

# Tritium Measurements After Enrichment in Precipitation Collected at SCK·CEN Mol

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## 1. Introduction

Tritium is produced naturally by the cosmic rays at an annual rate of 74 PBq ( $74 \times 10^{15}$  Bq).<sup>1</sup> The nuclear tests in the 1950s and 1960s had injected into the earth's atmosphere by 1963 an amount of tritium estimated at 190 EBq ( $190 \times 10^{18}$  Bq) and 50 EBq, respectively, in the northern and southern hemisphere.<sup>1</sup> Nuclear facilities that release tritium into the environment are nuclear power stations, nuclear fuel reprocessing plants and tritium production plants. The annual release from these industries can be estimated at 6.4 PBq using data from UNSCEAR 1993 Report.<sup>1</sup>

Isotope measurement finds application in hydrological studies. These studies follow the variation in the concentration of  $^2\text{H}$ ,  $^3\text{H}$  and  $^{18}\text{O}$  along with  $^{13}\text{C}$  and  $^{14}\text{C}$  in dissolved carbon, in natural water. For tritium measurements two basic assumptions are made: 1- H-free groundwater contains only precipitation water from the 'pre-bomb period' and is older than 50 years; and 2- groundwater with significant tritium activity (karstic aquifer) contains precipitation water from the 1960s.

Prior to the nuclear era, the tritium activity in the precipitation has been estimated to be between 0.06 to 2.4 Bq/l.<sup>2</sup> Kaufman and Libby<sup>3</sup> estimated this value to be 0.68 Bq/l. In the early 1960s, following the atmospheric tests, the tritium activity in the precipitation has risen to 700 Bq/l. The long-term trend in the  $^3\text{H}$  concentration in precipitation has been followed by Rank<sup>4</sup> from 1961 until 1991. Nowadays, following the gradual decrease in the concentration of bomb H, its activity in precipitation has nearly fallen to the value observed for the 'pre-bomb period' and thus local and regional contamination by tritium increases its influence on hydrological studies.

When it was decided to study the tritium activity in groundwater, the first thing to look at was the tritium activity in precipitation. This paper presents our results obtained since 1994.

## 2. Analytical Procedure

### 2.1. RAINWATER SAMPLING

At SCK·CEN Mol, rainwater is collected from a funnel of 0.5 m<sup>2</sup> area directly into a polythene bottle. The funnel is surrounded by a water bath which is triggered when atmospheric temperature falls below 4 °C. This ensures that all precipitation is collected in the bottle under the funnel.

Daily, the rainwater is gathered and 7 subsequent samples are combined to produce a week's sample. This sample is filtered and 250 cm<sup>3</sup> are taken out from the filtrate for global alpha and beta activity measurements. The rest of the filtrate is kept to produce a monthly sample for tritium determination.

Rainwater has also been collected at two other sites in the south of Belgium. Mont Rigi is a scientific station of the University of Liège where precipitation is collected in a similar procedure

as described for SCK·CEN but no global alpha and beta measurements are made on these samples (sampling area 0.1 m<sup>2</sup>). At Parete, run off water from the roof of a house is collected in a barrel and from this the monthly sample is taken out for tritium determination.

## 2.2. TRITIUM ENRICHMENT PROCEDURE

Each electrolysis cell consists of a glass vessel suitably shaped to maintain a high liquid level around the nickel electrode. The cell can contain a water sample up to 250 cm<sup>3</sup>. The volume surrounding the electrode is around 20 cm<sup>3</sup>.

A water sample of 250 cm<sup>3</sup> is poured into the cell and 2 g of Na<sub>2</sub>O<sub>2</sub> is added. Two control samples are similarly prepared with 245 cm of reference water and 5 cm of a tritium standard. This reference water originates from a deep underground well and has been found to contain no tritium after our enrichment procedure. The cells are closed with the nickel anode and cathode and immersed in water with a cooling circulator set up at 2.2 °C to avoid the decrease of the separation factor for tritium and the evaporation loss of water by heating during the electrolysis.

The cells are connected in series and the electrolysis is started with an intensity of maximum 4 A and reduced to 2 A before the level of the liquid reaches the top of the electrodes. A quantity of 15 to 20 g of water should be left at the end of the electrolysis. The cells are then transferred to a distillation ramp and the water is distilled under reduced pressure.

## 2.3. TRITIUM MEASUREMENT

An aliquot of 10 cm<sup>3</sup> of the distillate is transferred and mixed with 10 cm<sup>3</sup> of liquid scintillation cocktail (Hisafe 3®) into the counting vial. Each vial is counted for at least 300 min. in a LKB 1220 Quantulus. With this set up, the Lower Limit of Detection is 2.3 Bq/l. Some of the samples have been counted for a much longer period of time leading to an even lower LLD (< 1 Bq/l).

The activity measured in the control samples allows us to calculate the enrichment factor which is applied for the determination of the initial activity of the rainwater samples. The average enrichment factor for the rainwater sample measured is 12 (range 9–15). Using these enrichment factors, the LLD for rainwater is 0.19 Bq/l (range 0.15–0.26 Bq/l). Except for 2 series of rainwater from Mont Rigi, the enrichment factor difference between the two controls was less than 10%.

The volume reduction by electrolytic decomposition of water from the initial volume  $V_0$  to the final volume  $V_f$  is accompanied by an increase of concentration from  $T_0$  to  $T_f$  as shown by the following equation<sup>5</sup>

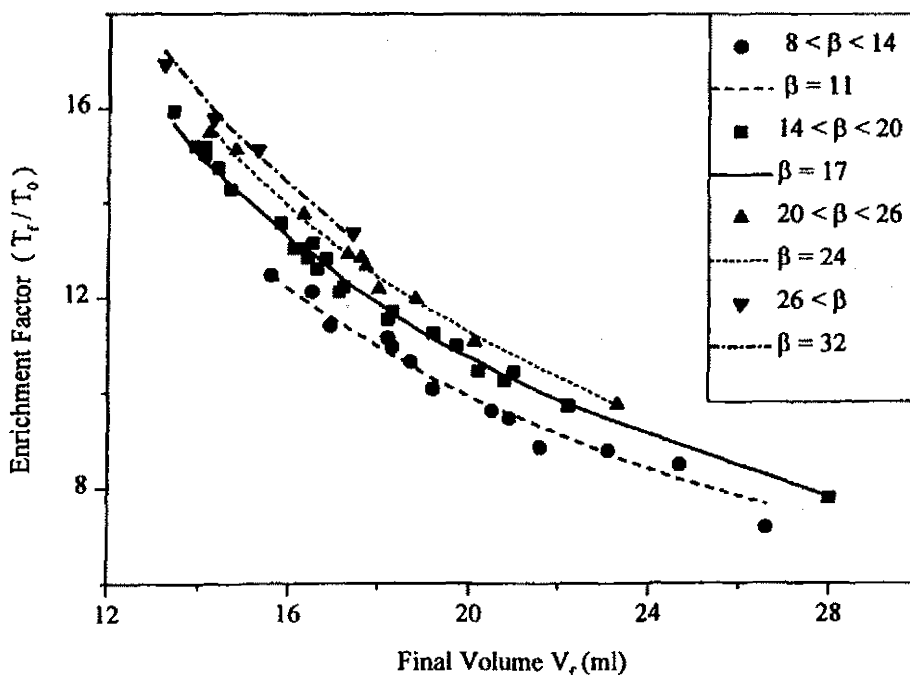
$$\log \frac{V_0}{V_f} = \frac{\beta}{\beta-1} \log \frac{T_f}{T_0} \quad (1)$$

where  $\beta$  is the separation factor for tritium. In our case,  $\beta$  is estimated by electrolysing simultaneously the two control samples containing a known amount of tritium.

The separation factor  $\beta$  will vary from cell to cell in a single run and also from run to run in a single cell. This factor also depends on the material used for the cathode. We have been using a pure nickel cathode but it has been shown that an iron cathode is more favourable because of its higher  $\beta$  value.<sup>5</sup>

The relationship of enrichment factor obtained in our experiments with volume reduction by electrolysis is shown in **Figure 1**. For each control sample, the separation factor  $\beta$  has been calculated from the experimental data and is represented by the points in **Figure 1**. These factors vary from 8 up to 36. The lines in the figure show the relationship obtained for the specific  $\beta$  values 11, 17, 24 and 32. These values are the average of the factor  $p$  for the chosen data range.

**Figure 1.** Relationship of enrichment factor with final volume obtained after electrolysis.



### 3. Results and Discussion

Monthly tritium activity in rainwater from March 94 until December 97 is given in **Table 1**. It must be said that while the precipitation samples have been collected very regularly at SCK·CEN, this has not been the case for the two other sampling points where some samples are missing.

Generally, the tritium activity observed at SCK·CEN is slightly higher than at the two other sampling sites. This is not surprising as, after all, SCK·CEN is a nuclear research centre and Belgoprocess, the Belgian radioactive waste handling facilities, is situated close by. However, most of the tritiated water (HTO) releases come from the stack of BR2.<sup>6</sup> BR2 is a high flux material testing reactor.

**Table 1.** Rainfall and tritium activity in precipitation.

Sampling date (mm)	Rainwater (Bq/l)	SCK·CEN (mm)	Rainwater (Bq/l)	Mont Rigi (mm)	Rainwater (Bq/l)	Parette

### 1994

Mar	97	$0.97 \pm 0.33$	190		108	
Apr	74	$1.43 \pm 0.36$	102		74	
May	44	$1.97 \pm 0.17$	72		75	
Jun	92	$2.1 \pm 0.2$	99		45	
Jul	16	$2.8 \pm 0.2$	82		21	
Aug	95	$2.5 \pm 0.2$	106	$1.54 \pm 0.14$	89	$1.21 \pm 0.25$
Sep	86	$3.6 \pm 0.4$	167		97	
Oct	77	$3.4 \pm 0.4$	118		121	$0.57 \pm 0.20$
Nov	60	$1.77 \pm 0.31$	115	$2.6 \pm 0.6$	71	$0.77 \pm 0.07$
Dec	85	$0.95 \pm 0.28$	189	$1.35 \pm 0.38$	154	$1.31 \pm 0.22$
Average 1994	73	2.15	124	1.83	85	0.97

### 1995

Jan	164	$1.91 \pm 0.46$	305	$1.69 \pm 0.38$	283	$0.91 \pm 0.08$
Feb	105	$1.38 \pm 0.41$	149	$1.34 \pm 0.38$	173	$1.84 \pm 0.25$
Mar	55	$< 0.05$	173	$1.55 \pm 0.38$	153	$2.8 \pm 0.3$
Apr	30	$< 0.05$	133	$1.83 \pm 0.39$	72	$2.5 \pm 0.3$
May	71	$1.72 \pm 0.43$	65		64	
Jun	78	$1.10 \pm 0.40$	128		46	$2.5 \pm 0.3$
Jul			141		57	$2.3 \pm 0.3$
Aug	87	$< 0.05$	77	$2.2 \pm 0.5$	45	
Sep			104	$1.25 \pm 0.38$	120	$1.75 \pm 0.17$
Oct	57	$< 0.05$	50	$1.52 \pm 0.26$	38	$2.5 \pm 0.3$
Nov	33	$1.59 \pm 0.36$	116	$0.87 \pm 0.22$	31	$2.1 \pm 0.3$
Dec	57	$3.5 \pm 0.5$	92	$1.20 \pm 0.23$	87	
Average 1995	74	1.87	128	1.49	97	2.14

### 1996

Jan			7		11	
Feb	32	$2.4 \pm 0.5$	104	$1.02 \pm 0.22$	93	
Mar	16.4	$2.9 \pm 2$	61	$1.14 \pm 0.23$	21	
Apr			260		208	
May	43	$1.53 \pm 0.35$	104	$1.08 \pm 0.22$	100	
Jun	41	$2.0 \pm 0.4$	46	$1.52 \pm 0.26$	21	
Jul	28	$2.5 \pm 0.5$	76		80	
Aug	166	$2.1 \pm 0.4$	189		102	
Sep	10	$0.73 \pm 0.29$	53		45	
Oct	37	$1.28 \pm 0.30$	165		88	$1.33 \pm 0.17$
Nov	62	$1.30 \pm 0.25$	153	$1.33 \pm 0.30$	141	
Dec	94	$2.8 \pm 0.4$	68	$2.3 \pm 0.3$	68	
Average 1996	53	4.6	107	1.39	81	

### 1997

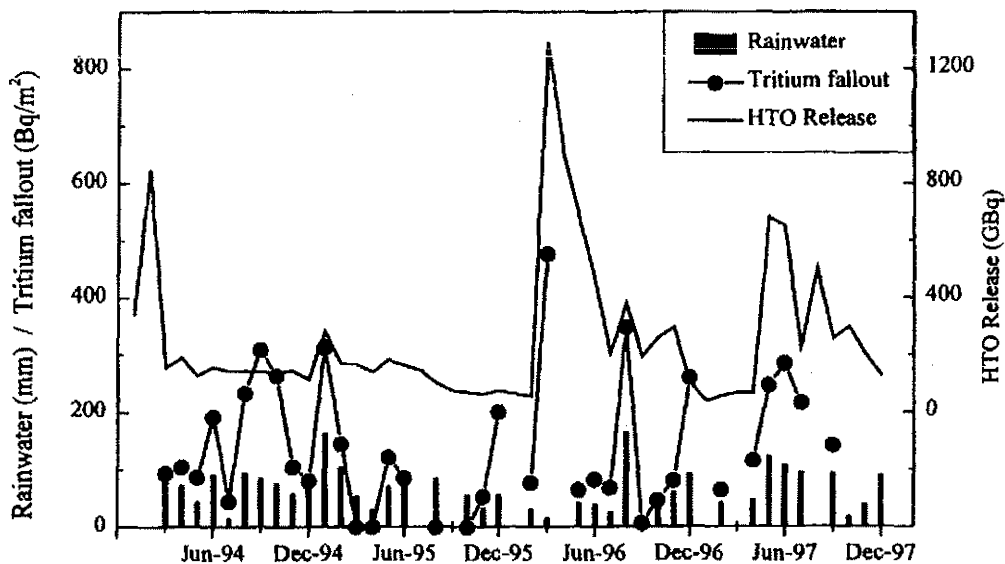
Jan			12	$1.24 \pm 0.24$	22	
Feb	43	$1.49 \pm 0.34$	167	$0.94 \pm 0.21$	169	
Mar			98	$1.19 \pm 0.27$	36	
Apr	48	$2.4 \pm 0.4$	127		35	$1.12 \pm 0.17$
May	124	$2.0 \pm 0.4$	130	$1.50 \pm 0.30$	93	

Jun	110	$2.6 \pm 0.4$	157		205	
Jul	96	$2.3 \pm 0.4$	128		44	$1.70 \pm 0.19$
Aug			37	$1.33 \pm 0.30$	43	
Sep	95	$1.51 \pm 0.34$	68		60	
Oct	19		108		88	$1.11 \pm 0.17$
Nov	41		84		123	$1.16 \pm 0.17$
Dec	91		167		152	$1.51 \pm 0.19$
Average 1997	74	2.05	107	1.24	89	1.32

The very high value of tritium in rainwater in March 1996, ( $29 \pm 2$  Bq/l) is, however, not due to reactor operation. At that time, the reactor was in refurbishment (from July 95 until March 97). The high HTO release (1292 GBq) observed in March 96<sup>6c</sup> was due to the cleaning up of several gloveboxes containing very high  $^3\text{H}$  activities. This is one of the reasons why the tritium enrichment procedure is not performed at SCK·CEN but at the University of Liège.

Following this, we have tried to correlate directly the tritium activity in rainwater with HTO releases from the stack of BR2. Besides the high value from March 96, no correlation could be observed. If instead of the  $^3\text{H}$  activity in rainwater (Bq/l) we look at the tritium fallout (Bq/m<sup>2</sup>), some correlation could be found with the HTO release and this is shown in **Figure 2**. Tritium fallout is defined as the  $^3\text{H}$  activity in rainwater (Bq/l) multiplied by the number of mm of rainwater falling on 1 m<sup>2</sup> or 1/m<sup>2</sup>. Tritium fallout is thus expressed in Bq/m<sup>2</sup>.

**Figure 2.** Tritium fallout and HTO release at SCK·CEN.



In **Figure 2**, it can be seen that the release from January 95, August 96 and May–June 97 are marked with a peak in the tritium fallout. On the other hand, the release from August 97 is not seen in the fallout as there was no rain or at least not enough rain during that month to perform any tritium measurement. The high release from March 96 is matched in the tritium fallout although the amount of rain which had fallen in that month was small (16.4 mm). In September 94, a peak in the fallout can not be matched with a particular peak release during that period. At

SCK·CEN, the tritium fallout ranges from 7.3 to 350 Bq/m<sup>2</sup> (excluding the value of 480 Bq/m<sup>2</sup> for March 96). At Mont Rigi and Parette, these values range from 15 to 520 Bq/m<sup>2</sup> and 40 to 430 Bq/m<sup>2</sup> respectively. With a few exceptions, high values of tritium fallout are due to high rainfall.

The tritium fallout depends not only on the HTO release from the reactor BR2 or other power plant, but also from the rainfall, the type of rainfall at the time of the release if there is one and the wind direction.

**Table 2** gives the average tritium activity in the precipitation and the average tritium fallout for the four years of observation. The values in brackets for Parette represent the single measurement performed that year. The 1996\* values for SCK·CEN are the average for 1996, excluding the very high tritium activity observed in March 1996.

**Table 2.** Average tritium activity in precipitation and average tritium fallout.

Year	SCK·CEN		Mont Rigi		Parette		
	Bq/l	Bq/m <sup>2</sup>	Bq/l	Bq/m <sup>2</sup>	Bq/l	Bq/m <sup>2</sup>	
1994		2.15	152	1.83	240	0.97	108
1995		1.87	92	1.49	201	2.1	201
1996		4.6	152	1.39	119	(133)	(117)
1996*		1.85	115				
1997		2.0	179	1.24	106	1.32	117

From this table, we can see that the average tritium activity in the precipitation is higher at SCK·CEN, but that the tritium fallout is much higher at Mont Rigi for the years 1994, 1995 and to a lesser extent in 1996 if the value of March 1996 is excluded. One of the reasons for this is that the rainfall at SCK·CEN is 30 to 40% lower than at Mont Rigi. It must be said that Mont Rigi and Parette are more or less surrounded by three nuclear power plants (Tihange in Belgium and Chooz and Cattenom in France) but it will be very difficult to correlate these observations.

## 4. Conclusions

The tritium activity in the precipitation at the three sampling points from Belgium ranges from 0.57 to 3.6 Bq/l with a tritium fallout range of 7 to 520 Bq/m<sup>2</sup>. Generally, high tritium fallout is associated with high rainfall. The tritium activity in precipitation generally observed is what can be expected nowadays. If sited near a nuclear facility, the sampling point can monitor the release from this facility at least through the tritium fallout but this fallout depends on many parameters.

Certainly more regular data are needed if extended hydrological studies are to be performed.

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## 5. References

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