameters

The dredging operations do not lead to modifications of the physico-chemical parameters, except for turbidity which can double or even quadruple compared to the initial values.

3.3.2: Tributyltin TBT

The dredging operation significantly increased the concentrations of organotin compounds including monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) in the water column during monitoring in the Port-Camargue marina. Formerly used in antifouling paints, TBT and its degradation products present in the sediments resuspended in Port Camargue and Pérols. The maximum concentrations in the dissolved phase measured were 13.4, 2.2 and 1.5 ng(Sn)·L⁻¹ respectively for MBT, DBT and TBT.

In the port of Pérols, the resuspension took place at the end of the dredging operation, probably linked to the dredging of a sedimentary zone more contaminated with TBT.

3.3.3: Trace metals

In Port Camargue, the concentrations of arsenic measured are systematically higher than the EQS. For copper, only one sampling point (PC7) systematically shows values above the EQS. For the other points and for Zinc only 25 % of the sampled points present values higher than the EQS. Concerning Palavas, the measured concentrations of arsenic are systematically higher than the EQS, while copper and zinc never exceed the EQS. Concerning Pérols, the measured concentrations are in 76 % for arsenic, 11 % for copper and 3 % for zinc above the EQS.
In order to quantify the impact of dredging operations, water enrichment factors (EF) of arsenic (Figure 4), copper (Figure 5) and zinc (figure 6) are calculated using as a reference the measured post-dredging concentration (Table 2) in the water columns of the four ports and compared with the concentrations measured during and after dredging:

$$EF = \frac{\text{Element}_i \text{ concentration}_{\text{post dredging}}}{\text{Element}_i \text{ concentration}_{\text{during dredging}}}$$

If the enrichment factor (EF) is greater than 1, then enrichment in the dissolved phase means that remobilization of metals from the sediment and suspended particles is occurring in the dissolved phase. Conversely, if the enrichment factor is less than 1, then there is no resuspension into the dissolved phase, which means re-adsorption onto the solid phase. The following graphs represent the dissolution (EF-1>0) or the sorption (EF-1>0) of Arsenic, Copper and Zinc in the different ports during dredging operations.

Figure 4 – Arsenic enrichment factors during dredging of Pérols (P), Palavas (PA) and Port-Camargue (PC).

Figure 5 – Evolution of Copper enrichment factors during dredging of Pérols (P), Palavas (PA) and Port-Camargue (PC).
It should be noted that the dredging operation of Port Camargue leads to a significant increase in the concentrations of As, Cu and Zn with enrichment factors ranging from 1.2 to 2.15 times the reference value inducing exceedance of the EQS.

The results of the EF calculations show a significant resuspension of As and Zn (EF>1) from the beginning of the dredging operation for the three ports with a more marked effect for the port of Pérols (Figures 4 and 6).

The behavior of copper is different in the three ports studied. A re-adsorption of Cu on the particulate phases (EF<1) seems to occur from the beginning of the dredging operations in the ports of Pérols and Palavas. In the case of Port Camargue an enrichment in the dissolved phase (EF>1) is observed. These phenomena are certainly related to the different natures of the sediments (sands, silts, clays, granulometry...).

3.3.4: Microbiological

The dredging operation do not lead to modifications of the microbiological quality.

4. Conclusion

The monitoring of all the chemical and microbiological contamination of the water during the dredging operations in three ports has made it possible to observe a certain number of phenomena, and in particular a resuspension of metallic trace elements and organotin compounds in the water column. The sometimes-high enrichment factors observed indicate that, in some cases, the environmental quality standards recommended by the Water Framework Directive have been exceeded.

The increase or decreasing of chemical element concentrations observed in the water column is directly related to the presence of these compounds in the sediments, which constitute both a sink and a source for (organo)metallic compounds. Indeed, the resuspension of sediments generates modifications of the physico-chemical conditions (oxygenation, modification of the redox conditions...).

The results obtained in this study show a potential for resuspension or readsorption of (organo)metallic compounds. The intensity of remobilization and reabsorption seems to depend, according to the elements considered, on the stability of the inorganic or organic complexes, the nature of the sediments and the particulate load. The environmental
monitoring carried out in the case of harbour dredging on even slightly contaminated sediments (level N1) must include the monitoring of these compounds in order to estimate and take into account the potential impact on the ecosystems.

These results will be particularly useful for the dredging works planned in the port of Carnon, which is more contaminated, taking into account the distribution of contaminants in the sediments.

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5. References


[2] Choueri, R.B.; Cesar, • A; Abessa, • D M S; Torres, • R J; Riba, • I; Pereira, • C D S; Nascimento, • M R L; Morais, • R D; Mozeto, A.A.; Delvalls, T.A. Harmonised Framework for Ecological Risk Assessment of Sediments from Ports and Estuarine Zones of North and South Atlantic., doi:10.1007/s10646-009-0442-y.
