

## Status and Trends of Iodine-129 Abundances in the European Environment

S. Szidat<sup>1</sup>, R. Michel<sup>1</sup>, J. Handl<sup>1</sup>, D. Jakob<sup>1</sup>, H.-A. Synal<sup>2</sup>, M. Suter<sup>3</sup>

<sup>1</sup>Zentrum fuer Strahlenschutz und Radioökologie, Universitaet Hannover, D-30167 Hannover, Germany

<sup>2</sup>Paul Scherrer Institut, c/o Institut fuer Teilchenphysik, ETH Hoenggerberg, CH-8093, Zuerich, Switzerland

<sup>3</sup>Institut fuer Teilchenphysik, ETH Hoenggerberg, CH-8093, Zuerich, Switzerland

### ABSTRACT

We report on investigations of  $^{129}\text{I}$  and  $^{127}\text{I}$  in the European environment. Results are presented concerning the verification of the natural  $^{129}\text{I}/^{127}\text{I}$  equilibrium ratio in the terrestrial biosphere, the development with time of  $^{129}\text{I}/^{127}\text{I}$  ratios in human and animal thyroid glands, the pre-nuclear abundance of  $^{129}\text{I}$  in soils, the deposition densities due to the atmospheric nuclear explosions and due to recent releases from European reprocessing plants, the migration behavior of stable and radio-iodine in soils, and the systematics of  $^{129}\text{I}$  and  $^{127}\text{I}$  in rain, surface and ground waters from Lower Saxony.

### INTRODUCTION

The long-lived radionuclide  $^{129}\text{I}$  ( $T_{1/2} = 15.7 \text{ Ma}$ ) occurs in nature at very low concentrations. Since the middle of the twentieth century the environmental levels of  $^{129}\text{I}$  have been dramatically changed as a consequence of civil and military use of nuclear fission. But, due to analytical and methodological problems the radioecology of  $^{129}\text{I}$  is still insufficiently known (1). We therefore started systematic investigations to establish reliable analytical protocols (1-4) for  $^{129}\text{I}$  and  $^{127}\text{I}$  analyses in various environmental materials and to close some gaps in our knowledge about the environmental abundance and behavior of  $^{129}\text{I}$ .

In nature, iodine-129 is produced by spontaneous fission of uranium in the lithosphere and hydrosphere and by interactions of cosmic ray particles with xenon in the atmosphere. Of the total inventory of approximately 326.8 TBq only about 1.7 TBq are estimated to be in the "free inventory" of atmosphere, hydrosphere and biosphere (5). Assuming a global equilibrium for the free inventory, equilibrium  $^{129}\text{I}/^{127}\text{I}$  ratios were estimated to be about  $10^{-12}$ ; e.g. (6).

To this free inventory, about 0.3 TBq were added by the atmospheric explosions of nuclear weapons (7). The Chernobyl accident added just a minor amount of 0.0071 GBq (2). The most important sources of anthropogenic  $^{129}\text{I}$  in the environment are releases from nuclear reprocessing plants. A complete balance of these latter emissions is not available, because of missing data for military installations. But, for example, the emission from the European reprocessing plants La Hague and Sellafield amounted to 15.4 TBq up to 1997. In 1997 this release amounted to 2.2 TBq with 75 % of the emissions being due to La Hague (8, 9). The total activity stored in spent fuel in 1990 was estimated to be 37 TBq (10).

Due to the emissions, the natural isotopic ratios were drastically changed. While the changes caused by the atmospheric explosions can be regarded to be fairly uniformly distributed with a certain preference of the northern hemisphere, the huge amount of emissions from reprocessing plants is extremely inhomogenous and differences by many orders of magnitude were and still are observed in the environment. The maximum  $^{129}\text{I}/^{127}\text{I}$  ratios measured are nine orders of magnitude higher than the natural ratios; see (1) for a recent survey.

From the radioecological point of view, our knowledge about  $^{129}\text{I}$  in the environment is still marginal. In 1962, radiochemical neutron activation analysis (RNAA) became available as a first analytical method to determine  $^{129}\text{I}$  in environmental samples (11). Manifold analyses demonstrated the extreme changes as a consequence of atmospheric weapon tests and even more pronounced due to releases from reprocessing plants. But, as discussed elsewhere in detail (1), RNAA is only capable of measuring  $^{129}\text{I}/^{127}\text{I}$  ratios above  $10^{-10}$  and the natural abundances and their transition to high contamination levels could not be quantified. Only by accelerator mass spectrometry (AMS) it became possible to determine all  $^{129}\text{I}/^{127}\text{I}$  ratios occurring in nature (1, 3).

The problem of quality assurance of  $^{129}\text{I}$  analyses remained, however, open (1). Missing standard reference materials, contamination problems and problems with chemical separation schemes for non-marine matrices make  $^{129}\text{I}$  analyses of environmental samples a sophisticated task. We shall not discuss these methodological problems in detail here, but rather refer to results of recent round robin exercises (12,13) and to earlier work of our group (1-4).

The theoretical estimates of the pre-nuclear equilibrium  $^{129}\text{I}/^{127}\text{I}$  ratio in the marine hydrosphere was verified experimentally by AMS measurements of pre-nuclear marine sediments and deep ocean waters yielding  $^{129}\text{I}/^{127}\text{I}$  ratios of  $(1.3 \pm 0.3) \cdot 10^{-12}$  (14) and  $(1.4 \pm 0.9) \cdot 10^{-12}$  (15, 16), respectively. AMS investigations showed further that  $^{129}\text{I}/^{127}\text{I}$  ratios of ocean surface waters remote from nuclear installations were changed to  $10^{-10}$ . This ratio is frequently used as an iodine unit for  $^{129}\text{I}/^{127}\text{I}$  ratios (IU). In the marine vicinity of the European reprocessing plants Sellafield and La Hague much higher isotopic ratios up to  $5700 \cdot 10^{-10}$  were measured 1984 - 1992 (17). Thus, the marine environment is in disequilibrium with respect to iodine isotopes, a fact which gives

rise to applications of  $^{129}\text{I}$  as a powerful tracer in hydrology (18).

Other information on the pre-nuclear abundance of  $^{129}\text{I}$  and on  $^{129}\text{I}/^{127}\text{I}$  isotopic ratios are scarce for other environmental compartments. For instance, there are no experimental results for pre-nuclear isotopic ratios in the terrestrial biosphere (1) and just a few investigations of environmental  $^{129}\text{I}$  levels in Europe remote from nuclear installations exist. To improve this situation four tasks can be identified. It is necessary to verify the pre-nuclear abundances for all relevant environmental compartments, to describe quantitatively their present status, to evaluate the radiological significance of environmental  $^{129}\text{I}$  levels, and to estimate the future trends.

## IODINE-129 IN HUMAN AND ANIMAL THYROID GLANDS

In order to establish the pre-nuclear ratios we investigated some old thyroid gland material from the United States using AMS. Results obtained are shown in Table 1. The up-to-now lowest isotopic ratio has been measured in a pig thyroid gland powder produced by Parke-Davis in 1943 in the USA. The mean of the two analyses of  $(0.058 \pm 0.012) \cdot 10^{-10}$  is still higher than the measured pre-nuclear ratios in ocean sediments. The thyroid glands sampled in 1947 in the USA turned out to have  $^{129}\text{I}/^{127}\text{I}$  ratios 10 to 60 times higher than the pre-nuclear marine equilibrium ratio and thus are suspect to be affected already by  $^{129}\text{I}$  releases during the Manhattan project and the onset of the nuclear age. The up-to-now lowest measured  $^{129}\text{I}/^{127}\text{I}$  ratio in biospheric materials remains with the Parke-Davis thyroid gland powder from 1943 which still is 5 to 7 times higher than the marine equilibrium value and which shows some variability among different aliquots.

The higher than expected isotopic ratios in the samples of 1947 cannot be explained by the analytical blanks which were regularly and carefully analyzed for the entire analysis and typically result in isotopic ratios below  $10^{-13}$ . The problem, however, is that one cannot be sure whether any contamination can be excluded during nearly 50 years of sample storage. Thus, in principle, the results for any pre-nuclear material can only be considered as upper limits of the intrinsic isotopic ratios.

Table 1. Verification of the natural  $^{129}\text{I}/^{127}\text{I}$  equilibrium ratio in the terrestrial biosphere.

| Material                   | Year | $^{127}\text{I}$<br>[g kg <sup>-1</sup> ] | $^{129}\text{I}$<br>[mBq kg <sup>-1</sup> ] | $^{129}\text{I}/^{127}\text{I}$<br>$10^{-10}$ |
|----------------------------|------|-------------------------------------------|---------------------------------------------|-----------------------------------------------|
| Animal thyroid powder, USA | 1943 | 3.0                                       | 0.14                                        | $0.070 \pm 0.015$                             |
|                            |      | $2.98 \pm 0.09$                           | $0.092 \pm 0.008$                           | $0.046 \pm 0.005$                             |
| Pig thyroid powder, USA    | 1947 | -                                         | -                                           | $0.58 \pm 0.20$                               |
| Horse thyroid powder, USA  | 1947 | 3.36                                      | 27                                          | $12.3 \pm 1.5$                                |
|                            |      | 3.36                                      | 34                                          | $15.4 \pm 1.8$                                |

Present days isotopic ratios in human and animal thyroid glands from Lower Saxony in Germany well away from nuclear installations emitting  $^{129}\text{I}$  show much higher ratios (Fig. 1). In bovine thyroid glands,  $^{129}\text{I}/^{127}\text{I}$  ratios of  $(110 \pm 10) \cdot 10^{-10}$ ,  $(47 \pm 5) \cdot 10^{-10}$ , and  $(400 \pm 196) \cdot 10^{-10}$  were observed in 1978 (n = 25), 1981 (n = 22), and 1992/93 (n = 9), respectively (19, 20). The fall-out caused by the Chernobyl accident in Western Europe just appeared as a short-term peak in the isotopic ratios (Fig. 1) as revealed by analyses of animal thyroids from Austria and Germany (21). Pre- and post-Chernobyl human thyroid glands from Germany analyzed at ZSR by RNAA showed  $^{129}\text{I}/^{127}\text{I}$  ratios of  $(216 \pm 114) \cdot 10^{-10}$  (n = 13) and  $(320 \pm 156) \cdot 10^{-10}$  (n = 26), respectively.  $^{129}\text{I}/^{127}\text{I}$  ratios are about one order of magnitude lower in thyroid glands from the southern hemisphere as revealed by analyses of human and animal thyroid glands from Chile (20). This is well in line with the general differences between global weapons fall-out in the southern and northern hemispheres, on the one hand, and the fact that the emissions from reprocessing plants mainly take place on the northern hemisphere, on the other.

With respect to the radiological significance of these  $^{129}\text{I}/^{127}\text{I}$  ratios, one can estimate the associated radiation exposure on the basis of a specific activity model (2). Assuming the data of ICRP reference man for human iodine content and uptake (22) and a dose factor for a child in its first year of  $2.8 \cdot 10^{-7}$  Sv/Bq (23), an equilibrium  $^{129}\text{I}/^{127}\text{I}$  ratio of  $100 \cdot 10^{-10}$  corresponds to an annual effective equivalent dose due to intake of  $^{129}\text{I}$  of  $H_{\text{eff}} = 6$  nSv/a. Thus, it can be concluded that the present situation is radiological not significant. It is to note, however, that this is just a coarse estimate which takes not into account the existing disequilibrium of  $^{129}\text{I}$  and  $^{127}\text{I}$  in the environment.

It cannot be concluded from the data of Fig. 1 that the  $^{129}\text{I}/^{127}\text{I}$  ratios in Europe remain constant at their present levels, since there appears a tendency of increase in spite of a considerable scatter of the data. Therefore, we shall look into other environmental compartments in order to describe the actual status and future development. Relevant compartments are the pedosphere, from the analysis of which integral deposition densities of  $^{129}\text{I}$  can be derived, and wet precipitation and other natural waters, which allow to determine deposition density rates and to investigate the pathways of  $^{129}\text{I}$  through the terrestrial hydrosphere.

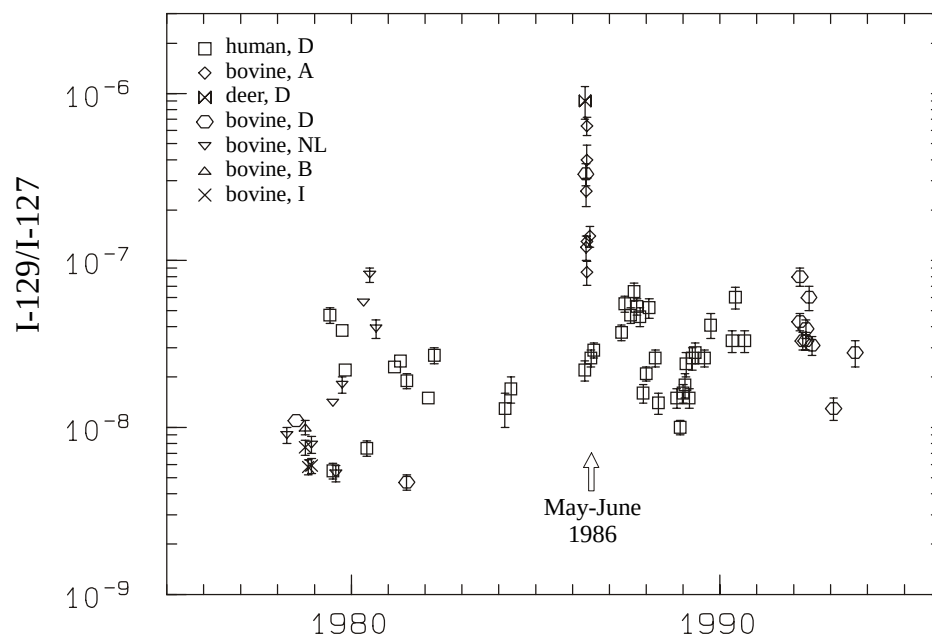


Figure 1. Development with time of biospheric  $^{129}\text{I}/^{127}\text{I}$  ratios as revealed by RNAA analyses of human and animal thyroid glands from Western Europe. All the analyses were performed by RNAA at the former Niedersaechsisches Intitut für Radioökologie (now Zentrum für Strahlenschutz und Radioökologie).

## IODINE –129 IN EUROPEAN SOIL SAMPLES

Also for the pedosphere, no measurements of the pre-nuclear abundances of  $^{129}\text{I}$  exist mainly because of the problem of contamination by ubiquitous man-made  $^{129}\text{I}$ . In this work, we analyzed samples from three soil profiles which were taken in Russia in 1909, 1910, and 1939, respectively. In table 2, the results are compared with  $^{129}\text{I}$  and  $^{127}\text{I}$  analyses of soils from Moscow, from the vicinity of Chernobyl and from Lower Saxony, Germany. For the pre-nuclear samples we were only capable of determining the total contents of the iodine isotopes, while for the others detailed depth profiles were measured (Fig. 2).

The range of  $^{129}\text{I}/^{127}\text{I}$  ratios and of  $^{129}\text{I}$  activity concentrations observed in soil samples cover five orders of magnitude. The up-to-now lowest activity per unit mass of  $0.14 \pm 0.03 \mu\text{Bq/kg}$  was found in the soil from Lutovinovo taken in 1939. This sample showed also the lowest isotopic ratio of  $(0.057 \pm 0.011) \cdot 10^{-10}$  which, again, is still a factor of five higher than the pre-nuclear marine equilibrium ratio. Generally, all the pre-nuclear soil samples showed  $^{129}\text{I}/^{127}\text{I}$  ratios between 5 and 170 times higher than the presumed natural equilibrium ratio. We therefore conclude that all the old soil are suspect to modern contamination during storage, but not during analysis since the complete analytical blanks typically yield  $^{129}\text{I}/^{127}\text{I}$  ratios below  $10^{-13}$ .

In order to estimate the total deposition density due to the atmospheric explosions of nuclear weapons we investigated two soil profiles taken in 1996 in Moscow which according to their  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$  activities could be estimated to be not affected by the fall-out of the Chernobyl accident. We chose Moscow because of the large distance to the Western European reprocessing plants and measured detailed depth profiles of  $^{129}\text{I}$  and  $^{127}\text{I}$ ; see table 2 and Fig. 2. The two determinations yield an average deposition density of  $50 \text{ mBq/m}^2$ . This result is significantly lower than the total deposition density of  $90 \text{ mBq/m}^2$  reported by Bunzl (24) for Munich, Germany as early as in 1986. It is, however, not clear whether average deposition densities due to atmospheric weapons tests of  $^{129}\text{I}$  can be determined at all given the strongly inhomogenous emissions from the reprocessing plants

which were not globally well mixed. In this sense, the value of 50 mBq/m<sup>2</sup> will have to be scrutinized by further investigations.

In order to estimate an upper limit of the pre-nuclear integral <sup>129</sup>I deposition density from the soil taken at Lutovinovo in 1939, we assumed that the average <sup>129</sup>I and <sup>127</sup>I in the sample analyzed represents an equilibrium between influx by fall-out of natural atmospheric <sup>129</sup>I and <sup>127</sup>I and outflux by migration into larger depths and into ground water with typical time constants of ~ 40 years deduced from the <sup>129</sup>I depth profiles from Moscow (2) (Fig. 2). Under these assumptions, one calculates an upper limit of the pre-nuclear integral <sup>129</sup>I deposition density of 0.084 mBq/m<sup>2</sup>.

Of particular interest is the analysis of soil samples in the highly contaminated areas around Chernobyl. In our investigations in Northern Ukraine, iodine isotopic ratios up to  $15,732 \cdot 10^{-10}$  and deposition densities of up to 1.4 Bq/m<sup>2</sup> were found in samples from Nosdrischtsche in contamination zone II (<sup>137</sup>Cs deposition density 555 - 1480 kBq/m<sup>2</sup>), much higher than those caused by the weapons fall-out. This <sup>129</sup>I offers the possibility to use <sup>129</sup>I as a tool for a retrospective dosimetry of the <sup>131</sup>I exposure in those areas long after the short-lived isotope decayed. Even in the samples from Nemirowka, located in zone III (<sup>137</sup>Cs deposition density 185 – 555 kBq/m<sup>2</sup>), the Chernobyl fall-out can clearly be distinguished from the weapons fall-out.

Table 2. <sup>129</sup>I and <sup>127</sup>I abundances, <sup>129</sup>I/<sup>127</sup>I ratios and <sup>129</sup>I deposition densities in various soils.

| Material                                  | <sup>129</sup> I<br>[μBq kg <sup>-1</sup> dry w.] | <sup>127</sup> I<br>[mg kg <sup>-1</sup> dry w.] | <sup>129</sup> I/ <sup>127</sup> I<br>10 <sup>-10</sup> | Integral <sup>129</sup> I<br>deposition density<br>[mBq m <sup>-2</sup> ] |
|-------------------------------------------|---------------------------------------------------|--------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------------------------|
| Bogoroditsk, 1909 <sup>a</sup>            | 0.86 ± 0.07                                       | 5.4 ± 0.3                                        | 0.25 ± 0.03                                             | not determined                                                            |
| Moscow, 1910 <sup>a</sup>                 | 0.88 ± 0.07                                       | 0.79 ± 0.02                                      | 1.7 ± 0.1                                               | not determined                                                            |
| Lutovinovo, 1939 <sup>a</sup>             | 0.14 ± 0.03                                       | 3.87 ± 0.13                                      | 0.057 ± 0.011                                           | 0.084 ± 0.017                                                             |
| Moscow VI, 1996 <sup>a,b</sup>            | 9.4 - 803                                         | 1.2 - 2.9                                        | 12 - 484                                                | 64 ± 5                                                                    |
| Moscow VII, 1996 <sup>a,b</sup>           | 17 - 562                                          | 0.74 - 3.5                                       | 35 - 282                                                | 37 ± 3                                                                    |
| Nemirowka II, 1995 <sup>a,b</sup>         | 9.0 - 2,660                                       | 4.5 - 7.9                                        | 3.0 - 631                                               | 186 ± 14                                                                  |
| Nosdrischtsche II,<br>1995 <sup>a,b</sup> | 73 - 6,142                                        | 0.5 - 0.72                                       | 224 - 15,732                                            | 1390 ± 100                                                                |
| Lower Saxony, 1998                        | 550 - 1,200                                       | 0.68 - 0.71                                      | 1,200 - 3,300                                           | not determined                                                            |

<sup>a</sup> range of data measured in 40 cm soil profiles; <sup>b</sup> for details see (2).

The <sup>129</sup>I/<sup>127</sup>I ratios within the individual soil profiles decrease by about a factor of 100 over 40 cm depth. The ratios observed in top-soils range from  $282 \cdot 10^{-10}$  (Moscow VII, 1996) over  $631 \cdot 10^{-10}$  (Nemirowka II, zone III, 1995) to  $15,732 \cdot 10^{-10}$  (Nosdrischtsche II, 1995, zone II). Two, recent top-soil from Lower Saxony showed ratios of  $1,200 \cdot 10^{-10}$  and  $3,300 \cdot 10^{-10}$ , respectively, significantly higher than the ratios measured up to 1993 in thyroid glands from Lower Saxony.

While from their <sup>129</sup>I, <sup>137</sup>Cs, and <sup>134</sup>Cs activity concentrations the soil profile from Nosdrischtsche appears to be disturbed, the other three <sup>129</sup>I profiles in Fig. 2 are seemingly undisturbed and allow to analyze <sup>129</sup>I migration in some detail (2). Further comprehensive measurements of soil profiles in Northern Ukraine are underway with the goal of retrospective dosimetry.

While the analysis of soil profiles yields information about integral deposition densities and about the migration behavior of <sup>129</sup>I, the actual fall-out rates can be determined by the analyses of wet precipitation. In addition, past annual deposition rates can be derived from the analysis of reservoirs such as ice cores which preserve the fall-out history.

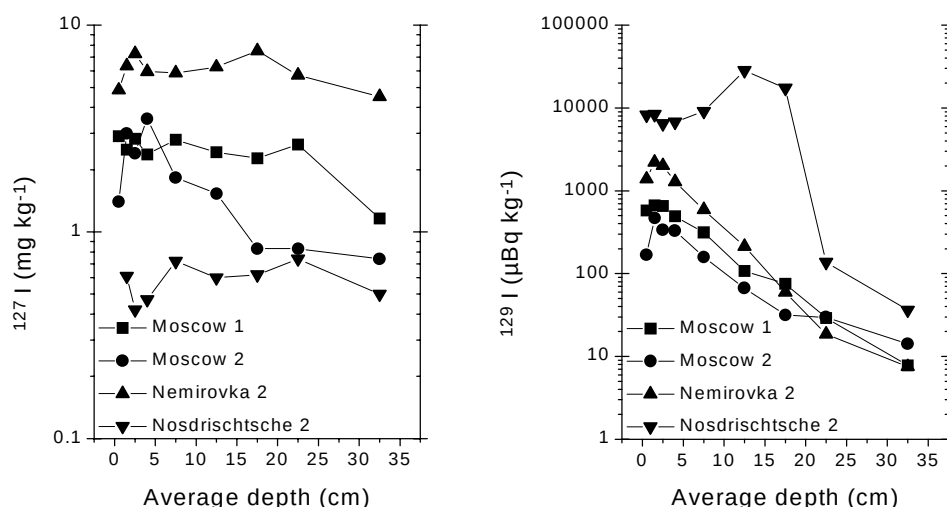


Figure 2. Distribution of stable iodine and of iodine-129 in soil profiles from Russia and Ukraine.

## IODINE –129 IN EUROPEAN NATURAL WATERS

We report here some results from a long-term project to investigate  $^{129}\text{I}$  and  $^{127}\text{I}$  in precipitation, surface and shallow ground water samples from Lower Saxony, Germany. In order to make a spatial separation, Lower Saxony was divided into four regions with sampling sites of every sample type each. In addition to open field precipitation sampled in each region, through-fall precipitation was collected in two regions; through-fall means rain that falls down on forests and interacts with the canopy of the trees on its way down. The four regions were chosen to represent the close proximity to the North Sea (region I), northern German low-lands distant from the North Sea (region II), the onset of the Harz mountains (region III) and the area of the Elbe river in Lower Saxony in the vicinity of Gorleben (region IV); for details of the sampling sites see (25).

Up to 10 L of precipitation were made available to us as quarterly composite samples. 2 L of surface water were collected as spot samples once a quarter and 10 L of ground water once every half year. A 1 L North Sea water sample was taken singularly near the shore on 12/7/99. Samples were made alkaline and stored in the dark in polyethylene containers until analysis. For determination of  $^{129}\text{I}$  with AMS, inorganic iodine was extracted from the samples by an anion exchange resin after carrier addition.  $^{127}\text{I}$  was measured with ICP-MS in the filtered samples. For sample preparation, AMS techniques and measurement details see (3, 4, 25, 28).

$^{127}\text{I}$  and  $^{129}\text{I}$  contents and  $^{129}\text{I}/^{127}\text{I}$  isotopic ratios of the samples analyzed are presented in table 3. Values are given as two years' geometric means of the quarterly or half-yearly measurements for sampling years 1997 and 1998. In addition, the results three older RNAA analyses of precipitation from Hannover collected in 1986 and 1987 are given. Geometric means were preferred to arithmetic means, because single values do not obey to a normal distribution, but rather to a log-normal one.

The iodine pathways through the environment are according to model estimations (26, 27) recognizable via the  $^{129}\text{I}/^{127}\text{I}$  ratios: The North Sea acts as a buffer reservoir for both, stable iodine and  $^{129}\text{I}$  the latter being mainly emitted by the European reprocessing plants. It is to point out that the ratio measured in sea water collected from the North Sea in 1999 is higher by a factor of 34 than those reported by Yiou et al. (17) in 1994. This increase points to the importance of recent releases from La Hague (8,9) and will be investigated in more detail soon.

The subsequent transfer of  $^{129}\text{I}$  and  $^{127}\text{I}$  through marine and land atmosphere takes place with a short residence time of about two weeks. Here, a mixing with iodine from other sources causes a lower  $^{129}\text{I}/^{127}\text{I}$  ratio than in sea water. After iodine is brought to the ground by wet and dry deposition it moves just very slowly into surface or ground waters. These compartments show distinctly lower  $^{129}\text{I}/^{127}\text{I}$  ratios which enables us to estimate residence times of iodine in catchments. As iodine is biophilic, these residence times may give evidence about the biological conditions of catchments if they are compared to tritium residence times. The significantly higher  $^{129}\text{I}/^{127}\text{I}$  ratio in precipitation from the North Sea shore area (region I) compared to the other areas may be explained in a significant portion of sea-spray since the samples were collected at Norderney airport which is just a few hundred meters away from the shore.

Table 3: Results of  $^{129}\text{I}$  and  $^{127}\text{I}$  analyses of natural waters from Lower Saxony, Germany. The results for regions I-IV of Lower Saxony are mean values for 1997 and 1998 unless otherwise stated.

| materials investigated      | region   | n | $^{127}\text{I}$<br>concentration<br>[ $\mu\text{g kg}^{-1}$ ] | $^{129}\text{I}$ activity<br>concentration<br>[ $\mu\text{Bq kg}^{-1}$ ] | $^{129}\text{I}/^{127}\text{I}$<br>atomic ratio<br>[ $10^{-10}$ ] |
|-----------------------------|----------|---|----------------------------------------------------------------|--------------------------------------------------------------------------|-------------------------------------------------------------------|
| Sea water, North Sea, 1999  | I        | 1 | 52.5 $\pm$ 4.9                                                 | 544.6 $\pm$ 36.4                                                         | 15300 $\pm$ 1700                                                  |
| Precipitation, 2/1986       | Hannover | 1 | 1.56 $\pm$ 0.12                                                | 1.69 $\pm$ 0.17                                                          | 1660 $\pm$ 230                                                    |
| Precipitation, 2-3/1987     | Hannover | 1 | 1.80 $\pm$ 0.08                                                | 6.57 $\pm$ 0.29                                                          | 5580 $\pm$ 350                                                    |
| Precipitation, 4/1987       | Hannover | 1 | 2.58 $\pm$ 0.19                                                | 8.76 $\pm$ 0.69                                                          | 5200 $\pm$ 580                                                    |
| Precipitation, open-field   | I        | 8 | 2.71 $\cdot$ 1.52 $^{\pm 1}$                                   | 17.8 $\cdot$ 1.37 $^{\pm 1}$                                             | 9680 $\cdot$ 1.28 $^{\pm 1}$                                      |
| Precipitation, open-field   | II       | 7 | 1.40 $\cdot$ 1.44 $^{\pm 1}$                                   | 6.87 $\cdot$ 1.33 $^{\pm 1}$                                             | 7260 $\cdot$ 1.45 $^{\pm 1}$                                      |
| Precipitation, open-field   | III      | 7 | 1.19 $\cdot$ 2.12 $^{\pm 1}$                                   | 4.70 $\cdot$ 1.87 $^{\pm 1}$                                             | 5860 $\cdot$ 1.59 $^{\pm 1}$                                      |
| Precipitation, open-field   | IV       | 7 | 1.21 $\cdot$ 1.60 $^{\pm 1}$                                   | 3.64 $\cdot$ 1.73 $^{\pm 1}$                                             | 3850 $\cdot$ 1.63 $^{\pm 1}$                                      |
| Precipitation, through-fall | II       | 7 | 6.83 $\cdot$ 1.30 $^{\pm 1}$                                   | 27.3 $\cdot$ 1.35 $^{\pm 1}$                                             | 5920 $\cdot$ 1.16 $^{\pm 1}$                                      |
| Precipitation, through-fall | III      | 8 | 4.75 $\cdot$ 1.22 $^{\pm 1}$                                   | 15.0 $\cdot$ 1.33 $^{\pm 1}$                                             | 4690 $\cdot$ 1.40 $^{\pm 1}$                                      |
| Surface water               | I        | 8 | 22.2 $\cdot$ 1.43 $^{\pm 1}$                                   | 5.96 $\cdot$ 2.04 $^{\pm 1}$                                             | 398 $\cdot$ 1.79 $^{\pm 1}$                                       |
| Surface water               | II       | 8 | 6.23 $\cdot$ 1.28 $^{\pm 1}$                                   | 0.97 $\cdot$ 1.83 $^{\pm 1}$                                             | 231 $\cdot$ 1.61 $^{\pm 1}$                                       |
| Surface water               | III      | 7 | 5.55 $\cdot$ 1.42 $^{\pm 1}$                                   | 514 $\cdot$ 1.72 $^{\pm 1}$                                              | 61.9 $\cdot$ 1.77 $^{\pm 1}$                                      |
| Surface water               | IV       | 8 | 6.36 $\cdot$ 1.40 $^{\pm 1}$                                   | 0.68 $\cdot$ 2.16 $^{\pm 1}$                                             | 159 $\cdot$ 2.01 $^{\pm 1}$                                       |
| Shallow ground water        | I        | 2 | 4.24 $\cdot$ 1.38 $^{\pm 1}$                                   | 514 $\cdot$ 1.48 $^{\pm 1}$                                              | 81.1 $\cdot$ 1.07 $^{\pm 1}$                                      |
| Shallow ground water        | II       | 3 | 3.60 $\cdot$ 1.22 $^{\pm 1}$                                   | 0.54 $\cdot$ 1.20 $^{\pm 1}$                                             | 226 $\cdot$ 1.50 $^{\pm 1}$                                       |
| Shallow ground water        | III      | 3 | 2.63 $\cdot$ 4.62 $^{\pm 1}$                                   | 432 $\cdot$ 5.40 $^{\pm 1}$                                              | 28.9 $\cdot$ 2.05 $^{\pm 1}$                                      |
| Shallow ground water        | IV       | 4 | 4.94 $\cdot$ 1.09 $^{\pm 1}$                                   | 0.0082 $\cdot$ 2.61 $^{\pm 1}$                                           | 2.49 $\cdot$ 2.49 $^{\pm 1}$                                      |

The mean  $^{129}\text{I}$  concentration is about four times higher in through-fall than in open field precipitation. This difference reflects the importance of evaporative concentration processes and the ability of the trees to scavenge fine mists and aerosol particles (16, 29). As the  $^{129}\text{I}/^{127}\text{I}$  ratios in through-fall and inland open field precipitation are the same it is obvious that the higher iodine content in through-fall originates from the same source. This excludes the possibility of canopy leaching or soil resuspension because in large amounts vegetation and soil have a lower  $^{129}\text{I}/^{127}\text{I}$  ratio than precipitation.

Taking together all results of analyses of precipitation from Germany, (30 - 32) and this work, and of an ice core from the Fiescherhorn in Switzerland (33) one can survey the development of  $^{129}\text{I}/^{127}\text{I}$  ratios (Fig. 3) and of annual  $^{129}\text{I}$  deposition rates (table 4) during the last five decades. After a dramatic increase of  $^{129}\text{I}/^{127}\text{I}$  ratios until the middle of the 1980s and a sharp peak due to the Chernobyl accident,  $^{129}\text{I}/^{127}\text{I}$  ratios have reached a constant plateau at  $\sim 8 \cdot 10^{-7}$  since 1987. Emissions of La Hague which increased about one order of magnitude since then (8,9) did not affect this stagnation up to now. There is no bomb peak in the annual deposition rates as observed for other man-made radionuclides such as  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{90}\text{Sr}$ , and  $^{137}\text{Cs}$ , but a continuous increase until the end of the 1980s. Since then, deposition rates have stabilized at a high level. They rose from 0.01  $\text{mBq m}^{-2} \text{a}^{-1}$  in 1950 by nearly three orders of magnitude to  $\sim 7 \text{ mBq m}^{-2} \text{a}^{-1}$  in 1997/98 (mean of open-field deposition rates from table 4). The present deposition is rather inhomogenous during the years showing even some seasonal dependence (25). There is also a high variability depending on the location and the distance from the North Sea. These investigations will be continued to survey the future development as well as to study the transfer mechanisms of iodine species from the North Sea into the atmosphere their deposition mechanisms. It is further needed to extend this coarse survey and to investigate different parts of Europe in more detail. Recent results from Spain (34) and unpublished data from Switzerland (35) point to the pertinent problem of ongoing  $^{129}\text{I}$  immissions which add to the  $^{129}\text{I}$  contamination of the terrestrial biosphere of Central Europe.

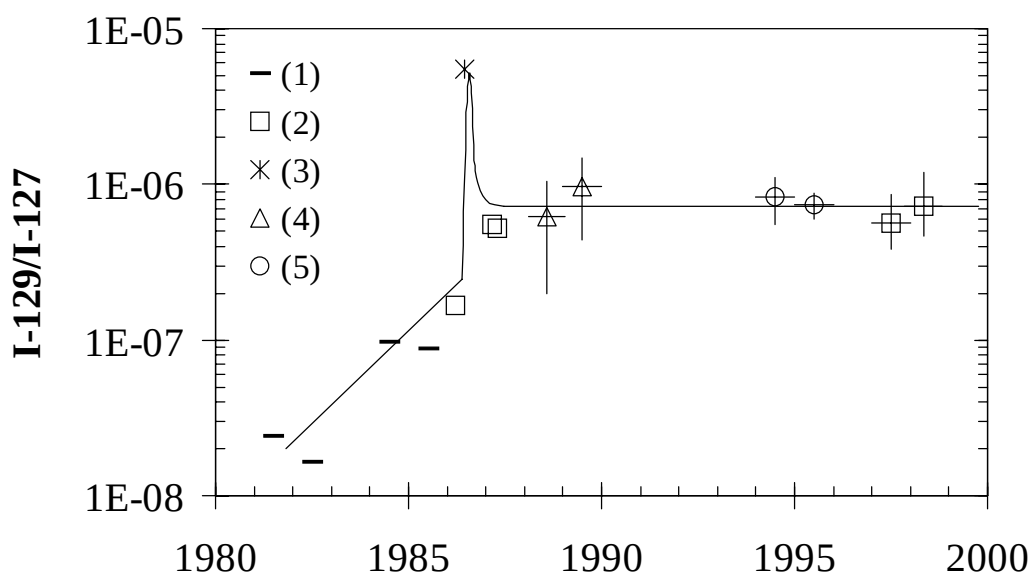


Figure 3. Development of  $^{129}\text{I}/^{127}\text{I}$  isotopic ratios in precipitation as revealed by analyses of precipitation from Switzerland and Germany. Data are coded 1 (33), 2 (this work), 3 (30), 4 (31), and 5 (32).

Table 4: Annual  $^{129}\text{I}$  and  $^{137}\text{Cs}$  deposition densities of the last 50 years at various European locations. Annual  $^{129}\text{I}$  deposition densities of this work were calculated by multiplying the geometric means of the  $^{129}\text{I}$  concentrations in precipitation with the actually measured precipitation depths at the respective sampling locations.

| location                   | material           | Year  | Ref. | annual $^{129}\text{I}$<br>deposition density<br>[mBq m <sup>-2</sup> a <sup>-1</sup> ] | annual $^{137}\text{Cs}$<br>deposition density<br>[kBq m <sup>-2</sup> a <sup>-1</sup> ] |
|----------------------------|--------------------|-------|------|-----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Fiescherhorn, Switzerland  | ice core           | 1950  | (33) | 0.014                                                                                   | 0.011                                                                                    |
| Fiescherhorn, Switzerland  | ice core           | 1983  | (33) | 0.92                                                                                    | <0.006                                                                                   |
| Mappenberg, Germany        | rain + aerosol     | 88/89 | (31) | 5.2 ± 2.1                                                                               | 0.010 ± 0.004                                                                            |
| Germany, various locations | precipitation      | 1995  | (32) | 7.4 ± 2.3                                                                               | n.a.                                                                                     |
| Lower Saxony (I), Germany  | rain, open-field   | 97/98 | this | 12.7 ± 3.4                                                                              | n.a.                                                                                     |
| Lower Saxony (II), Germany | rain, open-field   | 97/98 | this | 7.2 ± 1.5                                                                               | n.a.                                                                                     |
| Lower Saxony (IV), Germany | rain, open-field   | 97/98 | this | 2.0 ± 0.8                                                                               | n.a.                                                                                     |
| Lower Saxony (II), Germany | rain, through-fall | 97/98 | this | 17.1 ± 6.2                                                                              | n.a.                                                                                     |

## CONCLUSIONS

In Europe, as all over the world, the natural abundance of  $^{129}\text{I}$  have been sustainably changed. But, in Western Europe these changes are going on.  $^{129}\text{I}/^{127}\text{I}$  ratios in precipitation stabilized after a decades-long increase at a level of  $\sim 10^{-6}$ . These ratios are more than one decade higher than recent ratios of biosphere iodine measured in Germany. The different environmental compartments in Europe show severe disequilibrium of  $^{129}\text{I}$  and of stable iodine with the expected consequence of a further rise of biospheric  $^{129}\text{I}/^{127}\text{I}$  ratios. Assuming continuing emissions and today's annual deposition rates of  $^{129}\text{I}$ , the deposition densities due to global weapons fall-out of about  $50 \text{ mBq/m}^2$  will be doubled every decade in Western Europe, afforested and coastal areas being more affected.

In spite of the fact that the present biospheric  $^{129}\text{I}$  abundance does not give rise to a significant radiation exposure, the future development should be carefully surveyed. Given the long half-life of  $^{129}\text{I}$  the current practice of increasing emissions should be discontinued in order to prevent  $^{129}\text{I}$  from becoming significant. In this respect,  $^{129}\text{I}$  turns out to be an outstanding quantitative indicator of the long-term human impact onto the environment. But, there remains a lot of open questions with respect to the radioecology of  $^{129}\text{I}$  which have to be dealt with in the future.

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