## 7.10 Anthropogenic pollution of Kara Sea and estuaries of the Yenisei and Ob rivers based on data of the 2001 and 2000 cruises

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The great Siberian rivers jointly with the northern seas compose a part of the global hydrosphere within which the processes of continental erosion, transport and accumulation of sediments take place, i.e., the processes of geochemical interaction between the continent and ocean. The scale and nature of these processes in the territories of northern Russia and the Arctic seas remain rather uninvestigated.

From an ecological point of view the large Siberian rivers are potential sources of anthropogenic pollution of the Kara Sea and further of the Arctic basin. Therefore, the investigations connected with an assessment of levels of contents of radioactive and chemical admixing in surface sediments and in sediment cores obtained from fluvial medium, mixing zone and open part of the sea, help to estimate the modern ecological state of the local region and to reveal time intervals of massive fluvial input from radiochemical plants of Ural and Siberia into the marine area.

### Working Program

The main tasks of our radiogeochemical research of the cruise 2001 were to study the horizontal and vertical distribution of the Cs, Sr and Pu isotopes in water and sediments, and to estimate the influence of natural environmental parameters on laws governing the distribution and migration of radionuclides in the investigation area.

Other tasks are:

- the study of granulometric structure of upper layer sediments and level of radioactivity $^{137}Cs$;
- the study of role of suspended matter on the behavior and migration of some radionuclides;
- the estimate of the Yenisei river role as source of anthropogenic pollution of the Kara Sea water;
- the evaluation of spreading of heavy metals with riverine suspension into the Kara Sea and the determination of anthropogenic elements in the Kara Sea, as consequence of the Norilsk plants production.

### Sampling and Analytical Methods.

Sediments were sampled with a box corer (50x50x60 cm), with subsequent subsampling with a plastic tube having an inner diameter of 10 cm. The cores were cut in 1-2 cm slices, and samples were dried at a temperature of 60 - $80^0$ C. Water was sampled with a large volume sampler (200 l Batomat) or taken by a pump through a plastic pipe

system, and filled in storage tanks. Before analysis some samples were filtered through a cartridge filter to remove suspended matter >0.45μm.

The greatest amount of data was obtained for $^{137}Cs$ contents, and to a smaller extent for $^{90}Sr$ and $^{239,240}Pu$. $^{137}Cs$, $^{90}Sr$ and $^{239,240}Pu$ in water samples, and $^{90}Sr$ and $^{239,240}Pu$ in sediment samples were determined with a radiochemical method. For the analysis of $^{137}Cs$ in sediments we used direct γ-measurements without decomposition of the sample.

Measurement of the radioactivity of $^{137}Cs$ in sediment samples was carried out in a low-background installation with semiconductor Ge detector. $^{137}Cs$ was determined in water samples of 200 1 volume using the sorption method under dynamic conditions with subsequent γ-spectrometer measurements on concentrates. Co-ferrocianid, fixed on an organic matrix, was used as quality sorbent for concentrating Cs.

The determination of $^{90}Sr$ in the water samples included precipitation of strontium carbonate. Then we use extraction chromatographic procedure with crown-acther dicyclohexano-18-crown-6 permitting to separate $^{90}Sr$ from other radionuclides. At passage 2μ of solution on hydrogen nitrate keeping radionuclides through column on a column remain strontium and lead. After unabsorbtion of strontium from the column by hot water, we carried out a final precipitation of $^{90}Sr$ as strontium oxalatum.

The analysis of Pu in water samples consisted of precipitation of Pu with iron hydroxide (from a volume of 150 1), subsequent radiochemical cleaning and adsorption of Pu on $LaF_3$. Precipitates were separated on a membrane filter and activity measured on α-spectrometer. For extraction of Pu from sediments samples were boiled in 7M $HNO_3$ with $KBrO_3$, and then were further processed as water samples Pu analysis.

**Results and Discussion**

The data on $^{137}Cs$ distribution in the top layer (0-2cm) of the bottom sediments from all .stations are presented in Table 7.12. The data demonstrate that the distribution of $^{137}Cs$ in the upper (0-2 cm) layer is irregular. In the Yenisei Bay high concentrations of this radionuclide are observed. The lowest values of $^{137}Cs$ cluster are in the central part of our working area, and at some localities of the Ob Bay.

If we consider the data on $^{137}Cs$ radioactivity, which we obtained during this expedition, in combination with the lithology and geochemical activity of 1995-cruise data (Tab. 7.13), we can estimate the peculiarities in the distribution of this radionuclide in the estuaries of rivers Ob and Yenisei. Thus, in the studied part of the Ob Bay, the reduced sediments are represented by sandy mud that does not absorb Cs, consequently, the $^{137}Cs$ concentration is very low. On the contrary, in the Yenisei Bay, the bottom sediments are characterized by a high fraction of partially oxidized clays, with high capabilities of absorbing $^{137}Cs$, which resulted in the higher specific activity of $^{137}Cs$ in the bottom sediments.

In the upper sedimentary layer the Pu-radionuclides activity distribution is recorded, although we have for this radionuclide less number of analysed samples (Table 7.14).

The investigation of the distribution of Cs and Sr radionuclides in water samples showed, that the concentration of these two radionuclides are low in filtrited samples of water. The concentrations of water-soluble Cs-species increase with increasing salinity (Fig. 7.21), where as the concentrations of Sr decrease with increasing salinity (Fig. 7.22).

The results of the Cs and Sr radionuclides distribution of solution and suspended matter showed, that for the sea water the suspended matter may absorb up to 1-10% $^{137}$Cs and $^{90}$Sr, for the water samples of rivers these value can be reach 15-30% (Tab. 7.15-7.16). This means, that the coefficient of $^{137}$Cs concentration (the first time) by suspended matter may be as high as $10^3$-$10^4$. Therefore, suspended matter, together with mobile clay phase of the bottom sediments upper layer, may transfer considerable amounts of $^{137}$Cs (and other isotopes).

For $^{90}$Sr-radionuclide we confirm our previous data that $^{90}$Sr is able to form complex with dissolved organic matter (Tab. 7.16), especially in solutions with low salinity. These investigations are important for understanding of the behavior and transfer of radioactive elements – as marker of processes in the river-estuaries-sea geochemical system.

The second part of our investigations were to obtain additional analytical information about contents and distribution of heavy elements, including the presence of the anthropogeneous heavy metals in sea water which enters the Kara Sea as consequence of works of the mining plants. In this cruise, we have performed the determination of heavy metals in bottom sediments by X-Ray fluorescence method using X-Ray spectrometer SPARK-1.

The data of the Fe content in river and sea water show, that heavy metals together with the upper layer of bottom sediments spread far to north of the Sea (Fig. 7.23). The lateral distribution of the anthropogenic metals Pb and Cu and other elements are different (Fig. 7.24). We believe that the irregular distribution of Pb and Cu in the Kara Sea (Fig. 7.25) may be related to the influence of source-works mining plant in the town of Norilsk.

Thus, our studies yielded rather objective characteristics of the antrophogenic situation in the estuaries of the Yenisei and Ob rivers and adjacent part of the Kara Sea in 2001.

Table 7.12: The data on $^{137}Cs$ distribution in the top layer of the bottom sediments.

| | Number of station | Concentration of $^{137}Cs$ Bq/kg (P=0.95) |
|---|---|---|
| 1 | 01-01 | 8.0 ± 1.0 |
| 2 | 01-03 | 33.7 ± 3.0 |
| 3 | 01-04 | 8.6 ± 1.8 |
| 4 | 01-05 | 2.8 ± 0.6 |
| 5 | 01-05 | 4.4 ± 0.6 |
| 6 | 01-06 | 16.0 ± 1.5 |
| 7 | BP01-07 | 15.9 ± 2.2 |
| 8 | BP01-08 | 7.6 ± 1.1 |
| 9 | BP01-09 | 24.0 ± 2.0 |
| 10 | BP01-10 | 27.4 ± 2.2 |
| 11 | BP01-12 | 46.2 ± 3.7 |
| 12 | BP01-13 | 24.0 ± 2.2 |
| 13 | BP01-15 | 21.0 ± 3.0 |
| 14 | BP01-16 | 3.0 ± 1.0 |
| 15 | BP01-17 | 21.7 ± 3.0 |
| 16 | BP01-18 | 39.3 ± 4.5 |
| 17 | BP01-19 | 47.0 ± 5.0 |
| 18 | BP01-20 | 363 ± 4.0 |
| 19 | BP01-21 | 28.0 ± 4.0 |
| 20 | BP01-22 | 6.2 ± 1.5 |
| 21 | BP01-23 | 6.8 ± 1.4 |
| 22 | BP01-25 | 19.0 ± 2.0 |
| 23 | BP01-28 | 7.0 ± 1.2 |
| 24 | BP01-29 | 7.1 ± 2.3 |
| 25 | BP01-30 | 5.6 ± 0.9 |
| 26 | BP01-31 | 7.0 ± 1.4 |
| 27 | BP01-32 | 4.9 ± 1.0 |
| 28 | BP01-33 | 3.8 ± 0.5 |
| 29 | BP01-34 | 2.0 ± 0.4 |
| 30 | BP01-35 | 6.4 ± 1.0 |
| 31 | BP01-36 | 2.2 ± 0.6 |
| 32 | BP01-37 | 5.0 ± 1.1 |
| 33 | BP01-38 | 6.1 ± 0.9 |
| 34 | BP01-39 | 5.8 ± 0.9 |
| 35 | BP01-40 | 5.7 ± 0.8 |
| 36 | BP01-41 | 6.0 ± 0.8 |
| 37 | BP01-42 | 16.7 ± 2.0 |
| 38 | BP01-43 | 14.4 ± 2.0 |
| 39 | BP01-44 | 1.4 ± 0.5 |
| 40 | BP01-45 | 10.2 ± 1.4 |
| 41 | BP01-46 | 2.1 ± 0.6 |
| 42 | BP01-47 | 9,2 ± 0,9 |
| 43 | 01-48 | 6.0 ± 1.5 |
| 44 | 01-49 | 5.0 ± 0.8 |
| 45 | 01-50 | 3.8 ± 0.6 |
| 46 | 01-51 | 6.8 ± 1.6 |
| 47 | 01-52 | 7.1 ± 1.3 |

| | | |
|---|---|---|
| 48 | 01-55 | 5.6 ± 0.8 |
| 49 | 01-56 | 5.0 ± 0.8 |
| 50 | 01-57 | 5.2 ± 0.8 |
| 51 | 01-58 | 7.0 ± 2.0 |
| 52 | 01-59 | 7.6 ± 2.0 |
| 53 | 01-60 | 3.8 ± 0.7 |
| 54 | 01-61 | 11.9 ± 1.7 |
| 55 | 01-62 | 12.7 ± 1.6 |
| 56 | 01-63 | 5.2 ± 0.9 |
| 57 | 01-64 | 10.9 ± 13 |
| 58 | 01-65 | 4.2 ± 1.2 |
| 59 | 01-66 | 9.6 ± 1.2 |
| 60 | 01-67 | 11.7 ±1.5 |
| 61 | 01-68 | 4.5 ± 0.8 |
| 62 | 01-69 | 13.5 ± 2.0 |
| 63 | 01-70 | 7.2 ± 0.8 |
| 64 | 01-71 | 1.9 ± 0.5 |
| 65 | 01-72 | 2.1 ± 0.5 |
| 66 | 01-72 | 9.2 ± 1.2 |
| 67 | 01-73 | 10.1 ± 1.4 |
| 68 | 01-73-1 | 11.1 ± 1.3 |
| 69 | 01-73-2 | 9.5 ± 1.2 |
| 70 | 01-73-3 | 14.9 ± 1.7 |
| 71 | 01-73-4 | 9.8 ± 1.0 |
| 72 | 01-73-5 | 7.1 ± 1.0 |
| 73 | 01-74 | 10.8 ± 1.4 |
| 74 | 01-75 | 15.9 ± 2.0 |
| 75 | 01-76 | 14.4 ± 2.4 |
| 76 | 01-77 | 12.8 ± 2.1 |
| 77 | 01-78 | 11.8 ± 1.5 |
| 78 | 01-79 | 6.8 ± 0.9 |
| 79 | 01-80 | 2.4 ± 0.4 |
| 80 | 01-81 | 17.4 ± 2.6 |
| 81 | 01-82 | 14.4 ± 2.6 |
| 82 | 01-83 | 10.0 ± 0.9 |

Table 7.13: Equilibrium partition coefficient ($K_d$) of $^{137}Cs$ for various types of bottom sediments (treatment of the cruise-1995 data).

| Group no. | Type of bottom sediments | $K_d$ | Sorption effect |
|---|---|---|---|
| 1 | Coarse-grained sediments wih a low fraction of pelitic particles of organic-mintral composition of shallow bottom areas with intence exchange at media interface | 10-20 | Weak |
| 2 | Pelitic sediments of organic-mineral composition with high content of sand-silt fraction of shallow and moderately deep floor regions with an intense exchange of disperse phases at media interface | 40-70 | Medium |
| 3 | Pelitic sediments consisting mainly of organic-mineral colloids with intense exchange of disperse phases at media interface | >100 | Strong |

Table 7.14: Results of determination activity _u-239,240 in upper layer of bottom sediments.

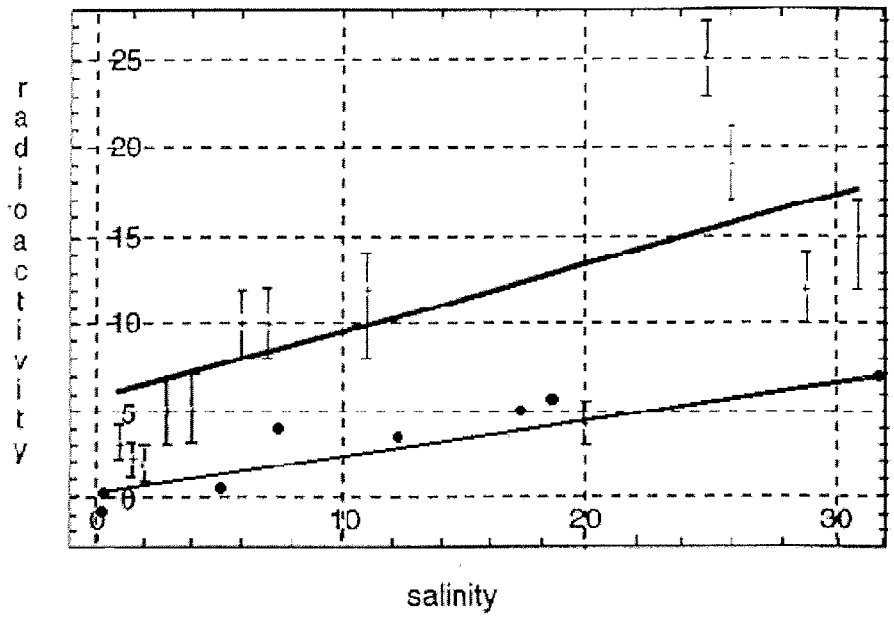
| Station | Activity _u-239,240, Bq/kg |
|---|---|
| BP2000-07 | 1.96 |
| BP2000-14 | 0.595 |
| BP2000-15 | 0.065 |
| BP2000-16 | 0.19 |
| BP2000-21 | 0.595 |
| BP2000-22 | 0.595 |
| BP2000-23 | 0.355 |

Table 7.15: Distribution of $^{137}Cs$ between water and suspended matter fractions.

| Number of station | Level of activity, Bq/sample. | |
|---|---|---|
| | Suspended matter | Water |
| BP95-36 (Kara Sea) | 0.2 | 33 |
| BP95-06 (Kara Sea) | 0.3 | 46 |
| BP01-70 (Ob bay) | 0.4 | 2.2 |
| BP01-25 (Yenisei bay) | 0.7 | 4.8 |

Table 7.16: Results of measurement of Sr-90 in water, filtered water (0,2 μm) and ultrafiltered water(2000 Da)

| Station | Depth, m | Salinity, ‰ | Activity Sr-90, Bq/m$^3$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | Not filtered water | Filtered water, (0,2 μrn) | Ultrafiltered water | | |
| | | | | | 2000 Da | 800 Da | 150 Da |
| BP01-08 | 3 | 0.1 | 3,9±1,1 | 3,1±0,6 | - | - | - |
| | 28 | 0,1 | - | - | 4,5±0,9 | - | 2,7±0,5 |
| BP01-72 | 3 | 0,1 | 9,7±1,9 | 8,0±1,6 | 6,4±1,3 | 5,9 | 3,7±0,7 |
| BP01-30 | 3 | 34,1 | 1,9±0,4 | 1,6±0,3 | - | 1,1±0,2 | - |
| BP01-70 | 3 | 1.5 | 7,0±1,4 | 5,8±1,2 | - | - | - |




Cs-137 concentration (dissolved) in samples as function of salinity.

Figure 7.21: $^{137}$Cs concentrations vs. salinity. ✖ - data 1995, 1997; _ - data 2001.

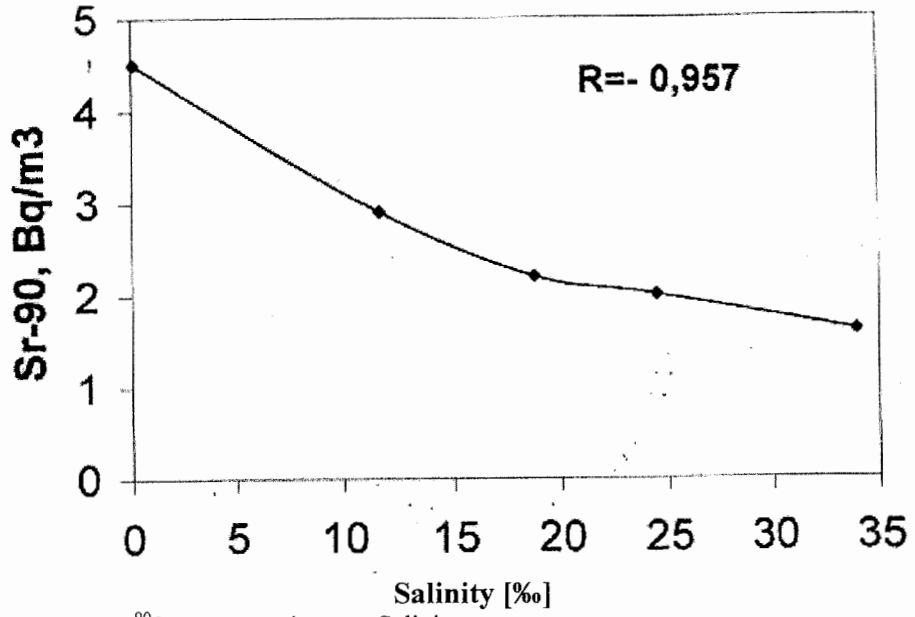



Figure 7.22: $^{90}Sr$ concentrations vs. Salinity

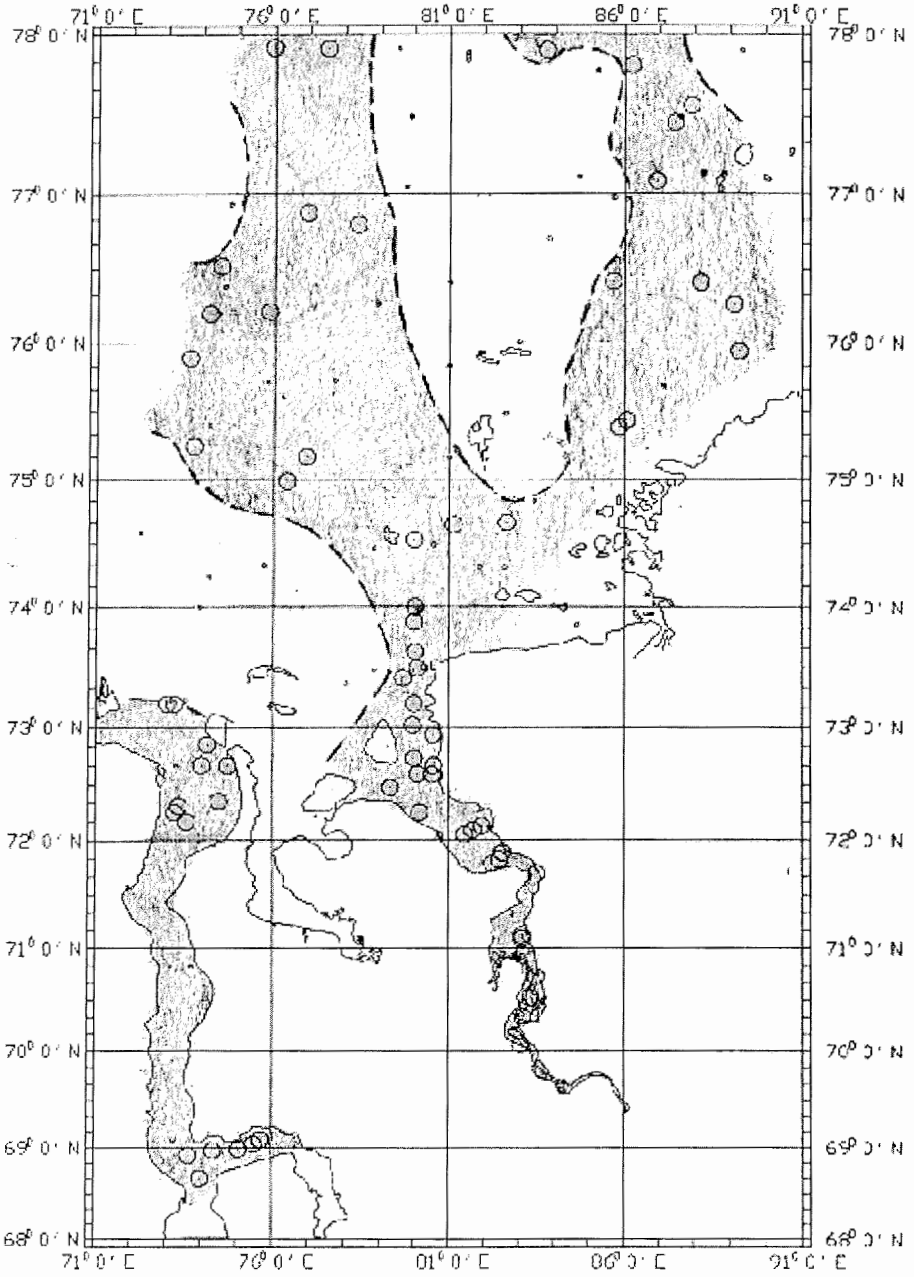



Figure 7.23: Spreading of the Yenisei river material to the Kara Sea on the Fe content in top layer of the bottom sediments.

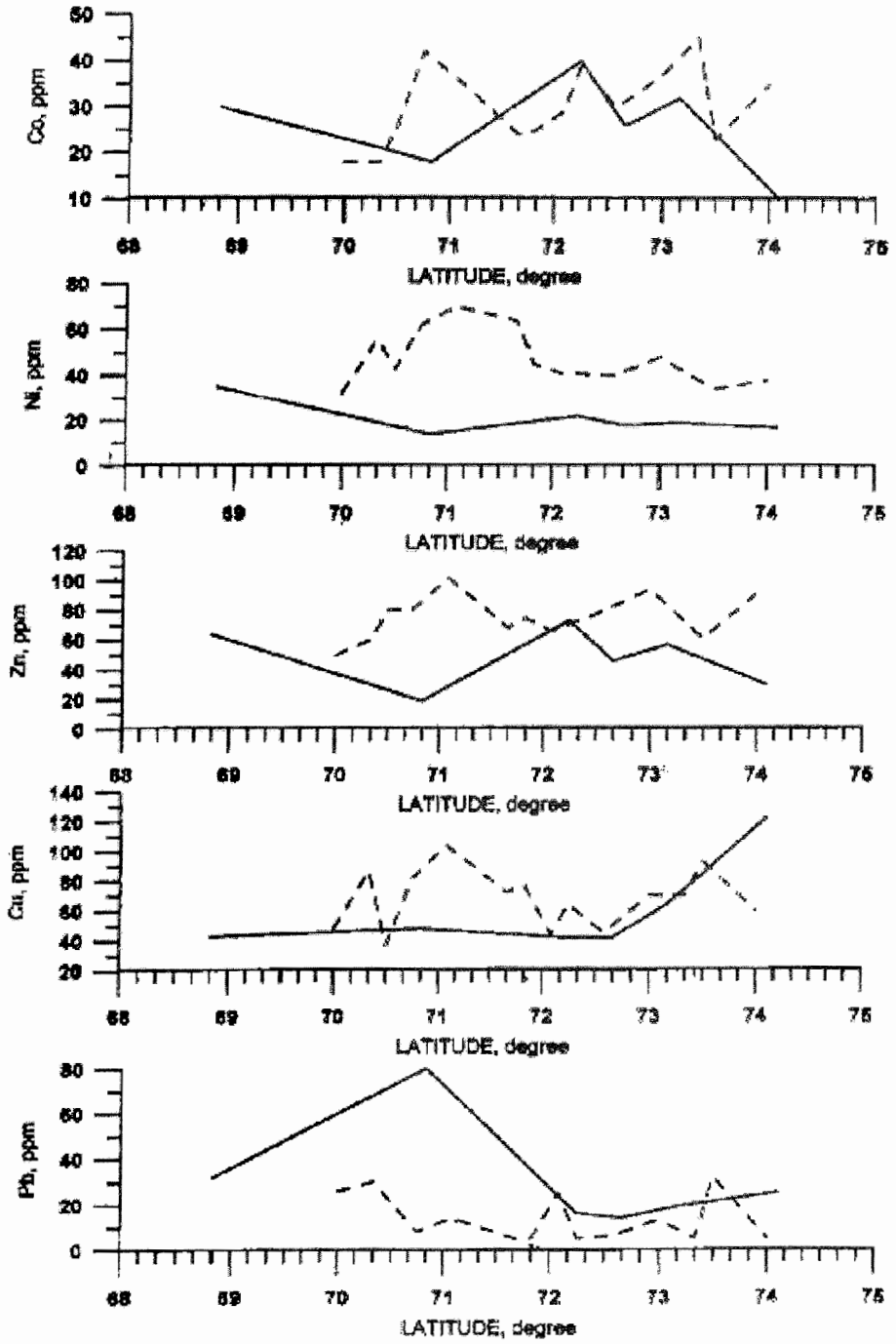



Figure 7.24: Lateral distribution of heavy metals in upper layer of bottom sediments. line: in Ob River; dotted line: in Yenisei River.

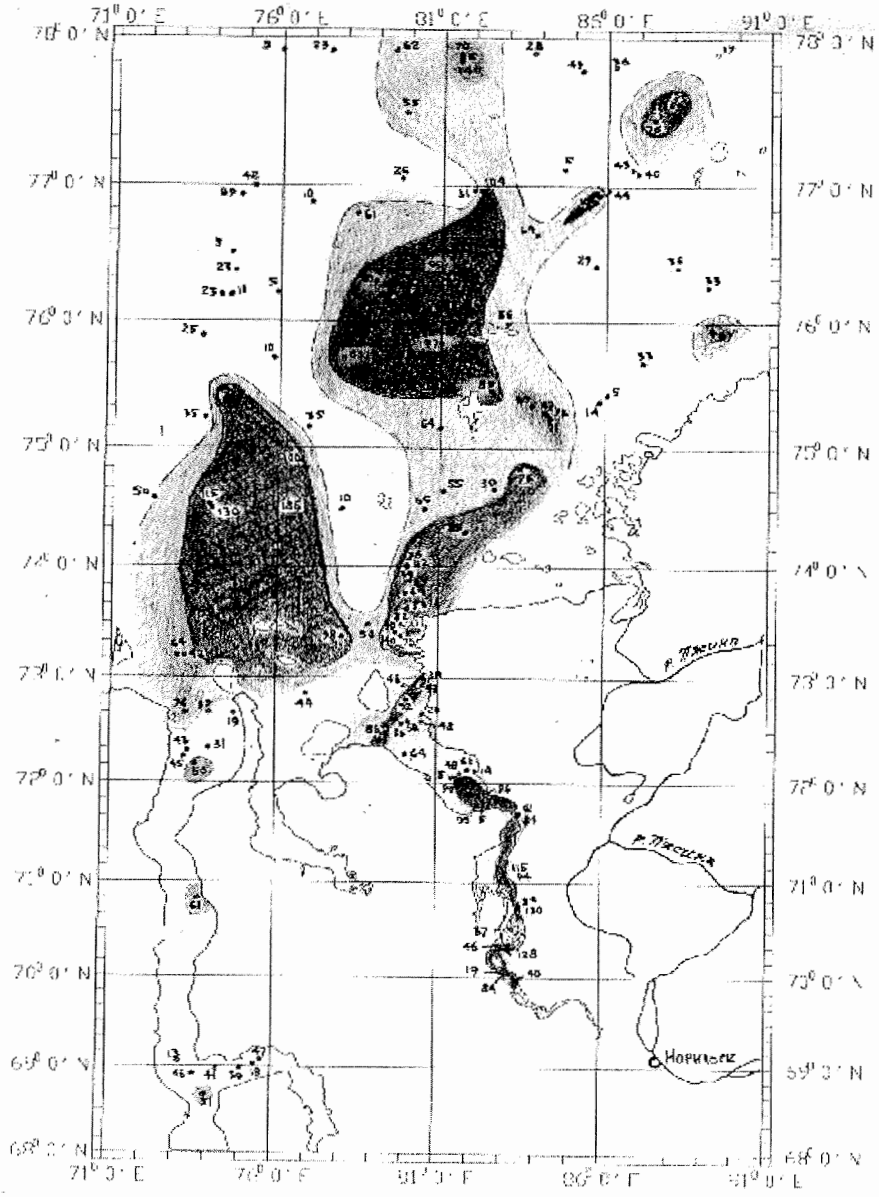



Figure 7.25: Distribution of the Cu in estuaries of the Yenisei and Ob rivers and adjacent area of the Kara Sea.

- < 50 ppm ; - 50 – 75 ppm ; - > 75 ppm .