

RADIOISOTOPE EXCITED X-RAY FLUORESCENCE AND NEUTRON ACTIVATION ANALYSES OF SURFACE SEDIMENTS COLLECTED ALONG THE TURKISH BLACK SEA COAST

D.S. Khamrayeva¹, T.Akyuz², S. Akyuz³

¹ Institute of Nuclear Physics, Tashkent, Uzbekistan,

² Cekmece Nuclear Research and Training Center, Istanbul, Turkey

³ Istanbul University, Istanbul, Turkey

Surface sediment samples collected from 18 sites of the Sea of Marmara and the Black Sea around Istanbul area in 1978, 1996 and 1999 years have been investigated. Radioisotope excited energy disperse X-ray fluorescence (EDXRF) method and neutron activation analysis were used for investigation of the impurity content of the samples..

Analytical results indicated that samples contain (mg/kg) Na (4900-15000), Ca (6800-66000), Sc (3.1-11), Ti (<10-3100), Cr (42-450), Mn (230-510), Fe (11500-27900), Co (3.2-8.7), Ni (45-83), Cu (<10-78), As (6.9-11), Se (≤ 1), Br (8.3-48), Sr (300-970), Zr (160-860), Mo (<10-95), Ag (0.36-1.4), Cd (<1), Sb (0.036-0.087), Cs (0.58-4.7), Ba (120-570), La (8.4-28), Ce (27-68), Sm (2.1-3.3), Hf (1-8), Ta (0.3-0.77), W (15-120), Au (0.0058-0.28), Hg (<1), Th (3.4-7.7), and U (2.0-5.9). Heavy metal pollution of the Marmara Sea sediments are founded to be higher than those of the Black Sea sediments around Istanbul Area. This is mainly due to the industrialised area situated around the Marmara Sea shore on the south part of Istanbul.

The results compare with those from other contaminated and uncontaminated sedimentary materials.

Black Sea is a unique, virtually enclosed water body shared between Romania, Bulgaria, Turkey, Georgia, Russia and Ukraine. Environmental problem in the Black Sea is serious. Major part of the pollutants transported by rivers are normally adsorbed on fine grained particles in suspension. Marine or lakes commonly accumulate deposits derived from bedrocks, soils and organic remains within the drainage basin, through fine particles can also be blown in by winds from distant natural, urban and industrial sources. These sediments provide a valuable record of

environmental change of conditions. Istanbul is the most heavily populated and industrialised metropolitan area of Turkey, situated on both sides of Bosphorus (Istanbul Strait). Bosphorus is narrow channel between the Black Sea and the Marmara Sea and is about 31 km long, 0.7-0.3 km wide an average dept of 35 m. The heavy metal pollution of the environment of the Black Sea and the Marmara Sea around Istanbul area is gradually increasing due to urbanisation and industrial activities in the region. On the other hand the pollutant levels in the Marmara Sea are greatly influenced by the opposite water currents between the Black Sea and the Aegean Sea, which is driven by the density differences between the adjoining seas. Therefore it is found to be interesting to compare the pollution levels between the Black Sea and the Sea of Marmara around Istanbul area using sediment samples. In this study surficial sediment samples, collected from 18 sites of the Black Sea and the Sea of Marmara nearby Istanbul area in 1996 and 1999 years, were analysed quantitatively by radioisotope excited energy dispersive X-ray fluorescence (EDXRF) method using fundamental parameter technique (FPT) and neutron activation analysis.

Surface sediments were collected from 18 sites of the Sea of Marmara and the Black Sea nearby Istanbul area in 1978, 1996 and 1999 years. The locations of the sampling sites are shown in figure 1 and given in Table 1. Surficial sediment samples were collected by Van veen grab on the board of Arar ship of Istanbul University¹. The investigated samples were taken from the uppermost part of the collected sediments for each site, with spatulas and deposited into plastic bags. The samples were dried at 40⁰C before being analysed.

The samples were excited using an ²⁴¹Am source (25 µCi) and a HPGe detector or a Cd source (15 µCi) and a Si(Li) detector for 50000 s with resolutions of approximately 350 eV and 185 eV FWHM, respectively, at 5,89 keV. The quantitative analyses were performed by the fundamental parameter technique (FPT), in order to minimize the matrix effects in X-ray fluorescence analysis. The details of this technique were given in references.

In the case of FPT, the geometric factors G_i for each element i { that were related to the incident-exciting X-ray intensity, the geometric factor of the spectrometer and the detection efficiency for the fluorescence radiation from element i } were first determined experimentally, by

using uniform thin standard samples, according to reference, and then a calibration graph for the spectrometer was drawn. The geometric factors for the other elements of the sample investigated were calculated by using this graph. Finally, the absorption corrections of the elements and then the concentration of each element i of the sample was determined. The reliability of the FPT was checked by several measurements on the standard reference materials (NBS SRM 1633a 1646 and SL-1, Soil-5 reference materials of International Atomic Energy Agency) and our results are found to be in confidence interval of SRMs. The over all error in the FPT is estimated to be less than +10%. This error has been calculated as a square root of sum of variances of different parameters used.

In the case of the NAA analysis samples were irradiated in the WWR-SM nuclear reactor in flux of 5.10 n.cm.s .

The EDXRF results of some elements of the Black Sea and the Marmara Sea sediments are given. Analytical results indicated that samples contain K (0.5 –2.22 %), Ca (0.90 –6.08 %), Ti (150-2870 $\mu\text{g/g}$), V (20-55 $\mu\text{g/g}$) etc.

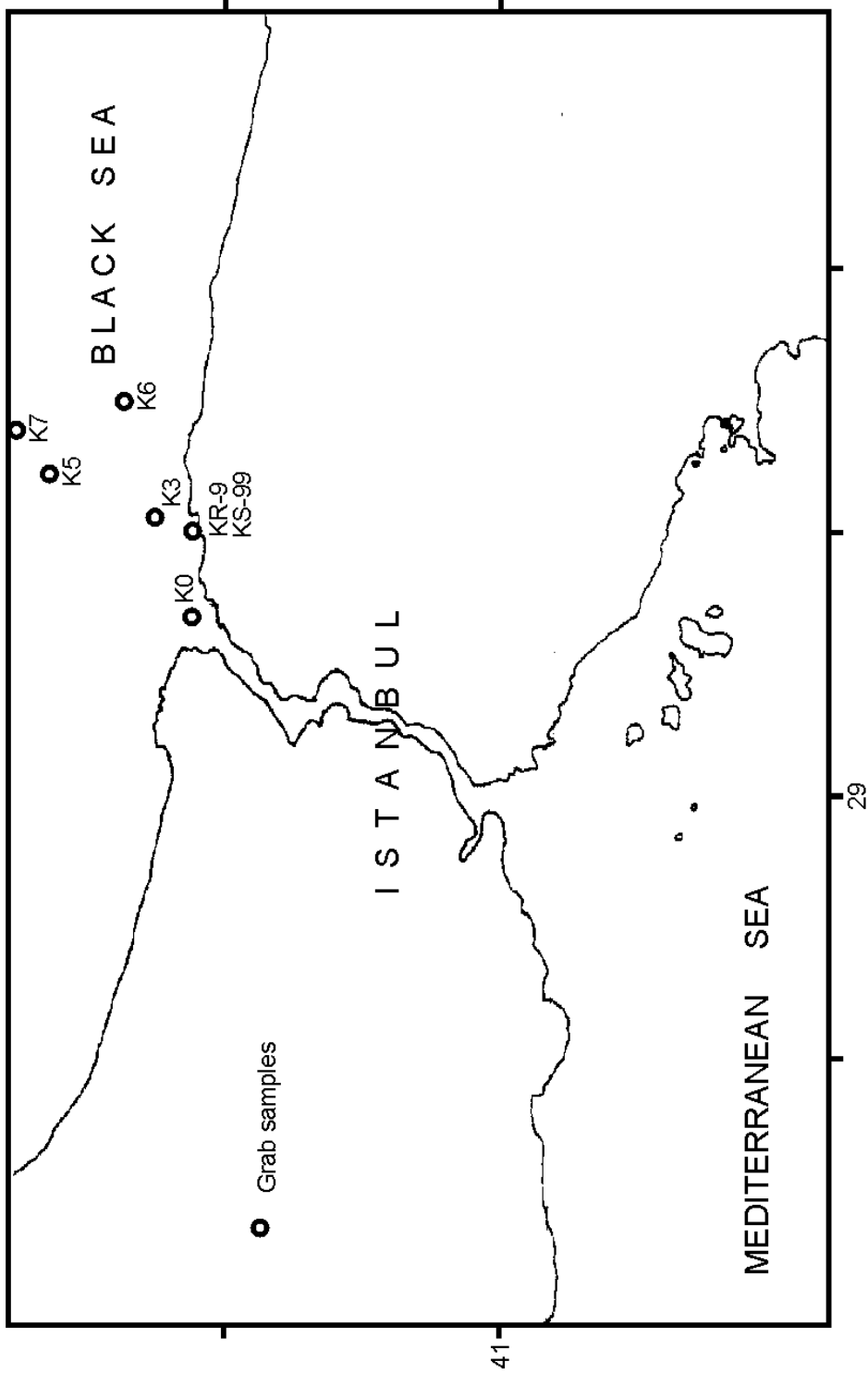
The NAA results of some elements of the Black Sea sediments are given.

Some metal concentrations of the surface sediments of the Black sea and the sea of Marmara around the Istanbul area are given in comparison. The same metal levels of the sediments, taken from Golden Horn and Izmit Bay sediments in which the vicinity of highly industrialised and densely populated regions of Turkey and those of coastal sediments of Southern California and Gulf of Venice. The comparison of heavy metal contents of the surface sediment samples around Istanbul area with those of other marine sediments, indicated that the sediments are not significantly contaminated with heavy metals. V,Cr, Fe, Cu, Pb and Zn concentrations of the Marmara Sea sediments are found to be higher than those of the Black Sea sediments. The results indicated that the heavy and toxic metal pollution of the Marmara Sea sediments are founded to be higher than those of the Black Sea sediments.

FIGURE CAPTION

Table 1. The locations (in degrees) of the sampling sites.

Sample No	Latitude	Longitude
1, K-0	41.1350	29.0800
2, K-3	41.1510	29.1260
3, K-5	41.1973	29.1455
4, K-6	41.1642	29.1778
5, K-7	41.2140	29.1631
6, KR-9	41.1900	29.5910
7, KS-99	41.1900	29.5800



Acknowledgement

This study was supported by NATO Grant EST.CLG 975645.

References

1. A.O. ALGAN, M.N. CAGATAY, H.Z. SARIKAYA, N. BALKIS AND E. SARI, Doga, Tr. J., Engineering and Environmental Science, 23 (1999) 39-48.
2. T.SALTOGLU,A.GEDIK, N.CAGATAY, H.KAPLAN,N.TULU and V.TOKER, Investigations of the Black Sea dip sediments, (in Turkish), Mineral Research and Expoloration Institute repor Ankara (Turkey, 1986).
3. P.M. VAN DYCK AND R.E.VAN GRIEKEN, Anal.Chem., 52, 1859 (1980).
4. R.D.GIAUQUE, R.B.GARRETT AND L.Y.GODA, Anal.Chem., 51,511 (1979).
5. J.OMOTE, H.KOHNO AND K.TODA, Anal.Chim.Acta, 307, 117 (1995).
6. T.AKYUZ, S.AKYUZ AND A.BASSARI, J. Radioanal.Nucl.Chem., 227,43 (1998).
7. T.AKYUZ, S.AKYUZ AND A.BASSARI, J. Radioanal.Nucl.Chem., 232, (1998) 251.
8. M. ERGIN, C. SAYDAM, O. BASTURK, E. EDEM, R. YORUK, Chemical Geology, 91 (1991) 269.
9. A. KATZ AND I.R. KAPLAN, Marine Chem., 10 (1981) 261.
10. R. DONAZZOLLO, O. H. MERLIN, L.M. VITTURI, A. A. ORIO, B. PAVONI, G. PERIN AND S. RABITTI, Mar. Pollut.Bull., 12 (1981) 417.