Man-made and natural radionuclides measured in the Danube River during 1991

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Abstract
Water and bed sediments sampled on principal cross-sections of the Danube River were analysed by gamma spectrometry. Cs-137 was present in low activity, while Th-232, U-238 and K-40 levels were typical of distributions normally encountered.

Introduction
Previous experimental research on the identification of man-made and natural radionuclides in the Danube River was carried out at the Polytechnical Institute of Bucharest with the objectives of determining, a) radioactive pollution at a specific time, b) estimation of the dilution capacity of the Danube River and, c) the elaboration of a mathematical model for transport of radionuclides to the Black Sea (GEORGESCU *et al.*, 1980, 1981). The aim of the present work was to identify the presence of Cs-137 ($T_{1/2}$=30.2 y) as well as U-238 and Th-232 after the Chernobyl accident.

Materials and Methods
Water (50 l) and sediments were sampled during June 1991 along major cross-sections of the Danube River and analysed for radionuclides using established procedures (GEORGESCU *et al.*, 1981). The gamma-emitting radionuclides were identified using a HPGe crystal coupled to a multi-channel analyser. Both samples and reference materials (IAEA-306) were counted in the same geometry for 18-24 hours.

Results and Discussion
Cs-137, Th-232, U-238, K-40 were identified in bed sediments (Table 1) and in unfiltered surface water (Table 2). Cs-134 ($T_{1/2}$=2.07 y) was present in the bed sediments of all the cross sections of the Danube River, but only in low activity, i.e. <0.2-<0.6 Bq/Kg dry. It should be noted that the sediments collected on the Romanian shore (left bank of River) are composed of silty clay, which may explain the somewhat generally higher accumulation of Cs-137 and other radionuclides.

Table 1. Activity in Bq/Kg dry sediment.

Sampling Site/ Date		^{137}Cs	^{238}U	^{232}Th	^{40}K
Upstream from	Left bank	8.2 ± 0.7	37 ± 2	22 ± 2	326 ± 16
Bechet Km 705	Centre	3.6 ± 0.3	20 ± 2	10 ± 1	261 ± 13
17.06.91	Right bank	2.2 ± 0.2	20 ± 2	12 ± 1	304 ± 15
Bechet	Left bank	5.6 ± 0.4	28 ± 2	20 ± 2	339 ± 17
18.06.91	Centre	3.8 ± 0.3	25 ± 2	8.7±1.3	260 ± 12
	Right bank	2.9 ± 0.3	18 ± 2	8.4±1.3	255 ± 10

The sediments, near the right bank have a higher granulometric composition and, therefore, do not readily accomodate the radionuclides in the crystalline lattice.

Table 2. Activity (Bq/m^3) of unfiltered Danube river surface water in 1991.

Sampling Site/ Date		^{137}Cs	^{238}U	^{232}Th	^{40}K
Entrance of	Left bank	<96	<27	<13	<95
Danube into	Centre	<48	<32	<12	<36
Romania, 9.06.91	Right bank	<46	<29	<14	<45
Upstream from	Left bank	<101	<27	<17	<99
Bechet Km 705	Centre	<55	<32	<14	<100
17.06.91	Right bank	<91	<29	<15	<103
Bechet	Left bank	<43	<31	<9	<56
18.06.91	Centre	<100	<36	<5	<115
	Right bank	<92	<29	<14	<101
Turnu-Magurele	Left bank	<81	<8	<10	<90
19.06.91	Centre	<41	<31	<16	<105
	Right bank	<95	<31	<15	<48

Conclusions
At the time when these Danube samples were collected (June 1991), the measured radioactivity in water and bed sediments ranged within the limits of the natural fluctuation. This was also the case at the Bechet site in front of the Kozlodui Nuclear Power Plant which is located on the right bank of the Danube River.

REFERENCES

1. GEORGESCU I.I., BONDAR C., ROMAN P. & BARAN Gh., 1980.- *In*: On a Monitoring Method for Radioactive and Chemical Pollution in Streams and Rivers. B. Patel, ed., Wiley Eastern Lmt. New Delhi, India, 302-309.
2. GEORGESCU I.I., DUMITRU C.I. & DEMETRESCU M., 1981.- On the presence in Danube River of some man made radionuclides and their transport to the Black Sea. *Rapp. Comm. int. Mer Médit.*, 27(3): 77-88.

Uranium as a pollutant from fertilizer industries located on the Black Sea shore and upstream from the Danube Delta

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Introduction
It is known that hazards can arise from the industrial plants using raw phosphorus materials to prepare fertilizers for agriculture purposes, due to release of dust and polluted waters into the environment. This waste contains not only toxic stable micro-elements such as As, Cd, Cr, Hg, Zn, etc., but also radioactive elements like U and Th in different concentrations. SALAGEAN *et al.* (1988) investigated U, Th and characteristic micro-elements in biota from the Romanian Black Sea shore, while others (FRONTASIEVA *et al.*, 1991) pointed out that phosphorus fertilizers contain some elements whose accumulation in vitally important media such as water, soil and food are undesirable from the medical-hygienic point of view. In the present work, we investigated only the U content of phosphorus raw materials and finite fertilizers obtained by nitric and sulphuric acid procedures in industrial plants located along the Romanian Black Sea coast and upstream from the Danube River Delta. Owing to contaminated radioactive water entering the sea either from direct discharge of the water or via migration through soil, we can gain information on the uranium concentration in the biota living in these waters.

Materials and Methods
Raw phosphorites imported from Algeria, Morocco, Tunisia, Jordan, Israel, U.S.A. (Florida) and apathite from the Kola Peninsula (Russia), as well as the finite fertilizers derived by nitric or sulphuric acid procedures were obtained as samples. About 100 g dry of each powdered sample was placed in a plastic bag and measured for uranium activity by gamma-spectrometry. All the samples were counted in the same geometry using a Phoswich (USA) detector of 127 mm dia. [3 mm NaI(T1)+50 mm CsI(T1)] coupled to a multichannel analyzer and personal computer. This system could detect either the 63 keV and 93 keV gammas from the Th-234 daughter of U-238 or the 186 keV from U-235.

Results and Discussion
The experimental data are shown in Tables 1 and 2. A significant quantity of uranium is noted in the final products. By correlating the chemical and radiological limits with the U content in the finite fertilizer products, it has generally been recommended to avoid the maximum possible uranium from all fertilizers. However, in our fertilizers U is not considered dangerous for several reasons. If we consider that 2-3 kg (case 1) or at maximum 200-300 kg (case 2) of finite fertilizer NPK2 nitric product (Table 2) with the highest U content (i.e. 28.85 mg/kg corresponding to an activity of 721.25 Bq/kg) is sprayed on 10,000 m^2, it means a variation of U activity ranging between 0.1442 to 0.21637 Bq/m^2 (case 1) or 14.42 to 21.637 Bq/m^2 (case 2). Upon the recommendations of ICRP-30 (1979), the Annual Limit on Intake (ALI) of natural U in critical organs (lungs, kidneys), is 1.5x10^3 Bq which corresponds to 60 mg natural U. However, an important quantity of U is retained by chemically complexed compounds such as humic acids in the soil and sediments of the Danube or Black Sea. Previous investigations by SALAGEAN *et al.* (1988) on U content in biota from the Black Sea have found 0.6 ppm in *Enteromorpha linza*, 2.8 ppm in *Ceramium rubrum* and <6 ppm (soft tissue) and <4 ppm (byssus) in *Mytilus galloprovincialis* from the Danube Delta near Sulina.

Table 1. Uranium content in raw samples

Sample	mg/Kg	Bk/kg*
Phosphorite Morocco	131.07	3276.75
Phosphorite Tunisia	40.42	1010.50
Phosphorite Jordan	73.21	1830.25
Phosphorite calcinated Morocco	148.58	3714.50
Phosphorite calcinated Algeria	56.37	1409.25
Phosphorite calcinated Israel	272.7	6817.50
Phosphorite calcinated U.S.A.	15.99	399.75
Apathite Kola (Russia)	141.46	3536.50

Table 2. Uranium content in fertilizers (finite products)

Fertilizer	mg/kg	Bk/kg*
NPK_2 nitric product	13.84	346.00
NPK_1 sulphuric product	15.27	381.75
NPK_2 nitric product	28.85	721.25
NPK_1 sulphuric product	27.30	682.50
NPK_2 nitric product	10.34	258.50
NPK_2 nitric product	2.82	70.50

* 1 mg U generates 25 Bq for natural uranium (88 - EHD - 139 Bioassay Guideline 4. Guidelines for U Bioassay. Health and Welfare - Canada)

REFERENCES

1. FRONTASIEVA M.V., GUNDORINA S.F., GORBUNOV A.V. & ONISCHENKO T.L., 1991.- Effect of the production of phosphorus fertilizers on environment. Conference paper. 8th International Conf. on Modern Trends in Activation Analysis, Physics Dep. Technical University of Vienna, Austria, 16-20 September 1991.
2. International Commission on Radiological Protection (ICRP), 1979.- Publication 30, Part 1., 1978. Limits for intake of Radionuclides by Workers. Vol. 2, Part 1. Pergamon Press, Oxford, New York, Frankfurt, 116 p.
3. SALAGEAN M., PANTELICA A. & GEORGESCU I.I., 1988.- Instrumental neutron activation analysis of two Macrophytes from the Romanian Black Sea beach. *Rapp. Comm. int. Mer Médit.*, 31(2): 326-327.

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