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TRITIUM IN THE ADRIATIC SEA

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Tritium activities were determined for the Adriatic Sea water in samples collected at four locations on the Adriatic coast. The tritium inventory for the Adriatic Sea mixed layer in 1991 was calculated to be $7.35 \cdot 10^{15}$ Bq (20.6 g). The net tritium input to the Adriatic through 1985–1991 period was estimated to be $5.53 \cdot 10^{15}$/yr (1.55 g/yr), being added through water vapour exchange, runoff and precipitation. The mean residence time of the mixed layer water was estimated for the Adriatic Sea to be 12.6 years.

1. Introduction

Tritium, the radioactive isotope of hydrogen, has chemical properties identical to those of light hydrogen. It has a radioactive half-life of 12.3 years, and decays to ^{3}He by the emission of a low energy beta particle, having maximum energy of 18.6 keV and average energy of 5.7 keV. The health hazard of tritium oxide – tritiated water (either HTO or T_20) to global population is a consequence of the ubiquitous nature of tritium, as it follows the global hydrogical cycle without discrimination. Until the nuclear weapons (H bomb) have begun to be tested in the atmosphere, the dominant source of tritium were nuclear reactions of cosmic ray protons and neutrons with hydrogen, oxygen and argon in the stratosphere. Nowadays, the major sources of environmental tritium are its production in the stratosphere, various consumer products and the nuclear fuel cycle. Looking at future, the first generation of fusion power plants is likely to have large inventories of tritium, leading to the possibility of major chronic and acute airborne releases of

tritium oxide as well as tritiated hydrogen gas (HT or T_2). Although environmental pathways and consequent impact of the tritium released to the atmosphere may strongly depend on its chemical form, eventually all tritiated hydrogen is oxidized to tritium oxide, which has been proved in number of field studies[1,2]. Possible future implementation of the world's nuclear energy production plan, or the future fusion power stations may affect the present environmental tritium levels. For assesing the tritium impact to environment and reliable evaluation of any increased dose contribution to the members of the general population it is indispensable to measure the equilibrium tritium levels in the various compartments of the ecosystem, among which oceans, i.e. sea-water, are the most important. Since 70% of the world surface is covered by water, the artificial radionuclides enter the oceans primarily through the air-sea interface. Furthermore, the sea is the ultimate recipient of the run-off from the land masses. In local waters such as the Adriatic Sea, the contamination originating from peaceful uses of nuclear energy may predominate over fallout. For the areas with short turn-over times, the levels of sea-water contamination may rapidly respond to variations in discharge rate and marine currents.

The Adriatic makes the northern part of Mediterranean, being a rather shallow sea enclosed by surrounding land masses. It is under the strong impact of the Po river which is the major source of fresh water in the Adriatic. Generally, the Adriatic Sea is characterized by relatively low precipitation, high evaporation, low tidal action, low nutrient content, low suspended load and the low biological productivity[3]. While these features result in hydrographical conditions quite different from those in other seas, the fundamental biogeochemical processes taking place in water columns are not to be considered basically different from those occurring in other seas.

As the study of marine radioactivity includes not only the monitoring and hazard assessment, but also studies related essentially to physical oceanographic investigations using radionuclides as tracers, tritium being water constituent is an ideal tracer. Investigations of the distribution and fate of natural, nuclear weapons produced and reactor released radionuclides in the Adriatic Sea have been conducted in the Department for Radiation Protection of this Institute, as a part of an extended monitoring programme. Strontium investigations have been going on since 1963 and those of tritium since 1985.

2. Material and methods

Samples of sea-water were collected twice a year (in May and October, if feasible) 3 km from the shore, at a depth of 0.5 meters, at four sampling sites (near the towns of Rovinj, Rijeka, Split and Dubrovnik). The same sea-water samples were used for radiochemical analysis of ^{90}Sr[4].

Analysis of HTO (tritiated water) was performed in a low-level tritium laboratory. Before mixing with scintillator, samples were distilled. Samples were counted on a Packard, Tri-Carb 2060 XL liquid scintillator spectrometer, coupled to an IBM PC 286 microcomputer. Counting was performed in the low-level mode. The sample

volume was 20 ml (8 ml of water and 12 ml of Instagel scintillator). The counting time was 1000 minutes. Efficiency was determined by internal spiking. Standards were obtained from Amersham and Atomic Energy of Canada Ltd., Chalk River, Ontario. Efficiency was $(21.5 \pm 0.1)\%$ and lower limit of detection 1 kBq m^{-3}. The water used for background determination was deep ocean water obtained from the World Health Organization (WHO), International Reference Centre for Radioactivity, Le Vesinet, France. Typical background activity was (2.00 ± 0.10) cpm.

Intercomparisons of tritium radioactivity measurements were performed also on samples provided by WHO.

3. *Results and discussion*

Surface water activity

All airborne tritium, both natural and the one produced by nuclear weapons, substantially combines to form tritiated water in the stratosphere, which is subsequently brought down into the troposphere, were both precipitation and water vapour exchange serve to transfer tritium into the surface ocean (sea) waters. Thus, the sea is the ultimate sink for tritium. Tritium activity in surface sea waters is a good representation of the tritium activity in the mixed layer (relatively warm waters in seas and oceans near the surface where rapid mixing occurs as a results of wind action). Mixed layer is divided from deep water layers by thermocline (the region of rapid temperature change).

Table 1 shows average tritium activities in the Adriatic Sea for the period 1985 – 1991.

TABLE 1.

Year	1985	1986	1987	1988	1989	1990	1991
Activity	2340	2350	2140	2210	2000	1720	1770
(Bq m^{-3})	±	±	±	±	±	±	±
	170	180	310	270	250	220	190

Tritium activity in the Adriatic surface waters
(Average of four locations).

In general, tritium activity has on average declined during the observed period. This can be explained by the decrease in the predominant H-bomb fraction by radioactive decay and removal to deep waters. For comparison, tritium activities in other seas have been approximately 7.0 – 9.0 kBq m^{-3} in the Baltic Sea[5)] in 1984, 0.5 – 0.7 kBq m^{-3} in the Japan Sea[6)] in 1984 and 1.0 – 2.1 kBq m^{-3} in the North Atlantic[7)] in late 1970s. But, for the Atlantic Ocean in 1989 are also reported values as high as 7.4 kBq m^{-3} (Gulf of Mexico) or 18.5 kBq m^{-3} in Southport[8)]. In the same year the Pacific Ocean activities were[8)] 3.7 – 11.1 kBq m^{-3}.

As the ^{90}Sr activities were determined in the same samples of the sea-water from the Adriatic, it was possible to estimate the $^{3}\mathrm{H}:^{90}\mathrm{Sr}$ activity ratio for the period 1985 – 1991. The ratio was found to be relatively constant, 850 ± 120. Data for the $^{3}\mathrm{H}:^{90}\mathrm{Sr}$ activity ratio are not often found in the literature because of the complicated and time-consuming ^{90}Sr analysis and large quantities of water ($\approx$ 150 l) needed for a single analysis. The $^{3}\mathrm{H}:^{90}\mathrm{Sr}$ activity ratio for the Japan Sea for 1984 was reported to be 238[6)]. However, the tritium concentrations from which the latter was estimated were lower, whilst global sea-water ^{90}Sr activity concentrations at that time were higher than those in the Adriatic in late 1980s, leading to lower value of $^{3}\mathrm{H}:^{90}\mathrm{Sr}$ activity ratio, compared to that in the Adriatic. The mean residence time of the water in the mixed layer can be estimated from the changes in tritium concentration in the mixed layer of the ocean. The mixed layer, whose tritium content can be ascertained from the surface-water data, is considered as one reservoir, the deep water as another. Tritium penetrates below the mixed layer only by diffusion or by sinking of the surface waters. Therefore, tritinm activities decrease with depth and there is no net inflow from the deep water into the mixed layer. Then, the change in tritium concentration per year in the mixed layer can be modelled as

$$\frac{\mathrm{d}C_{ml}}{\mathrm{d}t} = -\lambda_d C_{ml} - \lambda_{ml} C_{ml} + I \tag{1}$$

where:

C_{ml} is the tritium concentration in the mixed layer (surface waters),
λ_d is the tritium decay rate (0.055 yr^{-1}),
λ_{ml} is the turnover rate of the mixed layer (inverse of the mean residence time) given in yr^{-1} and
I is total annual tritium input into the Adriatic Sea.

Assuming the constant input, the solution of equation (1) is:

$$C_{ml} = K\mathrm{e}^{-(\lambda_d+\lambda_{ml})t} + \frac{I}{\lambda_d + \lambda_{ml}} \tag{2}$$

where K is the constant.

Tritium inventory in Adriatic

By making use of the concentration data for tritium in surface waters from Table 1, the total tritium activity in the Adriatic Sea mixed layer in respective years can be estimated by multiplying average tritium concentration by the volume of mixed layer. The thickness of the ocean mixed layer, Z_{ml}, varies geographically from 10 to 200 meters[9)]. In the Adriatic Sea average thermocline is about 30 meters[19)] under the sea surface, $Z_{ml} = 30$ meters. The North Adriatic has a surface area of 78750 km^2, a volume of 6795 km^3, and its average depth is 81.5 m[3)]. The South Adriatic has an area of 59850 km^2, a volume of 28182 km^3 and an average depth of

470.9 m^3[3]. Thus, the tritium inventory of the mixed layer in the Adriatic Sea can be calculated from the expression:

$$T_l = S_A \times Z_{ml} \times A_{ml} \tag{3}$$

where:
T_l is the tritium inventory in Bq,
S_A is the surface area of entire Adriatic Sea (138600 km^2),
Z_{ml} is the depth of the mixed layer and
A_{ml} is the tritium concentration in the mixed layer given in Bq m^{-3}.

From (3) tritium inventory in the Adriatic Sea mixed layer in 1991 is estimated to be $7.35 \cdot 10^{15}$ Bq (20.6 g). In order to obtain the upper limit of the total tritium inventory of the Adriatic Sea in 1991, its entire volume ($3.50 \cdot 10^{13}$ m^3) should be multiplied by mixed layer tritium concentration (1.77 kBq m^{-3}) which gives $6.2 \cdot 10^{18}$ Bq (173.4 g). For a more reliable estimation of the total Adriatic Sea tritium inventory, tritium profiles from several locations in the Adriatic Sea should be taken.

Input to the Adriatic Sea

The net input of tritium in the Adriatic Sea is affected by precipitation (P), evaporation (E), run-of (R) and water vapour (molecular) exchange (VE). Water vapour exchange arises from water molecules crossing the air-sea interface in both directions. Whereas the humidity gradient above the water surface is such that a net upward flux of vapour occurs, i.e. evaporation, the tritium gradient is opposite, so that there is net transport into the sea-water. Thus:

$$I = VE + P + R - E \tag{4}$$

a) Precipitation

Through the observed period (1985 – 1991) the average tritium activity in precipitation can be assumed to be approximately equal to average sea-water activity i.e. 2.1 kBq m^{-3}. This assumption is in agreement with data for tritium activity concentration in precipitation collected in Croatia[11].

The precipitation contribution to tritium to the Adriatic can be calculated from the exppression:

$$P = A_P \times H_P \times S_A = A_P \times V_P \tag{5}$$

where:
P is the total tritium annual activity delivered by precipitation to the Adriatic, in Bq yr^{-1},
A_P is the average precipitation activity concentration in Bq m^{-3},
H_P is the average precipitation rate (19 locations) for the Adriatic, i.e. (1.001 ± 0.038) m yr^{-1} [3],
S_A is the surface area of the Adriatic Sea and
V_P is the total annual volume of precipitation delivered to the Adriatic Sea $(1.39 \cdot 10^{11} \pm 0.05 \cdot 10^{11})$ m^3.

It follows from (5) that on average $2.9 \cdot 10^{14}$ Bq yr^{-1} of tritium entered to the Adriatic Sea by precipitation in 1985 – 1991 period.

b) Evaporation

The equation similar to (5) can be applied for tritium outflow from Adriatic by evaporation:

$$E = A_{ml} \times H_E \times S_A = A_{ml} \times V_B \tag{6}$$

where:

E is the total tritium activity removed from the Adriatic Sea by evaporation given in Bq yr^{-1},

A_{ml} is the sea-water tritium activity concentration in the mixed layer, given in Bq m^{-3},

H_E is the average evaporation rate for the Adriatic Sea, calculated from 15 locations, i.e. (0.580 ± 0.085) m yr^{-1} [3] and

V_E is the total sea-water volume evaporated from the Adriatic Sea in one year $(8.04 \cdot 10^{10} \pm 1.18 \cdot 10^{10})$ m^3 yr^{-1}.

It follows from (6) that in 1985 - 1991 period $1.67 \cdot 10^{14}$ Bq yr^{-1} of tritium was removed from the Adriatic Sea by evaporation.

c) Run-off

The Po river outflow is the most important source of fresh water in the Adriatic Sea. The average flow rate is about 1000 m^{3}s^{-1} [12]. The tritium data for the Po river are not available, but they may be assumed not to differ significantly from those of other major rivers in Europe. For example, the tritium concentration in the Sava river upstream Nuclear Plant Krsko ranged from 2 to 4kBq m^{-3} in 1990[12] If the average tritium activity in the Po river is assumed to be approximately 3 kBqm m^{-3} i.e. slightly higher than tritium sea-water activities, then the total annual input to the Adriatic Sea by the Po river can be estimated to be $R \approx 1.0 \cdot 10^{14}$ Bq yr^{-1}.

d) Water vapour exchange

The input by water vapour exchange, as the predominant mechanism by which tritium enters the oceans, is about 60% of the total input[14]. Taking into account H_P, A_P, H_E, A_{ml} and relative humidity (which is for the Adriatic Sea 70%[3]), this is also in agreement with the prediction by the hydrological model developed by Weiss[7].

Upon substituting $V_E = 0.6 \cdot I$ into equation (4) and using data for P, E and R, the total input of $5.53 \cdot 10^{14}$ Bq yr^{-1} is estimated, being $VE = 3.32 \cdot 10^{14}$Bq yr^{-1}.

Turnover rate of mixed layer

For conversion of total tritium activity to mass units, the equation for specific activity is used:

$$S_A = \frac{\ln(2) \times N_A}{T_{1/2} \times M} \tag{7}$$

where:
S_A is the specific activity given in Bq g^{-1},
N_A is the Avogadro number ($6.023 \cdot 10^{23}$ mol^{-1}),
$T_{1/2}$ is the tritium half-life of 12.35 years and
$M = 3$ is the atomic number of tritium.

Various modes of tritium input into the Adriatic Sea are summarized in Table 2.

TABLE 2.

	Activity (Bq)	Mass (g)	Inventory (%)	Total Input (%)
Vapour Exchange	$3.32 \cdot 10^{14}$	0.93	4.5	60.0
Precipitation	$2.88 \cdot 10^{14}$	0.81	3.9	52.1
Run-off	$1.00 \cdot 10^{14}$	0.28	1.4	18.1
Evaporation	$-1.67 \cdot 10^{14}$	-0.47	2.3	30.2
Total Annual Input	$5.53 \cdot 10^{14}$	1.55		

Modes and balance of tritium input into the Adriatic Sea for the 1985 – 1991 period.

If the annual tritium input to the Adriatic Sea over the period 1985 – 1991 is assumed to be constant and equal to 1.55 g, by fitting the tritium mixed layer mass concentration data for respective years, using the Simplex method of function minimization to relation (2), the values of the constant $K = 16.8$ g and the turnover rate of the mixed layer water $\lambda_{ml} = 0.08$ yr^{-1} are obtained. Data for the mixed layer concentration and fit are shown in Fig. 1. The mean residence time of water in the mixed layer, $1/\lambda_{ml}$, is thus 12.6 years.

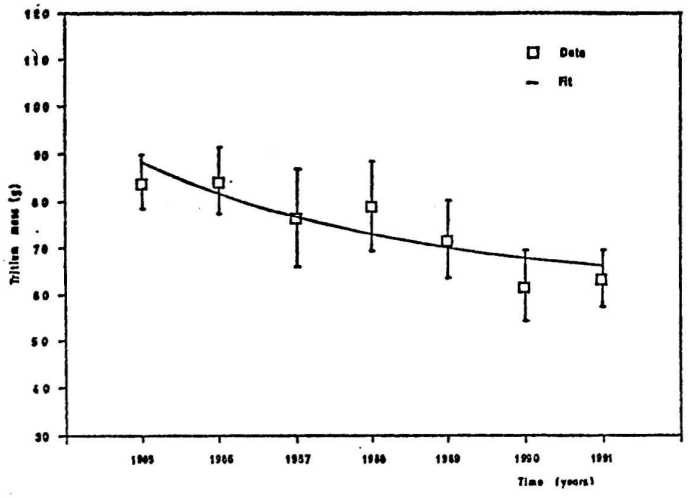

Fig. 1. Tritium mass data in the Adriatic Sea through period 1985 – 1991 (average of four sampling locations). Bars indicate 1 σ errors.

That value excellently corresponds to overall mean residence time of water in the mixed layer of the world ocean which is according to Fasterley[15] estimated to be 13.8 years. However, in the shallow, local seas, characterized by relatively fast vertical mixing (e.g. Adriatic) mean residence time of mixed layer water should be expected to be shorter than estimated above. Thus, it is likely that mean residence time of 12.6 years is overestimation, since data prior to 1985 needed for more reliable fit of the equation (2) are lacking.

4. Concluding remarks

The Adriatic Sea may still be considered to be unperturbed either by global or local discharge of tritium. In estimating the net tritium input to the Adriatic, the tritium inflow from the Mediterranean through the straight of Otranto is taken to be equal to outflow. It is thus implicitly assumed that the tritium concentrations in the Adriatic and the Mediterranean are comparable. The estimated total annual tritium input in the Adriatic Sea, most of which takes place through water vapour exchange, is equal to only few percent of the mixed layer inventory. The Adriatic Sea, with the average annual relative humidity of about 70% is the region of the Mediterranean Sea where the precipitation rate is higher than the evaporation rate ($H_P - H_E > 0$) and the H_P/H_E ratio is 1.7. Since the tritium concentration in precipitation is approximately equal to that in the water activity, (i.e. $A_P \approx A_{ml}$), in case that $H_P - H_E \approx 0$, the net tritium input would be about half lower, i.e. $\approx$ 0.8 to 0.9 g.

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TRICIJ U JADRANSKOM MORU

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Određivane su aktivnosti tricija u morskoj vodi na četiri lokacije duž jadranske obale. Ukupna količina tricija u miješanom sloju Jadranskog mora procijenjena je za 1991. godinu na $7,35 \cdot 10^{15}$ Bq (20.6 g). Neto unos tricija u Jadran za period od 1985. do 1991. godine, kroz molekularnu izmjenu, riječne vode i oborine, procijenjen je na $5,53 \cdot 10^{15}$/god (1,55 g/god). Srednje vrijeme boravka vode u miješanom sloju mora za Jadransko more procijenjeno je na 12,6 godina.