CASE STUDY OF CONTAMINATED ORGANIC-RICH SEDIMENTS IN A NARROW BAY

Masaharu FUKUE, Department of Marine Civil Engineering, Tokai University, Shimizu-ku, Shizuoka, Japan
Yoshio SATO, Department of Marine Science, Tokai University, Shimizu-ku, Shizuoka, Japan
Toshihide FUJIKAWA, Graduate Student, Hokkaido University, Sapporo, Japan
Tomohiro INOUE, Graduate Student, Tokai University, Shimizu-ku, Shizuoka, Japan
Catherine N. MULLIGAN, Department of Building, Civil and Environmental Engineering, Concordia University, Montreal, Quebec, Canada
Kouji UEHARA, Japan Industrial Land Development Co., Tokyo, Japan

ABSTRACT
A case study of sediment contamination was made in one of the 23 specific designated important ports in Japan. The study focuses on the relationship between contaminants and organic matter in terms of ignition loss. Since the inner part of Shimizu Port has been used as wood pool for a long period, organic matter has existed as forms of suspended solids and deposits. The analyses showed that many properties of the sediments, such as water content and sulfide content are correlated with ignition loss. Of particular importance is that the concentrations of heavy metals such as zinc, copper, and lead for sediments are also correlated with ignition loss. As the ignition loss decreased with distance from the wood pool, other properties including the concentrations of trace metals also decreased with the distance.

RÉSUMÉ
Un cas d'étude de la contamination des sédiments a été réalisé dans un des 23 ports importants désignés au Japon. L'étude a visé la relation entre les contaminants et la matière organique en termes de perte au feu. Étant donné que l'intérieur du port Shimizu a été utilisé en tant qu'étang pour le bois sur une période prolongée, la matière organique a été présente sous forme de solides en suspension et de dépôts. Les analyses ont montré que plusieurs des propriétés des sédiments, tels que les contenus de l'eau et des sulfures, ont été corrélés avec la perte au feu. Plus particulièrement, les concentrations de métaux lourds comme le zinc, le cuivre et le plomb, dans les sédiments ont été corrélées avec la perte au feu. Tant que la perte au feu diminuait en fonction de la dimension de l'étang, les autres propriétés incluant les concentrations de métaux traces diminuaient également.

1. INTRODUCTION
Shimizu Port is one of the 23 specifically designated important ports in Japan. Orido Bay is located in the inner part of Shimizu Port. The bay has been used as a pool in which wood is floated for pest control since 1927. However, since the bay has become surrounded by many industries, it might have become contaminated. An integrated investigation is therefore needed to assess its potential for the following uses: the farming of fish and shellfish, tourism, anchorage, moorage, and roadside areas for ships and seaplanes or a waterfront public park.

The properties and contamination of sediments obtained from Orido Bay were investigated (Fukue et al. 2006b) and it was extended to the rivers that feed the Orido Bay and Shimizu Port as sources of contaminants. The objective of this research therefore was to determine the impact of the wood pool in Orido Bay and also to investigate the impact of this area on the Shimizu Port.

2. SITE LOCATIONS
The investigation sites were within a wood pool that occupies most of Orido Bay and Shimizu Port, as shown in Figure 1. The inner part of the wood pool has been enclosed by breakwaters and used as a pool in which wood is floated for pest control since 1927. The wood pool has an area of 717,000 m² and a maximum water depth of 8 m. Therefore, wood chips have accumulated on the bottom and have been subjected to degradation. The pool is fed by two streams, the Ohashi River and the Hamada River, both of which run through residential districts and small factory sites, as shown in Figure 1. The flow rates of the streams are relatively low (i.e. 0.17–0.76 m³/s and 0.02–0.24 m³/s, respectively). The wood pool contains several breakwaters and many driven mooring piles, to which wood rafts are moored. The Tomoe River, which is larger than the two streams mentioned above, flows into Shimizu Port, as shown in Figure 1. The flow rate of the Tomoe River is approximately 6.0 m³/s. The properties of discharged suspended solids and sediments were also determined for the samples from each of the river mouths, as indicated by the circles in Figure 1.

Nineteen surface sediment samples were obtained using a grab sampler from the bottom of the wood pool (Orido bay) and Shimizu Port. The sampling depth was less than 8 cm from the top surface. Because of the presence of wood and ropes discarded on the bottom, it was difficult to obtain sediment samples at some sites, as shown in Figure 2. The sampling site locations were designated as 1 to 12 for the Orido Bay and S1 to S7 for Shimizu Port, as indicated in Figure 1.
Sato et al. (2006) investigated the transport mechanisms and contamination of suspended solids in a wood pool as a case study for environmental assessment of an enclosed sea area. Phytoplankton was also found in the suspended solids. In order to assess the present contamination of Shimizu Port in Japan, seawater, suspended solids and settling particles were collected from the three rivers, the wood pool and Shimizu Port. Physical and chemical properties of the water samples were analyzed. Furthermore, a tidal current was observed to investigate the transport process of chemical substances by suspended solids. The results showed that the amount of lithogenic particles into Shimizu Port was approximately 12,000 kg/day. The suspended solids discharged from the rivers and the biological particles produced in the port cause a reduction of transparency of seawater and an increase in COD. Trace metals, such as Mn, Co and Pb, were highly concentrated in the suspended solids.

3. TESTS AND MEASUREMENTS

Physical tests on the sediment samples were carried out to obtain the specific gravity of particles, grain-size distribution, water content and so on. These tests were carried out using the methods provided by the Japanese Industrial Standards (JIS) and the Japanese Geotechnical Standards (JGS), except for grain-size analysis, which was performed using the laser diffraction method (Furukawa et al., 2001). Ignition loss, concentrations of sulfide, heavy metals and tributyltin (TBT), redox potential and pH were measured by chemical tests and analyses.

A temperature of 750°C was used to determine the ignition loss. The chemical analyses of some metals—i.e. iron (Fe), lead (Pb), copper (Cu), zinc (Zn), manganese (Mn) and cobalt (Co)—were carried out using inductively coupled plasma atomic emission spectrometry (ICP-AES), after digestion with HNO₃, HF and HClO₄. As some metals appeared to be present at relatively high concentrations, a cross check was made using atomic-absorption analysis. This technique was also used to measure the concentrations of elements such as cadmium (Cd), arsenic (As), aluminum (Al) and chromium (Cr).

4. RESULTS AND DISCUSSION

4.1 Physical and Chemical Properties

Table 1 indicates the ignition loss and concentration of metals for both suspended solids and sediments obtained from the mouths of the three rivers. Since the properties of sediments obtained from Orido Bay have been presented in a previous study (Fukue et al. 2006b), these data will not be discussed unless required.

For example, the data of ignition loss for Orido Bay sediments are plotted at the same site in Figure 3. Figure 3 shows the relationships between ignition loss and distance from S1 site, which is located just outside of Orido Bay, as shown in Figure 1. The distance between S1 and S7 is approximately 5000 m. As can be seen in Figure 3, the ignition loss of the sediments decreases with distance from the S1 site. This indicates that the source of the organic matter is mainly within Orido Bay.
Figure 2. Example of samples containing wood.

The ignition loss of soils can represent the organic matter content. Organic matter contains organic carbon. Therefore, the ignition loss can be correlated with the total organic carbon (TOC) for soils. Figure 4 shows the relationship between the ignition loss and TOC for various types of soil (Japanese Geotechnical Society 2000). The data obtained for the Orido Bay sediments (Sites 10 to 12) and the Lake Sanaru sediments are also presented in Figure 4 (Fukue et al. 2006b). The figure shows a strong correlation between ignition loss and TOC for various soils and sediments ($R^2 = 0.809$). When the ignition loss is high, the organic carbon content is also high.

Because organic matter can contain more water, a higher ignition loss usually leads to higher water content. Furthermore, a lower specific gravity of organic matter can also make the water content higher. A similar pattern is seen in peat, which consists mainly of organic matter. The relationship between ignition loss and water content is shown in Figure 5.

The specific gravity of sediments depends mainly on the organic matter content. As the organic matter content is reflected by the ignition loss value, there is a correlation between specific gravity and ignition loss (Fukue et al. 2006b).

As a low $Eh$ value means a reducing anaerobic condition, the sediments of S1, S2 and Orido Bay are now under anaerobic conditions. Figure 7 shows that sediments with a low $Eh$ value contain a high concentration of sulfide. The sulfide concentration is very low at S4 to S7 where $Eh$ values are relatively high.

Table 1. Properties of the flow rates, SS and sediments from the three rivers.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Water Flow (m³/s)</th>
<th>Metal content (mg/kg dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Hamada R</td>
<td>0.02 - 0.24</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>2.5</td>
<td>177</td>
</tr>
<tr>
<td>Sediments</td>
<td>7.0</td>
<td>164</td>
</tr>
<tr>
<td>Ohashi R.</td>
<td>0.17 - 0.76</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>6.9</td>
<td>255</td>
</tr>
<tr>
<td>Sediments</td>
<td>3.1</td>
<td>52</td>
</tr>
<tr>
<td>Tomoe R.</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>2.0</td>
<td>150</td>
</tr>
<tr>
<td>Sediments</td>
<td>9.6</td>
<td>79</td>
</tr>
</tbody>
</table>

Figure 3. Distribution of ignition loss for Shimizu Port sediments. Orido Bay samples are shown at a distance of ~ 400 m.

Figure 4. Relationship between ignition loss and TOC.

Figure 5. Relationship between ignition loss and water content.
4.2 Oxidation – Reduction Potential

At the bottom of the water column, degradation of organic matter will lead to low levels of oxygen in the sediments. The degree of oxygen consumption can be measured as the oxidation-reduction potential, \(Eh\) (mV). Figure 6 shows a variation in the \(Eh\) value with distance from the S1 site. It seems that the \(Eh\) value increased with distance from Orido Bay, though there is some scattering in the data. This is because the organic content would decrease with the distance, as deduced from the variation of ignition loss (Figure 3).

The relationship between \(Eh\) and sulfide concentration obtained in this study is shown in Figure 8. The figure shows that if the \(Eh\) value is greater than approximately 80 to 100 mV, no sulfide can be produced. This range of \(Eh\) levels for sediments can only be obtained at open sea bottoms and clean sand beaches (Fukue et al. 2004). The change in \(Eh\) influences the precipitation and dissolution of minerals in the sediments. Under anaerobic conditions, pyrite is often formed in marine sediments (Fukue et al. 2003, Fukue et al. 2004).

4.3 Heavy Metals and Ignition Loss

As might be expected, the metal concentrations increased with increasing ignition loss (IL). As the background value of Zn is 130 mg/kg dry for silty sediments (Fukue et al. 2006a), the rate of increase in the amount of Zn due to ignition loss is approximately 28 mg/kg/ %. The background values for Cu and Pb are 20 mg/kg, respectively (Fukue et al. 2006).

The organic component of sediments has a high affinity for heavy metal cations because of the presence of ligands or groups that can form chelates with the metals (Yong et al. 1992). If this is the case, the heavy metal contents must increase with increasing ignition loss. Figure 9 shows the concentrations of copper, lead, and zinc versus the ignition loss for sediment samples from Orido Bay and Shimizu Port.
Orido Bay. This may be dependent on the organic content, but not on the distance. There is a correlation between the concentrations of metals and ignition loss for Orido Bay sediments only (Fukue et al. 2006b).

By contrast, there was no significant correlation between Fe concentration and ignition loss for the Orido Bay sediments (Fukue et al. 2006b). The correlation coefficient $R^2$ was only 0.064. As Fe exists as oxides, pyrites or hydroxides in sediments, its concentration is largely independent of the amount of organic matter. Some studies reported that Fe and Al concentrations could be used for normalization when the sediment contamination was evaluated (Cobelo-Garcia and Prego 2003, Din 1992). However, normalizing techniques with elements such as Fe and Al could not be used in the present study, because no data were obtained on uncontaminated sediments.

Biodegradation of organic matter in sediments can release the adsorbed metals and nutrients into water column. This phenomenon can be one of the serious problems for contaminated sediments regarding the natural attenuation capabilities of sediments (Yong and Mulligan 2004). There is also the possibility that organic matter, i.e., detritus, can be taken by benthos, thus the contaminants adsorbed on organic matter can be accumulated in the benthos. Eventually, the contaminants can be taken up in the food-chain. In addition, oxidation of the sediments through resuspension during dredging operations can also potentially enhance degradation of the organic matter. Subsequent enhancement of leaching of the contaminants and their bioavailability would also occur (Cappuyns et al. 2006). Clearly then, the organic content must be considered when evaluating the remediation or management of contaminated sediments. Some of these alternatives are discussed in more detail in Yong et al. (2006).

4.4 Correlations Between Concentrations of Various Heavy Metals

In general, the type and level of hazardous materials released into the environment depend on the characteristics of the districts. On the other hand, similar types of hazardous materials have been released at the same time. Figure 11 shows a correlation between the concentrations of two elements, Cu and Pb, for the same sediments. The coefficient of correlation for this case is quite high, i.e., $R^2 = 0.901$. The coefficient of correlations between Cu and Zn, and Pb and Zn are also high, as shown in Figures 12 and 13. These facts indicate that the metals may be discharged from the same source.
On the other hand, iron and manganese do not show high coefficients of correlations with other metals. This may be because iron exists as a form of oxide or hydroxide or is a constituent of minerals, while manganese changes with a relatively high rate due to oxidation or reduction. By contrast, copper, lead and zinc can be elements mostly discharged through human activities and adsorbed on suspended solids which are deposited on the bottom.

5. CONCLUDING REMARKS

A case study of sediment contamination was made in one of the 23 specific designated important ports in Japan. The results show that the origin of contamination may be the Orido Bay which is located on the inner part of Shimizu Port. The concentrations of heavy metals such as copper, lead and zinc show a strong correlation with ignition loss, i.e., organic content. Though the concentrations of these elements decreased with distance from the Orido Bay, it is basically dependent on the organic content. High organic content in Orido Bay results from that the bay has been used as wood pool since 1927. Thus, the clean-up of Orido Bay is the best way to remediate the sediments in Shimizu Port and Orido Bay itself. The source of high concentrations of heavy metals may be small factories, because Orido Bay has been fed by two rivers, the Ohashi River and the Hamada River.

References


