The Chemical Composition and Nickel, Cobalt, Copper, Zinc and Lead Contents of Nanao Bay Sediments*

Yoshikazu YAMAMOTO**, Yukitaka TANAKA** and Shunzo UEDA**

Abstract: The contents of major and some of the minor elements, nickel, cobalt, copper, zinc and lead were studied on sediments collected from three inlets of Nanao Bay located at eastern side of Noto Peninsula. Little variation was found on the average contents of silicon, iron, titanium, aluminum, manganese, magnesium and potassium among the sediments of West, South and North Bays in Nanao Bay. Whereas significant difference was found on the contents of calcium, chloride, sulfur and nitrogen among sediments of three bays.

As to the minor elements, the average contents of nickel (20±5 ppm), cobalt (5±1 ppm), copper (18±5 ppm) and lead (17±8 ppm) are relatively low but zinc content is high in these sediments comparing with those of coastal deposit around Japan Island. From the results obtained here, it became clear that no environmental contamination of nickel, cobalt, copper and lead, and a little organic pollution were found in Nanao Bay sediments.

1. Introduction

In recent years the problem on contamination of marine environment, especially in coastal area, has begun to arise public attention. Marine sediments in coastal area or in bays, as well as sea water or marine organisms, seem to play an important role as geochemical and environmental discriminators. From the above point of view, the authors already reported on the contents of the major and minor elements in Nanao Bay sediments (YAMAMOTO, 1968a, b) and also the contents of cadmium, chromium and vanadium in Tokyo Bay sediments (ISHIBASHI et al., 1970).

The present paper describes on contents of the major, some of the minor elements and organic nitrogen in the sediments of three inlets of Nanao Bay, West, South and North Bays located at eastern side of Noto Peninsula.

2. Sample and method of analysis

The nineteen sediments samples were collected in August and October 1974 from the shallow area of Nanao Bay, using an Ekman-Birge sediment sampler. Fig. 1 shows the sampling localities. The samples were classified into three groups as follows: West Bay (Sample No. 1-6), South Bay (Sample No. 7-10) and North Bay (Sample No. 11-19). The average depth of sampling in West, South and North Bays are 8, 17 and 29 meters respectively. The samples were thoroughly air-dried, pulverized and subjected to the chemical analysis. The contents of the major and minor elements in the top 5 cm thickness of the sediments are given.

Absorbed water and ignition loss were determined by drying for 5 hours at 105-110°C and heating at 900-950°C respectively. Silicon, iron, titanium, aluminum, calcium and magnesium were determined by X-ray fluorescence method by using fused cake with lithium borate and potassium phosphate. Sodium and potassium were determined by flame photometry. Manganese and phosphorus were determined colorimetrically by potassium periodate and phosphomolybdate methods respectively. Total nitrogen was determined by Kjeldahl method.

The analytical procedure involves decomposition of the sample with hydrofluoric-perchloric acid and extraction of nickel, cobalt, copper, zinc and lead from the ammoniac solution of citrate with dithizone in chloroform. The chloroform solution of the dithizonates is evaporated to dryness, organic matter in the residue is decomposed by nitric-perchloric acid oxidation. Nickel, cobalt, copper, zinc and lead are pre-
cipitated with ammonium pyrrolidinedithiocarbamate (APDC) as a complexant. The precipitate of metal-APDC complex was collected on a membrane filter and dried. The APDC complexes of nickel, cobalt, copper, zinc and lead are then determined by X-ray fluorescence analysis with coefficients of variation of 2.0 to 3.6%.

3. Results and discussion

The average chemical composition of 19 samples of Nanao Bay are presented in Table 1, in which the averages of major elements of West, South and North Bays sediments are given for comparison.

From the above analytical results, no remarkable differences were found on the average contents of silicon, iron, titanium, aluminum, manganese, magnesium, potassium and phosphorus among the sediments of West, South and North Bays. Whereas significant differences are found on the contents of calcium, chlorine, sulfur and nitrogen among the sediments of three bays. Of these elements, average sulfur contents of West and South Bays sediments, $0.92 \pm 0.39 \%$ and $1.19 \pm 0.04 \%$ are 2-2.5 times higher than that of North Bay sediments ($0.47 \pm 0.17 \%)$. This may be due to the shallow depth, narrow entrance of bay and little exchange of sea water between the inside and the outside.
Table 1. The average chemical composition of the shallow-water sediments of Nanao Bay.*

<table>
<thead>
<tr>
<th>Drying loss</th>
<th>Sediments of West Bay (6 species)</th>
<th>Sediments of South Bay (4 species)</th>
<th>Sediments of North Bay (9 species)</th>
<th>All Sediments of Nanao Bay (19 species)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ignition loss</td>
<td>14.04</td>
<td>12.42</td>
<td>12.70</td>
<td>13.16</td>
</tr>
<tr>
<td>SiO₂</td>
<td>49.32±6.55</td>
<td>49.15±2.06</td>
<td>49.66±4.54</td>
<td>49.45±4.92</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.70±1.06</td>
<td>6.16±0.46</td>
<td>6.72±1.07</td>
<td>6.60±1.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.81±0.13</td>
<td>0.72±0.04</td>
<td>0.85±0.15</td>
<td>0.81±0.14</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.73±0.47</td>
<td>13.85±0.75</td>
<td>14.60±1.55</td>
<td>14.48±1.20</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03±0.01</td>
<td>0.03±0.01</td>
<td>0.02±0.01</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>3.85±1.20</td>
<td>2.77±0.79</td>
<td>4.73±1.67</td>
<td>4.04±1.58</td>
</tr>
<tr>
<td>MgO</td>
<td>2.00±0.32</td>
<td>2.01±0.04</td>
<td>2.02±0.34</td>
<td>2.01±0.29</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.33±0.12</td>
<td>1.47±0.60</td>
<td>1.66±0.46</td>
<td>1.51±0.45</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.35±0.12</td>
<td>1.52±0.09</td>
<td>1.44±0.24</td>
<td>1.43±0.19</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.92±0.39</td>
<td>1.19±0.04</td>
<td>0.47±0.17</td>
<td>0.76±0.39</td>
</tr>
<tr>
<td>Cl</td>
<td>3.81±1.09</td>
<td>5.53±0.97</td>
<td>2.84±0.95</td>
<td>3.71±1.44</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.20±0.04</td>
<td>0.20±0.04</td>
<td>0.16±0.02</td>
<td>0.18±0.04</td>
</tr>
<tr>
<td>N</td>
<td>0.25±0.06</td>
<td>0.31±0.04</td>
<td>0.20±0.06</td>
<td>0.24±0.07</td>
</tr>
</tbody>
</table>

* Sea salt free and dry basis.

Table 2. The contents of minor elements in the sediments of Nanao Bay.

<table>
<thead>
<tr>
<th>Elements</th>
<th>West Bay (ppm)</th>
<th>South Bay (ppm)</th>
<th>North Bay (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>range</td>
<td>average</td>
<td>range</td>
</tr>
<tr>
<td>Ni</td>
<td>6~ 20</td>
<td>16± 5</td>
<td>16~ 23</td>
</tr>
<tr>
<td>Co</td>
<td>3~ 6</td>
<td>5± 1</td>
<td>4~ 6</td>
</tr>
<tr>
<td>Cu</td>
<td>7~ 22</td>
<td>17± 1</td>
<td>16~ 25</td>
</tr>
<tr>
<td>Zn</td>
<td>91~ 204</td>
<td>159±39</td>
<td>97~ 273</td>
</tr>
<tr>
<td>Pb</td>
<td>10~ 16</td>
<td>11± 4</td>
<td>23~ 31</td>
</tr>
</tbody>
</table>

Table 3. The contents of the average minor elements in Nanao Bay sediments, other coastal deposits and marine sediments.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sediments of Nanao Bay (ppm)</th>
<th>Sediments of Nanao Bay (ppm)</th>
<th>Coastal deposits around Honshu Island, Japan (b)</th>
<th>Sediments of Gulf of Paria, USA (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>range</td>
<td>average</td>
<td>range</td>
<td>average</td>
</tr>
<tr>
<td>Ni</td>
<td>20± 5</td>
<td>14± 5</td>
<td>20±14</td>
<td>11± 8</td>
</tr>
<tr>
<td>Co</td>
<td>5± 1</td>
<td>6± 2</td>
<td>7± 5</td>
<td>4± 5</td>
</tr>
<tr>
<td>Cu</td>
<td>18± 5</td>
<td>27±16</td>
<td>35±45</td>
<td>13±20</td>
</tr>
<tr>
<td>Zn</td>
<td>139±60</td>
<td>51± 7</td>
<td>114±51</td>
<td>73±74</td>
</tr>
<tr>
<td>Pb</td>
<td>17± 8</td>
<td>55± 6</td>
<td>21±12</td>
<td>11± 9</td>
</tr>
</tbody>
</table>


of South and West Bay compared with North Bay which is deep and has wide entrance of the bay and higher exchange rate of sea water between the inside and the outside of the bay. The average nitrogen contents of 0.25±0.06 % and 0.31±0.04 % for West and South Bays sediments are close to the average of 0.23 % for Wakasa Bay sediments (Ohta, 1954) and to the values of 0.16-0.32 % for Tokyo Bay sediments (Esumi, 1975).

Table 2 shows the average contents and ranges of Ni, Co, Cu, Zn and Pb in the sediments of West, South and North Bays of Nanao. Table 3 gives the average contents of Ni, Co, Cu, Zn and Pb in Nanao Bay sediments together with the result of previous study.
in 1964 (YAMAMOTO, 1968a, b) and of coastal deposits of Honshu, Japan (ISHIBASHI et al., 1968, 1959a, b and 1960).

Nickel The contents of Ni in Nanno Bay sediments are in the range 6–27 ppm. The average Ni content of these sediments, 20±5 ppm, is a little higher than that of our previous study (YAMAMOTO, 1968a, b). The average level of Ni in these sediments is close to that of the coastal deposits of Honshu (20±14 ppm), where seem to be affected by little pollution (ISHIBASHI et al., 1959b).

Cobalt The contents of Co in these sediments ranges from 3 to 7 ppm with the average value of 5±1 ppm. No difference was found on the contents of Co among the sediments of West, South and North Bays, as shown in Table 2. There was also no variation in the average content of Co compared with that of the previous study in 1964 (YAMAMOTO, 1968a, b). The average content of Co in these sediments was in the same level as those of the coastal deposits of Honshu (ISHIBASHI et al., 1959a), as shown in Table 3.

While, SANDELL and GOLDLICH (1943) pointed out that Co varies linearly with magnesium over a wide range of concentrations in the silicic rocks, but no relationship between the contents of Co and magnesium was found in these sediments.

Copper The content of Cu in these sediments is in the range from 9 to 29 ppm with slight variation. The same values of Cu concentrations, the averages of 17±5 ppm and 17±6 ppm, are found in West and North Bays sediments. While slightly higher content of Cu, the average value of 20±4 ppm, is found in South Bay sediments. The average content of Cu in Nanno Bay is 18±5 ppm which is a little lower than that of the previous study (YAMAMOTO, 1968a, b). However, it is close to the average values of 13±20 ppm and 17 ppm for the coastal deposits (sands) of Honshu (ISHIBASHI et al., 1958) and for the sediments from the Gulf of Paria (HIRST, 1962) respectively.

Zinc Relatively high level of Zn was found in these sediments, ranging from 60 to 273 ppm with the average value of 130±60 ppm.

The average Zn content of these sediments increases more than twice as much as that of 51±7 ppm determined in 1964 (YAMAMOTO, 1968a, b).

Lead The content of Pb in these sediments ranged from 4 to 29 ppm with the average value of 17±8 ppm, which is close to the average Pb content of 21±12 ppm in the coastal deposits (muds) of Honshu (ISHIBASHI et al., 1960). Compared with the average Pb content of 55±6 ppm obtained in 1964 (YAMAMOTO, 1968a, b), the average Pb content of these sediments is one fourth of the previous result. The average value of 17±8 ppm for these sediments corresponds to the background values of 11–22 ppm Pb reviewed by KITANO et al. (1975).

From the data described above, it became clear that no environmental contamination of Ni, Co, Cu and Pb and a little organic contamination appeared in sediments of Nanno Bay, while relatively high level of Zn was observed in sediments of South and West Bays.

References


ISHIBASHI, M., S. UEDA and Y. YAMAMOTO (1960): Studies on the utilization of the shallow-water
七尾湾海底土の化学組成ならびにニッケル，コバルト，銅，亜鉛，鉛含量

山本善一*，田中幸隆*，上田俊三*

要旨：七尾湾西湾，南湾および北湾から採取した19種の海底土試料の化学組成と微量元素としてニッケル，コバルト，銅，亜鉛，鉛含量を調べた。西湾，南湾，北湾の試料中のケイ素，鈣，チタン，アルミニウム，マンガン，マグネシウム，カリウム，リンの平均含量はほぼ類似の値を示し，各湾の水深や堆積環境との関連は認められなかった。これに対し，各湾の試料中のカルシウム，塩素，イオウ，窒素の平均含量には有意の差がみられた。

微量元素については，ニッケル（平均値 20±5 ppm），コバルト（平均値 5±1 ppm），銅（平均値 18±5 ppm），鉛（平均値 17±8 ppm）で，これらの平均値は底質中のそれぞれの元素のパックグラウンド値に近い，これに対し，亜鉛含量は一般に高く（平均値 139±60 ppm），とくに南湾と西湾の底土に高い。一方，北湾の底土には100 ppm 以下のものが多い。

以上の結果から，亜鉛含量のやや高いのを除いて，七尾湾海底土中には，ニッケル，コバルト，銅，鉛などの重金属による底質汚染は認められなかった。

* 金沢大学工学部工業化学科
〒920 金沢市小立野 2-40-20