ON THE PRESENCE IN DANUBE RIVER OF SOME MAN MADE RADIONUCLIDES AND THEIR TRANSPORT TO THE BLACK SEA

by

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Abstract : Water and bed load sediment samples of Danube river on "significant verticals" and cross-sections, were collected during 1979, in view to compute a mathematical model concerning the man made radionuclides transport into the Black sea. The liquid and solid discharge of the Danube, simultaneously with the sample prelevation were determined. The fission and neutron induced nuclides after radiochemical separation by their characteristic gamma lines were identified by means of a high resolution Ge(Li) detector coupled to a multichannel analyzer. A simplified model for longitudinal dilution coefficient is given. Taking into account the chemical composition and the grain size of the bed load sediments correlated with the hydraulic parameters, the possible radionuclides accumulation was discussed.

INTRODUCTION

Due to the increasing nuclear plants in the catchment area of Danube river, man made radionuclides were identified on the carriers : water, suspended matter and bed load sediments. Though in very low activity, this are possible to accumulate in a greater quantity in the biota.

Previous works carried out at Polytechnical Institute of Bucharest (Romania) on the monitoring of radioactive pollution of Danube river, concluded that instead to oollect many samples and avoid a laborious work in the laboratory, one could make use of only 3 or 4 "significant verticals" that could characterize the total radioactivity of that cross section /1/,/2/. Between two cross sections one could compute the longitudinal coefficient dilution of any radionuclide /3/.

The purpose of the present work is to have a clearer understanding of the possible occurrence of the man made isotopes in the mouth of Danube river and Razelm lagoon of the Black sea, Romanian shore-known as rich fishery sites.

As some years ago, ten man made fission and neutron induced nuclides into special consideration were taken : ^{144}Ce, ^{125}Sb, ^{22}Na, ^{1o6}Ru, ^{137}Cs, ^{54}Mn, ^{11om}Ag, ^{89}Sr, ^{65}Zn and ^{6o}Co. The behaviour of some of this radionuclides were discussed in relation with their stable counterparts into the Black Sea /4/, /5/, now they will be in the Danube river. In this view analyses of micro and macroelements were performed and correlations are given with the grain size of the sediments.

All the data obtained concerning the radionuclide transport by Danube river in the Black sea at low and high liquid discharges and different degree of radioactive pollution will be included in a mathematical model, now in progress to elaborate.

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MATERIALS AND METHODS

During spring and autumn 1979, surface Danube water as well as their corresponding bed load sediments on every of the three "significant verticals" named I(left), II(middle) and III(right) belonging to two selected cross sections of the Danube river, were collected as materials under investigations. A "significant vertical" could represent the average value of the radioactivity only if the radionuclides are present about 100% or almost 85%. The "significant vertical" position on a cross section is determined by the geomorphogeometry and by the liquid discharge. The flow Danube river data were measured simultaneously with the collection of river samples, by applying the Romanian methods worked out by the Meteorological and Hydrological Institute in Bucharest.

The man made radionuclides were identified by radiochemical analyses of 100 l water and about 1 kg bed load sediment for each sample /6/. The isolated radionuclides by their characteristic gamma lines that couldn't interfere were identified. For this purpose it has been used a high resolution Ge(Li) detector of 38 cm^3 of 2.6 keV at ^{60}Co gamma lines, coupled to a multichannel analyzer SA-42 Intertechnique of 800 channels.

The stable microelements concentration in water and sediments were determined by a GPS-2 grating spectrograph while Zn by a VARIAN AA-5 type Atomic Absorption Spectrophotometer. Natrium and potassium by a flame photometer Zeiss and other macroelements were determined by usual analytical chemistry./7/

In evaluating the longitudinal coefficient dilution of the radionuclides, the method indicated in /3/ has been applied also for ^{144}Ce but for other and activity hydraulic parameters. Assuming the river bed to be stable and water and suspensions rate to be permanent, the radionuclides transfer between water and suspended matter could be explained by a simplified model to compute the longitudinal dilution for every carrier type. Noting by c_w and c_s the radionuclide concentration in water and suspensions, by 1 and 2 subscripts up and down stream respectively, by Q liquid discharge in m^3/s by R the solid discharge in Kg/s, the radionuclide discharges (pCi/s) in the two cross sections will be :

$$C_1 = Q_1 c_{w1} + R_1 c_{s1} \quad ; \quad C_2 = Q_2 c_{w2} + R_2 c_{s2} \qquad (1)$$

The river bed is participating into the exchange of radionuclides by a factor $c_b \Delta L$, where ΔL represents the distance between the two cross sections.

From the continuity Equation (1), in the hypothesis :

$$Q_1 = Q_2 = Q \qquad \text{and} \qquad R_1 = R_2 = R$$

it results :

$$c_b \Delta L = Q \Delta c_w + R \Delta C_s \qquad (2)$$

where

$$\Delta c_w = c_{w1} - c_{w2} \quad ; \quad \Delta c_s = c_{s1} - c_{s2}$$

From Equation (2), the longitudinal dilution coefficient is obtained :

$$c_b = Q \frac{\Delta c_w}{\Delta L} + R \frac{\Delta c_s}{\Delta L} \qquad (3)$$

The dilution coefficient has the following dimensions : pCi/m.s., or pCi/Km. day in the case of mentioned hypothesis.

RESULTS AND DISCUSSIONS

Man made radionuclides were investigated upon some years ago concerning their evolution on the principal carriers of Danube water : suspended matter, filtered water and sediments. During 1979 again it has been confirmed the presence of the following radionuclides : ^{144}Ce-^{144}Pr, ^{125}Sb, ^{22}Na, ^{106}Ru-^{106}Rh, ^{137}Cs, ^{54}Mn, ^{110m}Ag, ^{89}Sr, ^{65}Zn and ^{60}Co but in very low activity. It must be outlined their permanently presence, even in low activity, especially in the bed load sediments of the Danube river sector selected for computing the longitudinal dilution coefficient of the radionuclides.

The following flow Danube river parameters were used in computation the longitudinal dilution coefficient :

Q, liquid discharge $(7190 \div 9100)m^3/s$,

R, solid discharge $(140 \div 595)Kg/s$,

$c_{w1} = 0.68 \cdot 10^3 pCi/m^3$ ^{144}Ce concentration in water upstream,

$\Delta c_w = 0.57 \cdot 10^3$ pCi/m^3 ,

$c_{s1} = 0.41 \cdot 10^3$ pCi/Kg ^{144}Ce concentration in suspensions upstream,

$\Delta c_s = 0.31 \cdot 10^3$ pCi/Kg.

The product c_b ΔL varied between $(0.6 \div 4.5)10^6$ pCi/s at high discharges and $(50 \div 740)10^6$ pCi/s at low discharges of Danube. Its variation depends on the initial radionuclide concentration on suspended matter, water and sediments, liquid and solid discharge. This computation could be applied to every radionuclide. The biological factor was not considered.

The concentration factor, $CF = \frac{\text{Activity/Kg bed load sedimen}}{\text{Activity/Kg water}}$

had the following values :

- ^{144}Ce, CF varies from 148 to 700 on the left river side (vertical I) and from 311 to 400 on the right river side (vertical III), while in the middle of the river (vertical II) is 1000 to 4000.

- ^{137}Cs. On the first vertical upstream to downstream, CF is increasing from 50, 100 and 3000, while in the vertical II (middle) is about constant 100 ÷ 200 and in the third vertical, CF is 1000 constant upstream and downstream. It must be outlined the chemical analyses carried out on this sediments shown illite $(AlSi_3O_{10})_nH_2O$, where frequently, aluminium is replaced by K and Fe. Radiocesium was found to have an uptake proportional to the illite content of the sediments, probably involving an ion - exchange with potassium /8/, /9/.

- ^{65}Zn. In the vertical I (left river side), CF vary from 1000 ÷ 2000 ; 300 in the middle (II) and 330 ÷ 990 in the third vertical. The uptake of stable and radioactive zinc depends on pH, salinity, temperature, concentration of the iron in medium and the physico-chemical state of Zn and ^{65}Zn. At higher salinity, it is well known that the water contains many more ions which compete with ^{65}Zn ions for sorption sites, hence would suppress concentration of ^{65}Zn. The same reaching holds for the effect of Zn concentration in water /4/.

Though the concentration factor of ^{65}Zn is high in sediments the specific activity of water, i.e. pCi ^{65}Zn/l water : µgZn/l water is very low, $1.1 \cdot 10^{-4} \div 4.10^{-4}$. In a previous work, in the upper layers of the Black sea, a specific activity of ^{65}Zn from $0.014 \div 0.35$ has been identified, in 1974. The specific activity of ^{65}Zn from Dabe river observed in spring 1979 is with 2 order of magnitude lower /8/ , /10/.

Recently, it has been shown, that in marine environment ionic zinc is more available for bioaccumulation than chelates of organic bound zinc (SCOTT and HEYRAUD,1980)/11/. This would be true also in rivers.

Concerning the concentration of stable microelements as : Ce, Zn, Co, Cr, Sr, Ag, etc., that could take an important place in the behaviour of their radioactive counterparts, in Table 1, are listed the results of the 27 microelements investigated by spectral analyses of the 11 samples of bed load sediments. This were simultaneously collected together with the surface Danube water on the same verticals and cross sections, used for computation the longitudinal dilution coefficient of radionuclides.

The following 9 elements were considered "lack" of the total samples because their concentration were under detection limit of the spectrophotometer : Sb, W, As, Ge, Bi, Cd, Be, Nb and Sm. The following elements were present in different concentrations of ppm in the all bed load sediments samples : Zr, Cu, Pb, Mn, Cr, Ni, V, Co, Ag, Ba, Sr, Ce, Y and Yb. Others were considered "lack" from only some verticals, for instance cerium concentration varied between $50 \div 150$ ppm and was under detection limit in six samples ; zinc varied from $45 \div 60$ ppm and in one

TABLE 1. Spectral analysis in parts per million dry weight of the bed load sediments from selected cross-sections.

No.	Cross section	Date of sampling	Zr	Cu	Pb	Sn	Mn	Cr	Ni	Mo	V	Co	Zn*	Ag	Ba	Sr	Ce	La	Y	Yb	Sb	W	As	Ge	Bi	Cd	Be	Nb	Sm
1.	Bechet I upstream	Spring 1979	100	10	30	-	450	50	21	1	15	7	-	0.1	1300	80	-	-	12	1.7									
2.	Bechet II upstream	Spring 1979	100	4	13	-	180	35	16	1	13	4	52	0.1	1000	70	-	-	12	1									
3.	Bechet III upstream	Spring 1979	100	50	18	-	350	25	40	1	60	5	-	0.1	1100	7	150	70	15	1.5									
4.	Bechet I downstream	Spring 1979	100	3	12	-	180	35	17	1	13	5	45	0.1	1200	75	-	-	8	1									
5.	Bechet II downstream	Spring 1979	110	3	20	-	200	40	18	1	12	4	-	0.1	900	120	50	-	8	1.0									
6.	Bechet III downstream	Spring 1979	225	110	18	-	900	160	17	1	22	6	90	0.1	1200	180	60	70	40	6.0	under detection limit								
7.	Giurgiu I downstream	Spring 1979	110	40	50	3	1500	170	22	1	18	8	45	0.2	1300	80	55	65	28	1									
8.	Giurgiu II	Spring 1979	100	4	32	-	350	25	17	1	13	5	45	0.1	900	85	-	-	14	1.5									
9.	Giurgiu III downstream	Spring 1979	135	35	22	3	1800	150	16	1	32	6	60	0.1	1200	90	-	60	35	1.3									
10.	Sediment Giurgiu II downstream	Autumn 1979	100	5	28	-	400	35	18	1	14	6	-	0.1	1300	140	-	-	6	1.0									
11.	Sediment Giurgiu III downstream	Autumn 1979	125	50	25	-	220	38	22	1	15	5	-	0.1	1000	70	50	50	7	1									
	Detection limit		100	3	3	3	3	3	3	1	3	3		0.1	3	3	50	30	1	1	100	300	100	3	3	10	10	300	100

*Atomic absorption.

sample 90 ppm. It must be outlined the values of zinc concentrations in dry residue of 1 l total surface water (always determined by atomic absorption) in the "significant verticals" : in spring 140 ÷ 270 μg/l upstream and 240 ÷ 270 μg/l downstream, while in autumn lower values were registered, i.e., 30 ÷ 150 μg/l upstream and 90 ÷ 240 μg/l downstream Danube river.

The variations of the grain size diameter of the bed load sediments at Bechet station - upstream cross section -, are included in Table 2. One can conclude the d_{50} diameter i.e., the 50% of the granulometric curve of one vertical, has 0.72 mm near the VIII-th vertical (right river side), while the lowest value of 0.28 mm is in the middle of the river. The maximum grain size diameter has 2 mm, while the minimum 0.05 mm in six of eight verticals. As has mentioned before the principal component of the bed load sediments is illite with different degree of impurities.

The radioactivity at Bechet cross section in spring 1979, even very low, was greater for ^{137}Cs, ^{110m}Ag and ^{65}Zn in the third "significant verticals" (right river side), while the activity of ^{60}Co was greater in the first "significant vertical", i.e. the left river side.

CONCLUSIONS

During 1979 the following man made radionuclides were identified in low activity under (below) the permissible international level : ^{144}Ce, ^{125}Sb, ^{22}Na, ^{106}Ru, ^{137}Cs, ^{54}Mn, ^{110m}Ag, ^{89}Sr, ^{65}Zn and ^{60}Co.

The longitudinal dilution coefficient of radionuclides was determined, but for higher liquid discharge of Danube river. This is constant as order of magnitude, i.e. 10^6 pCi/m.s. .

Concentration Factors, CF of some selected radionuclides as ^{144}Ce, ^{137}Cs, ^{65}Zn and ^{60}Co were determined for the bed load sediments upstream and downstream the two cross sections where the longitudinal coefficient dilution was measured.

Chemical analyses shown the bed load sediments of Danube upstream and downstream of Bechet - cross section under study were made of illite with different impurities. The diameter of the grains varied from a minimum value of 0.05 mm, maximum 2 mm and d_{50} mean value of 1.70 mm on 8 verticals of Bechet cross sections.

TABLE 2. Grain size of the bed river Danube at Bechet during May 1979.

Vertical Number / diamater mm	I	II	III	IV	V	VI	VII	VIII
d_{50} mean	0.14	0.28	0.38	0.24	0.58	0.54	0.74	0.72
$d_{(maximum)}$	1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0
d_{minim}	0.05	0.05	0.05	0.04	0.10	0.05	0.10	0.05

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Paper presented by S.W. Fowler (Monaco)

Discussion

No comment.