Stable Element Variation in Sediments and Macrophytes from Rumanian Black Sea Coast the Last Decade

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Bottom sediments on the Rumanian Black Sea coast as well as the algae Enteromorpha linza and Ceramium rubrum sampled during 1989 from the sea beach were analysed by INAA for determining certain selected stable elements. During the last ten years an increasing concentration in Zn, Cr, As, Sb, Se and Hg was observed. Co was found decreasing in sediments and Enteromorpha linza but increasing in Ceramium rubrum. Sc was found decreasing in sediments but slightly increasing in algae.

Sediment samples from the bottom of the Rumanian Black Sea (45°08'N, 29°57'E, to 44°08'N, 28°57'E, 12-17 nautical miles offshore and 29-43 m depth were collected together with E. linza and C. rubrum on the sea side beach during March-June 1989. After rinsing the algae the samples were dried. The samples were analysed by INAA. About 100 mg of each sample were irradiated along with an equal quantity of standards under same conditions in the VVRS-2 reactor in Bucharest (flux 10^{12-13} n/cm²sec). Counting has been performed by using a Ge(Li) detector (2.8) keV resolution coupled with a pulse height analyser.

The results obtained in this work concerning As, Co, Cr, Cs, Hg, Sb, Sc, Se, Th, U and Zn are given in Table 1. In a previous paper it has been outlined that the content of the selected stable elements was increasing in E. linza and C. rubrum during 1986 (SALAGEAN et al., 1988). Nowadays, four years later, the concentration of As, Co, Sb, Hg and Zn was found increased. Also Sc was found increased in C. rubrum while in E. linza was decreased at S. Eforie but increased at Mangalia. The mean value as a whole of Sc in E. linza is about the same as before. Uranium is almost constant in both algae while Th is slightly increased in C. rubrum. In the bottom sediments at Portitza sampling site at the south of Danube river, higher concentration of the elements was observed than at the other sampling sites: Zn (615 ppm), Cr (130 ppm), As (8.4 ppm) (SALAGEAN et al. 1988). The Cs value (8.9 ppm) related to illite presence explains the highest accumulation of Cs-137 at Portitza site.

Table 1. Stable element content (ppm dry matter) in sediments and algae sampled from the Rumanian Black Sea coast during 1989

ELEMENT	SEDIMENTS				Enteromorpha linza		Ceramium rubrum	
	Sulina	Sf.Gheorghe	Portitza	Constantza	South Eforie	Mangalia	South Eforie	Mangalia
As	6.2±1.7	11.2±2.7	18.4±4.4	5.7±1.4	<5	<4	<7	<4
Co	7.3±0.2	7.5±0.2	15.5±0.4	5.2±0.1	1.7±0.1	2.8±0.2	5.1±0.3	4.4±0.2
Cr	75 ± 3	50 ± 2	130 ± 5	27 ± 1	5.2±0.7	16 ± 1	31 ± 1	24 ± 1
Cs	2.9±0.1	3.0±0.2	8.9±0.4	1.9±0.1	0.54±0.12	0.81±0.10	2.3±0.2	1.6±0.2
Hg	<1.8	<2.1	<2.0	<1.9	<2.1	<1.5	2.6±0.9	<1.7
Sb	0.9±0.1	0.94±0.09	2.2±0.1	0.56±0.06	0.4±0.1	0.48±0.07	1.4±0.1	0.75±0.09
Sc	6.5±0.2	5.9±0.2	15.4±0.5	3.5±0.1	0.06±0.02	1.52±0.04	4.6±0.1	3.1±0.1
Se	<1.3	1.2±0.6	<3	<1.5	<2.5	<1.6	<3.3	1.3±0.5
Th	4.8±0.1	4.5±0.1	11.5±0.3	2.9±0.1	0.52±0.06	1.6±0.07	3.6±0.1	2.5±0.1
U	1.1±0.2	1.7±0.2	2.8±0.4	0.9±0.2	<1	1.1±0.4	1.4±0.6	1.5±0.5
Zn	296±18	133±21	615±43	155±15	150±9	230±14	298±30	310±23

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Modelling Cesium, Cobalt & Strontium Accumulation in Painted Comber, *Serranus scriba*

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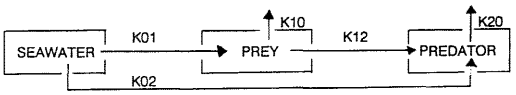
Radionuclides of cesium, cobalt and strontium may be introduced into the marine environment in global fallout and in civil nuclear discharges. Since they may be accumulated by biota and transferred through marine food chains, it is important to quantify relevant transport processes in order to predict any risks to consumers which may be associated with such transfers. This involves identifying pathways as well as determining the extent of accumulation at different trophic levels. One approach used in assessing the accumulation of radioactivity involves the use of concentration factors (CF) - defined as the radioactivity per unit wet mass of an organism divided by the concentration of radioactivity in the water. CFs have been determined for radionuclides in many species both *in situ* and in laboratory experiments. Generally, laboratory exposures tend to lead to underestimates of CFs measured *in situ* - perhaps because of too-short exposure periods in laboratory aquaria or because of non-representative diets of the test animals or of the physicochemical speciation of the radionuclides in the test system (1). In this presentation we report the application of a three-compartment model which allows the CF of a radionuclide to be predicted in fish predator species. The model also allows estimates to be made of the time required to reach steady-state conditions and differentiates between the contributions of food and of water vectors to total uptake. Here it is used to predict the accumulation of 134-Cs, 60-Co and 85-Sr in the painted comber, *Serranus scriba*, using laboratory-determined accumulation and excretion rate data as well as the assimilation efficiency for these radionuclides after ingestion of a radiolabelled prey organism - juvenile flathead grey mullet, *Mugil cephalus*.

Description of Model: The model is a slight modification of that described by Aoyoma & Inoue (2). From water, of radionuclide concentration W, both predator and prey accumulate radioactivity at the rate K20 and K10 respectively. Both species also excrete accumulated radioactivity at the rates K20 and K10. In addition the predator accumulates radioactivity at the rate K12 through consumption of the prey organism. The parameter K12 is equivalent to the product of the assimilation efficiency and the feeding rate (expressed as the daily ration as percent of the total body weight). The radioactivity in the predator at any time (t) is equivalent to the sum of water (WATER) and food (FOOD) vectors.



WATER = W*K02/K20 * (1-EXP(-K20*t))
FOOD = W*K01*K12*{[1/(K10*K20)] + [EXP(-K10*t)/(K10*(K10-K20))] + [EXP(-K20*t)/(K20*(K20-K10))]}
Since the uptake and loss rates in the prey can be expressed in terms of those of the predator then the expression describing uptake from food can be reduced to:
FOOD = 2.09*W*K02*K12*[1.8 + EXP(-2.8*K20*t)-2.8*EXP(-K20*t)]/[5.04*K20*K20]

Estimation of parameters: *Serranus scriba* (28±4 g) captured near Monaco were used. (i) Accumulation from water: Four fish were exposed to 60-Co (450 Bq/l), 134-Cs (450 Bq/l) and 85-Sr (7500 Bq/l) for 30 days in individual 20-litre aquaria containing 10μm-filtered seawater. The water was changed and the radionuclide concentration re-established every second day. The animals were routinely wholebody-counted under anaesthesia in a calibrated 2"x3"NaI well-type detector and the radionuclide content determined by comparison with known standards. The accumulation rates, normalised to unit radionuclide concentrations in the water, were calculated by linear regression of radionuclide content *vs.* time (Table 1); (ii) Excretion: Four fish were fed a single ration of grey mullet containing 92.5 kBq 60-Co, 18.5 kBq 134-Cs and 18.5 kBq 85-Sr. The animals were maintained for 37 days in aquaria with constantly flowing seawater and were fed daily with non-contaminated mullet. They were regularly wholebody-counted as described above and the loss rates were determined by fitting a double-exponential decay curve to the data (Table 1); (iii) Assimilation efficiency for a single feeding could be estimated from the equation of the excretion curve. A second estimate was made using linear regression of wholebody-counting data for four fish which were fed daily for 75 days with radiolabelled mullet (20% of the radioactivity used for the single feeding) *vs.* time (Table 1).

Table 1. Laboratory values for the parameters used and the consequent predictions.

	^{60}Cobalt	^{134}Cesium	^{85}Strontium
Uptake	0.087*t - 0.024	0.201*t - 0.036	0.024*t + 0.014
K02	0.087	0.201	0.024
Loss (Fast Pool)	0.91*EXP(-2.1*t)	0.53*EXP(-12*t)	0.98*EXP(-2.6*t)
Loss (Slow Pool)	0.09*EXP(-0.015*t)	0.46*EXP(-0.018*t)	0.02*EXP(-0.026*t)
K20	0.032	0.0175	0.0256
Assim. Eff. (loss)	9.5%	46%	2.0%
Assim. Eff. (uptake)	9.3%	35%	3.8%
K12	0.0942	0.4410	0.0292
CF (from Water)	5.7	11.5	0.93
CF (Food & Water)	32.0	33	1.02
Cont. of Water	18%	35%	91%
90% St.-State at	170 days	150 days	90 days

Assumptions made in model: It was assumed that (a) in an exposure situation the radionuclide concentration in the water would remain constant with time (this is considered to be valid for global fallout and for routine civil nuclear discharges but is not necessarily so for accidents *etc.*); (b) the excretion rate is independent of the route of uptake of the radionuclide; (c) in the natural environment the predator consumes a daily ration equivalent to 10% of its body weight in four separate feeds (each feed equivalent to 2.5% of the body weight of the predator); (d) the accumulation and excretion processes in the prey organism are functionally identical to those of the predator and are proportional to a power function of body weight i.e. Accumulation Á Weight$^{0.80}$ and Excretion Á Weight$^{0.72}$ (3). Thus the accumulation rate from water in the prey would be 2.09 times that of the predator and the excretion rate would be 2.8 times that of the predator (4).

Simulations and Predictions of Model: Accumulation of the radionuclides by *Serranus scriba* during 300 days of exposure was simulated using this model with initial conditions of zero radioactivity in predator and prey at time zero and assuming that the concentration of each radionuclide in the water remained constant at unity (W = 1) during the exposure. The predictions of the model are presented in Table 1. Accumulation is given in terms of CF. No accumulation of strontium beyond the levels in the water is seen (CF = 1) and more than 90% of the strontium uptake in the animals is from the water. Both cesium and cobalt are accumulated predominantly from the diet (CF = 33 and 32 respectively) although water is a more important vector for the former during accumulation (35% *vs.* 18% of total uptake). In all three cases more than 90 days are required to reach CF values equivalent to 90% of the steady-state values. The predicted CF values are in excellent agreement with field-measured CF values for these radionuclides in fish (1, 5) and both the time required to reach steady-state values and the significant contribution of diet to total uptake of cesium and cobalt may explain why laboratory-determined CF values tend to underestimate those measured *in situ*. This work demonstrates the value of simple laboratory studies and their application in relatively unsophisticated models in the prediction of pathways of accumulation and the importance of trophic transfer in the movement of radionuclides through marine food chains.

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