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Chapter 5

Fate of Radiopharmaceuticals in the Environment

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Additional information is available at the end of the chapter

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Abstract

After World War II, the use of artificially produced radionuclides in medicine began and led to great success in the fight against cancer and other diseases. However, the highly radioactive compounds had to be handled with great care to protect patients and hospital personnel from radiation. The survey of these radionuclides in the environment followed some years later. In Switzerland, double-tracked monitoring programs were started. On the emission side, hospitals and industries handling radiopharmaceuticals had to report their consummation of radionuclides yearly. A monitoring program of their waste waters and solid wastes was also started. On the immission side, the remaining radioactive wastes, which were released to the environment, had to be surveyed. Overall, only a few violations of the limits for radiopharmaceuticals were observed over the last 30 years in Switzerland. Nevertheless, the monitoring of radioactivity in the environment remains an important task as long as radionuclides are used in medicine.

Keywords: radiopharmaceuticals, y-90, Lu-177, I-131, sewage sludge, sewer sludge, suspended matter

1. Introduction

Radiopharmaceuticals were first synthesised back in 1933. In Paris, Irène and Frédéric Joliot-Curie produced the first synthetic radionuclide by irradiating aluminium foil with alpha particles. They obtained a radioactive phosphor nuclide (^{30}P). The irradiation of boron resulted in a radioactive nitrogen nuclide [1]. Soon after their discovery of synthetic radionuclides, first applications were published (e.g., studies of metabolism with radioactive tracers and the use of radionuclides in diagnosis and therapy started). After World War II, the nuclear pharmacy industry started in USA. In the 1960s, a group of scientists founded the "radiological chemistry" at the University of Basel. Their focus was on the synthesis and applications of

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protein-bound radionuclides. They were the first to develop DOTATOC[1]-bound ^{111}In and ^{90}Y and apply them with success against tumours.

1.1. Application of radiopharmaceuticals

i. Today, a broad range of radiopharmaceuticals are used for diagnostics and the fight against cancer and other diseases. Radionuclides are either used in their pure form (e.g., $^{223}RaCl_2$) or bound on a carrier. For diagnosis, they are used in scintigraphy, positron emission tomography (PET), single photon emission computed tomography (SPECT) and others. Specific radionuclides that are in use include the following:^{99m}Tc (technetium-99m), which is used for the scintigraphy of the skeleton, heart, lung, brain, liver, kidney, marrow etc. It is also used in techniques, such as myocardia- and parotid scintigraphy.

ii. For the detection of neuroendocrine tumours, ^{111}In (indium-111) and ^{68}Ga (gallium-68) can be used.

iii. For the diagnosis of prostate tumours, brain tumours and metastases in bones, ^{18}F (fluorine-18) is commonly used as the radionuclide in scintigraphy.

Specific radionuclides used in therapeutical applications include the following:

^{131}I (iodine-131), a thyreostatica which is administered in the form of swallowable ^{131}I–capsules, is used to treat diseases of the thyrea (hyperthyroidism and Basedow's disease). In Switzerland, 200 MBq may be applied for ambulatory treated patients. For higher activities, patients have to stay at specially isolated rooms, until the required dose becomes less than 5 μSv/h at a distance of 1 m. ^{131}I is also applied bound with MIBG (metaiodobenzyl-guanidine).

i. ^{90}Y (yttrium-90) and ^{177}Lu (lutetium-177) are applied successfully against neuroendocrine tumours. These radionuclides are bound to DOTATOC, an octapeptide, which has a similar structure as the hormone somatostatin. ^{90}Y is applied in selective, internal radiotherapy (SIRT) bound on spherical polymer particles.

ii. ^{90}Y–Zevalin is used against lymphoma.

iii. Other radionuclides, such as ^{90}Y, ^{188}Re (rhenium-188), ^{169}Er (erbium-169), are applied for radiation synovectomy[2].

iv. A recently available radionuclide is ^{223}Ra (radium-223). In the form of radium dichloride, Xofigo, it can be used against prostate tumours that have spread to the skeleton. In Basel, it has been administered since 2013.

1.2. Use of radiopharmaceuticals in Basel and Switzerland

The Federal Office for Public Health, Radioprotection Section, publishes annually the consumption of radionuclides and radiopharmaceuticals by industry and hospitals together with data from the radioactivity monitoring of the effluents of waste water treatment plants (WWTP) and other emission sources in Switzerland [2].

[1]DOTATOC: 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate coupled with an octapeptide.
[2]An application of radiopharmaceuticals to fight arthritis and arthrosis.

Today, 33 Swiss hospitals use radionuclides. Twenty-three of these hospitals discharge their contaminated waste waters to WWTPs, which are connected to the Rhine/Aar River system. **Table 1** lists the most used radionuclides in Switzerland and the percentage of their use in Basel compared to the whole Switzerland [3].

As can be observed, the Basel University Hospital is highly specialised in applications of ^{90}Y and ^{177}Lu. Only a few GBq of ^{177}Lu are applied in hospital centres at Bern, St. Gallen, Lausanne and Zurich. ^{90}Y is used in many hospitals, but in remarkably lower activities than in Basel. **Figure 1** shows consumption of radionuclides of radionuclides over the last 18 years. The consumption of ^{131}I is almost stable between 300 and 500 GBq/year. ^{90}Y shows a maximum in 2009 (2500 GBq/year); its use has been reduced since 2009 to almost 1000 GBq/year. Applications of

	Switzerland	Hospitals in Basel City	Percentage of Basel City
^{131}I ambulant appl.	25.2	0	0
^{131}I hospitalised appl.	2.593	221	9
^{186}Re	2.3	0.4	16
^{169}Er	1.0	0	0
^{90}Y	1.099	568	52
^{153}Sm	4.0	0	0
^{177}Lu	3.040	2.608	86
^{223}Ra	4.1	0.2	3

Data from [2]. appl: applications for ambulatory or hospitalised patients; LE: exemption limit.

Table 1. Applied radionuclides in Switzerland 2016, in GBq.

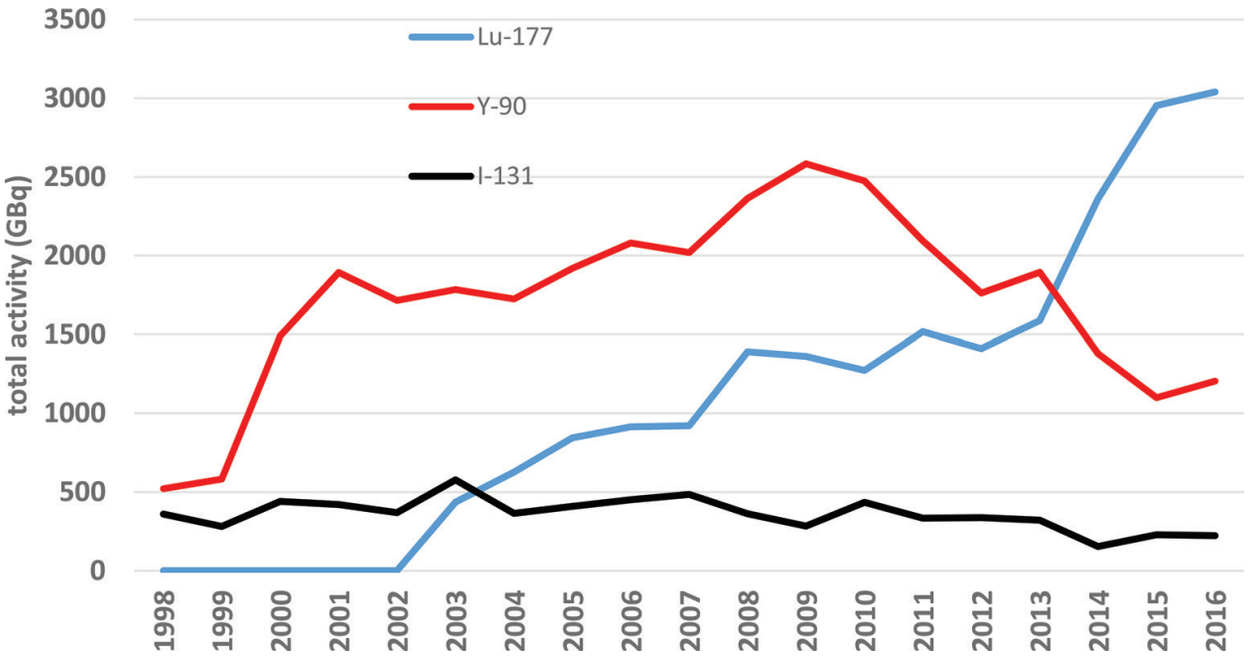


Figure 1. Yearly consumed activities of radiopharmaceuticals at Basel hospitals since 1998.

^{177}Lu started in 2002 and started to rise over the years to 3000 GBq/year in 2016. In that year, the hospitals of Basel used overall 4.5 TBq activity. In Basel, more than 8000 persons per year were treated with radiopharmaceuticals for diagnosis and therapies against cancer and for other applications [4].

Waste water and other wastes of patients are collected in special stainless steel tanks, while the patients are hospitalised. Due to their short half-lives, the activity of the radionuclides declines very fast. Cooling time in the storage tanks is several weeks. Once a week, tanks are discharged into the waste net when the activity of the radionuclides falls below a specified activity level. This level is fixed in such a way that the limit values for rivers cannot be reached.

2. Legislation in Switzerland

Since 1991, in Switzerland, radionuclides are regulated by the Radioprotection Act (from 22 March 1991) [5] and the Radioprotection Ordinance (RPO) (from 22 June 1994) [6]. In Annex

Radionuclide	Half-life	decay	LE Bq/kg	Activity limit (Bq/kg)[1]	Activity load per month[2] (kBq)	Limit value for surface water[3] (Bq/kg)
^{18}F	109.8 m	β^+	200.000	2.000	20.000	4.000
^{44}Sc	3.93 h	β^+, γ	30.000	300	3.000	600
^{67}Ga	78.3 h	γ	50.000	500	5.000	1.000
^{68}Ga	68 m	β^+, γ	100.000	1.000	10.000	2.000
^{85}Sr	65 d	γ	20.000	200	2.000	400
^{90}Y	64 h	β^-	4.000	40	400	80
^{99m}Tc	60.2 h	γ	500.000	5'000	50.000	10.000
^{110m}Ag	249.9 d	β^-, γ	4.000	40	400	80
^{111}In	2.83 d	γ	30.000	300	3.000	600
^{131}I	8.04 d	β^-, γ	500	5	50	10
^{133}I	20.8 h	β^-, γ	2.000	20	200	40
^{153}Sm	46.7 h	β^-, γ	10.000	100	1.000	200
^{169}Er	9.3 d	β^-, γ	30.000	300	3.000	600
^{177}Lu	6.71 d	β^-, γ	20.000	200	2.000	400
^{177m}Lu	160.9 d	β^-, γ	6.000	60	600	120
^{186}Re	90.6 h	β^-, γ	7.000	70	700	140
^{188}Re	17.0 h	β^-, γ	7.000	70	700	140
^{223}Ra	11.4	α, γ	100	1	10	2

Source: Swiss Radioprotection Ordinance [6].

[1]About 1% of the exemption limit (LE).

[2]About 100 fold of LE for waste water.

[3]About 1/50 of LE for rivers and lakes.

Table 2. Limits for radionuclides used in medicine.

2 of the RPO, solid and liquid wastes may not reach activities higher than a permitted limit (EL[3]). For higher activities, the material has to be treated as "radioactive" according to the Ordinance. For waste water, the activity limit is set to 1% of the EL of each radionuclide. Mixtures of radionuclides are considered as follows (summation rule):

$$a_1/EL_1 + a_2/EL_2 + \ldots + A_n/EL_n < 0.01 \quad (1)$$

with axe: activity of radionuclide x, EL_x: exemption limit of radionuclide x.

The sum in Eq. (1) has to be below 0.01; then, the activity of the waste water is under the limit value. Further, a specific discharge limit per month for treated and untreated waste water has to be fulfilled. A violation is present when both limits are overridden. The aim of these restrictions is to guarantee a limit value of 1/50 of EL for each radionuclide in rivers and lakes (according to Art.102. Par. 2 of the RPO). The Federal Office of Public Health uses the same limits for treated waste waters that are discharged to rivers and lakes (**Table 2**).

3. The waste treatment in Basel City

3.1. The waste water treatment: The municipal WWTP of Basel

The whole waste water of the city of Basel is treated at the *WWTP Pro Rheno*. In this plant, the waste water (A) is treated in three main steps (see **Figure 2**): First solids are taken out by a coarse screen (3). Yearly, 370 tonnes of solid wastes are extracted in that way and burnt at the incineration station *KVA Basel* (a) [7]. Then, the waste water runs through degritters (4). The filtered off solid materials are disposed at a nearby landfill site (b). The pre-cleaned waste water undergoes a preliminary cleaning with a primary clarification step (5). Then follows a biological treatment of

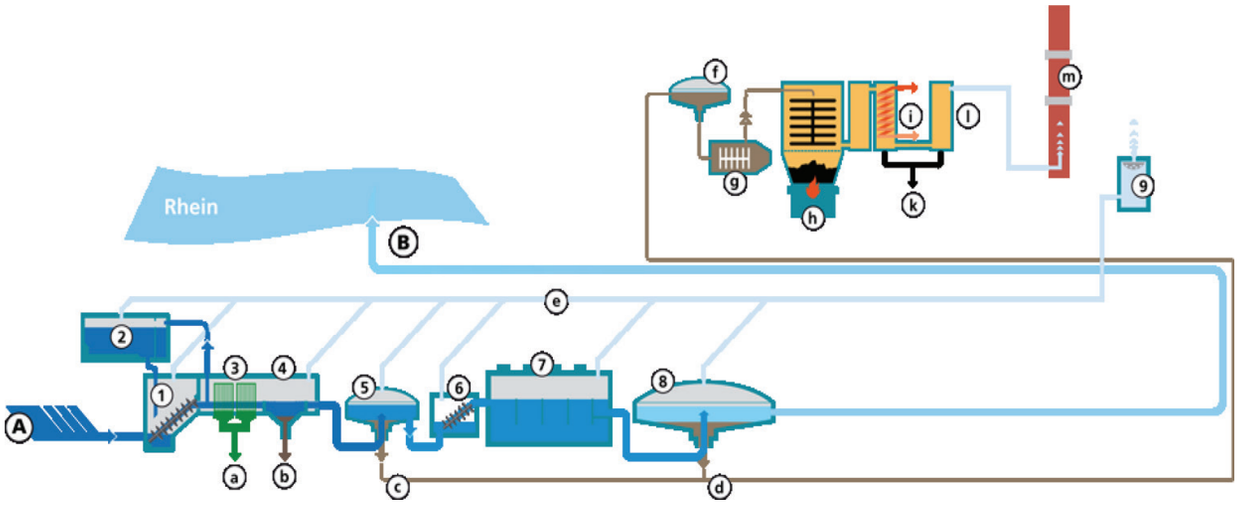


Figure 2. Scheme of the municipal WWTP of the city of Basel, *ProRheno* (source: *ProRheno* AG (with the kind permission of *ProRheno AG* [7]). Details explained in the text.

[3]EL: exemption limit. The ingestion of 1 kg of a radionuclide with a specific activity of 1 EL yields a committed effective dose of 10 μSv [6].

the waste water with activated sludge and oxygen, where most organic substances are degraded (7). The produced sewage sludge is isolated by sedimentation. At last, the waste water undergoes a secondary clarifying step (8). Over 90% of the organic carbon is degradable. Phosphates, which are the most important nutrient for algae, are eliminated by chemical precipitation. Nitrogen is not eliminated (e.g., by a nitrification/denitrification process). The so treated waste water is then released to the Rhine River below the city of Basel, near the border to Germany and France (B). The isolated sewage sludge is centrifuged (c, d). This thickened sludge is then burnt in fluidized bed furnaces (9). The ashes are disposed at a nearby landfill site (**Figure 2**).

A total of 270,000 inhabitants of Basel City and surrounding villages (several villages of France and Germany included) release their waste waters to the waste net of the city, which has a length of about 360 km. It ends at the WWTP in the north of the city. The WWTP treats 82,000 m^3 of waste water a day; 30 million m^3 waste water a year, respectively. About 40% of the waste water originates from households (170 L of water are used per person per day). Special waste waters are discharged by the hospitals and industries. Waste waters from chemical industries in Basel are treated in a separate, independent WWTP, especially built for the treatment of chemical waste waters. For more details about the WWTP, visit the website of *ProRheno* [8].

3.2. The solid waste treatment at Basel: The municipal waste incineration plant of Basel

The waste incineration plant *KVA Basel* has a capacity of 230,000 tonnes/year for burning wastes from households and permitted wastes from industries (that means 103 tonnes a day) [9]. Only 29% of the wastes are from the city of Basel. About 54% of the wastes are delivered from the state of Basel-Campaign and other Swiss states. The German Landkreis Lörrach delivers another 17%. The wastes originate from about 700,000 persons. They are burnt in two oven lines, which produce 537 GWh/year of heating energy (the value for energy consumption is 76%). The fire gases are cleaned in several steps: dust is eliminated by electrofilters. Nitrogen oxides are neutralised with ammonia. To destroy toxic dioxins and furans, special catalysts are used. The pre-cleaned air then undergoes a wet scrubbing with water. This waste water is treated on site with the incinerator's own treatment plant. The chemical quality of the cleaned water (about 190 m^3/d) satisfies the quality criteria for treated waste water and can therefore be discharged directly to the Rhine River. The ashes are cooled down with water and stored in bunkers. About 43,800 tonnes of ashes are disposed of at a nearby landfill site. For more information, see [10].

4. Materials and methods

4.1. Swiss monitoring programme

Since 1956, environmental radioactivity has been continuously monitored in Switzerland. The motivation for the programme was the occurrence of the global fallout from bomb tests. Since 1986, the Federal Office of Public Health (BAG) is authorized to survey the ionising radiation and radioactivity in the environment. It has to organise a yearly monitoring programme. Part of this programme is the survey of the consumption of radiopharmaceuticals from hospitals and their discharge to the environment. The basic data are delivered by the hospitals (yearly

consumption of radiopharmaceuticals and the discharge of total activity in ^{131}I–equivalents to the rivers). Several Swiss WWTPs and waste incineration plants, which are in the catchment area of hospitals, chemical radionuclide producing industries and watch industries are monitored continuously. Yearly, the BAG publishes the data [2].

4.2. Sampling

4.2.1. Water samples

For balancing radionuclides in waste water, a permanent sampling is necessary. This is only possible by using automatic water samplers. At the WWTP *ProRheno*, several samplers continuously collect water samples at several locations. Most important is the sampling of the untreated, raw waste water, before it enters the WWTP, and the treated waste water, before it is discharged to the Rhine River. The sampling rate of the samplers is fixed by the continuously recorded water flow rate. At higher rates, more water is sampled. Other samplers are necessary to control and optimise the waste water treatment processes inside the WWTP. At the waste incineration of Basel *KVA Basel*, the treated waste water from wet scrubbing of the flue gases is sampled permanently over 24 hours a day. This sampling is not operated by the water flow rate. The monitoring programmes of WWTP *ProRheno* and the waste incineration plant *KVA Basel* are based on water samples, which are representative for the whole time period (24 hours or a week). The water samples are delivered once a week to the State Laboratory of Basel City. The cleaned waste water from WWTP *ProRheno* consists of a 1 L sample, which was sampled over a whole week. The cleaned waste water contains a small amount of insoluble material (20–40 mg/L). The water samples from *KVA Basel* are daily samples, which are mixed in the laboratory to get a week sample. These samples are free from insoluble materials. The water samples are filled into 1 L Marinelli beakers for gamma ray spectrometry.

4.2.2. Solid samples

For the balancing experiments at WWTP *ProRheno*, sewage sludge and ash samples have to be analysed. These samples are filled into cylindrical beakers of 500 mL volume or, where possible, into 1 L Marinelli beakers. Sewer samples (sewer sludge or sewer slime) are collected in the waste net of the city of Basel. The sewer is filled into petri dishes (6.5 cm Ø). Considering the short half-lives of the radionuclides of interest (e.g., ^{99m}Tc), the gamma ray counting has to be started immediately after having received the samples. All solid samples were counted without drying to take into account the short half-life of some radionuclides and the volatility of certain radionuclides (e.g., ^{131}I). Afterwards, all solid samples were dried at 110°C. All activities were calculated back to a dry-weight basis.

In 1980–2012, suspended matter of the Rhine River was collected in 50 L barrels in three months periods upstream of the city of Basel. The suspended matter was then co-precipitated with potassium zinc hexacyanoferrate-(II), clarified using Carrez solutions, dried and analysed with gamma ray spectrometry. After 2002, the suspended matter from Rhine River was sampled once a month at the *International Monitoring Station (Rüs) at Weil am Rhein*, Germany, near Basel. To filter off the suspended matter from the water, a centrifuge was continuously loaded with Rhine water. This water was a mixture of the Rhine water over the whole profile of the river. Depending on the water flow, the sampling time took one to several days.

The suspended matter was freeze-dried in the laboratory of the Office for Environmental Protection and Energy Basel City. The dried material was ground and filled into petri dishes (6.5 cm Ø and 4 cm height, volume: 77 mL) for gamma ray counting [11]. The counting time for suspended matter was 2–3 days.

4.3. Gamma ray spectrometry

The water samples are filled without filtration into 1 L Marinelli beakers and counted for 24 hours with high resolution gamma ray spectrometers (Ge detectors). Different Ge detectors from Ortec and Canberra are used at the State Laboratory of Basel City (25–50% relative efficiencies, all detectors are of coaxial type). For recording and analysis of the pulse high spectra, Maestro Dspec jr. from Ortec combined with Interwinner-software from ITEC is used. Regularly, all detectors are recalibrated with calibration sources from Czech Metrology Institute at Prague (mixtures of ^{241}Am and ^{152}Eu). All spectra are background subtracted. For water samples, no density correction is necessary because of the same density of the calibration sources (d = 1.0). Solid samples are corrected according to their density and composition. No summation corrections are done. Experimental details are described in [12]. For the identification and quantification of the most important radionuclides, the following emission lines (with emission probability in %) are used: ^{131}I: 284.3 keV (6.2), 364.5 keV (81.6) and 637.0 keV (7.1), ^{177}Lu: 112.95 keV (6.4) and 208.4 keV (11.0), ^{177m}Lu: 208.4 keV (62.2), 228.4 keV (37.8) and 378.5 keV (28.3), ^{111}In: 171.3 keV (90.2) and 245.4 keV (94.0), ^{186}Re: 63.0 keV (1.9) and 137.2 keV (9.4), ^{99m}Tc: 140.5 keV (89.0), ^{153}Sm: 69.7 keV (5.3) and 103.2 keV (28.3), ^{67}Ga: 93.3 keV (39.0), 184.6 keV (21.3), 300.2 keV (16.8) and 393.5 keV (4.6), ^{110m}Ag: 657.8 keV (94.4), 763.9 keV (22.5), 884.7 keV (72.2) and 937.5 keV (34.3) and ^{223}Ra: 81.1 keV (14.9), 83.8 keV (24.5) and 94.9 keV (8.5).

4.4. Beta ray spectrometry

Radionuclides, such as ^{90}Y, are pure beta-emitters. Therefore, pre-treatment is necessary before a sample can be analysed with beta-spectrometry. Hospitals usually convert these activities into ^{131}I–equivalent values. For a specific analysis of ^{90}Y, samples of 50–100 mL are prepared as follows. First, the ^{90}Y is co-precipitated with oxalic acid in the presence of a non-active Y-carrier (Y_3Cl). The precipitates are isolated and ashed at 850°C. They are then dissolved in HCl and precipitated again at a pH of 5. ^{40}K and most of the alkaline earth metals are isolated in this step. The ^{90}Y is then precipitated in a strong alkaline medium as Y_2Ox_3. The decay of ^{90}Y in these pure beta-sources is measured in 10 consecutive runs of 400 minutes each by means of a gas proportional counter (LB 4000 from Canberra). Beta-background and relative efficiencies of the beta-detectors (30–40%) have to be considered. The beta-efficiencies of the detectors are regularly tested using own ^{90}Sr/^{90}Y oxalate sources [13].

5. Results

5.1. The waste water monitoring at WWTP *ProRheno*

In 1997, a monitoring programme for cleaned waste water was started in Basel. This treated waste water is analysed on a weekly basis for ^{3}H and gamma-active radiopharmaceuticals. In

1998, higher activities for ^{131}I near the limit value were noted. The activity limit of 5 Bq/L was not crossed, but the discharge activity of 12 GBq exceeded by far the limit of 50 kBq for ^{131}I. In that year, four violations were noted. Three of the four violations were due to discharges of waste water from the University Hospital. The reasons for the violations were diverse: overfilling of waste water storage tanks, emptying of a wrong tank and technical problems with tank filling indication devices at the University Hospital. The State Laboratory Basel City started disciplinary proceedings against the responsible personnel [14]. The fourth violation was caused by the waste incineration plant of *KVA Basel*. At that time, the WWT at *KVA Basel* was stopped for revision works and the uncleaned waste water of the wet scrubbing was redirected for treatment to the WWTP *ProRheno*. This fourth violation demonstrated that radioactive contaminated wastes are also disposed of at *KVA Basel*.

Since 1999, no more violations of the limit values (e.g., 5 Bq/L for ^{131}I, see **Table 2**) have been noted. In 2005, first activities of ^{111}In were detected in the treated waste water of the city. In 2003, the University Hospital of Basel started applications of ^{177}Lu, which were growing over the years. This can clearly be seen in **Figure 3**. Besides ^{177}Lu, ^{131}I and ^{111}In, other radionuclides are detected sporadically, such as ^{188}Re, ^{67}Ga, ^{153}Sm and ^{99m}Tc (**Table 3**). Radionuclides with very short half-lives, such as ^{99m}Tc or ^{18}F, normally are not detected in the waste water [15].

At the hospitals, only a part of the applied radioactivity is released to the waste net. A non negligible amount of radioactive wastes is released at homes. Here, all treated patients remain emission sources for the following weeks. In Section 5.3, we present measurements in the waste net that clearly show this fact. Most of the patients treated at the local hospitals live in the vicinity of Basel. Their wastes are also treated at *ProRheno* and at *KVA Basel*.

5.2. Waste water monitoring at the incineration plant *KVA Basel*

Originally, the monitoring programme of cleaned waste water from wet scrubbing of flue gases was focused on the survey of the beta-nuclide ^{3}H (tritium). From time to time, violations of the limits occurred, but no polluter could be identified. In 2001, the monitoring was extended for the survey of radiopharmaceuticals. To date, ^{131}I is the only radionuclide that caused several violations of the limit values. In April 2008, a violation of both limits for ^{131}I was noted. The activity of the effluent was 30 Bq/L and the discharge was calculated to be 15 MBq/month; both values were clearly over the limit [16]. In May 2014, a further violation of ^{131}I was noted. The mean activity then was 24 Bq/L (limit value: 5 Bq/L) and the discharge was 6.4 MBq per month (limit: 50 kBq/month) [17]. In both cases, no specific polluter could be found. We suppose that the ^{131}I–containing wastes were delivered by the local hospitals. Other radiopharmaceuticals were only detected sporadically (**Figure 4**, **Table 4**). Without specific indications, it is almost impossible to find a polluter. *KVA Basel* has to deal with over 500 waste deliveries per day. In 2018, according to the revised Radioprotection Ordinance, waste incineration plants are obliged to install a gamma-detecting portal where all wastes are monitored for gamma rays when delivered at the plant. Overall, the detected activities in the effluent of the waste incineration plant *KVA Basel* were of minor concern due to the low discharge volume of about 500 m^3/day of waste water to Rhine River.

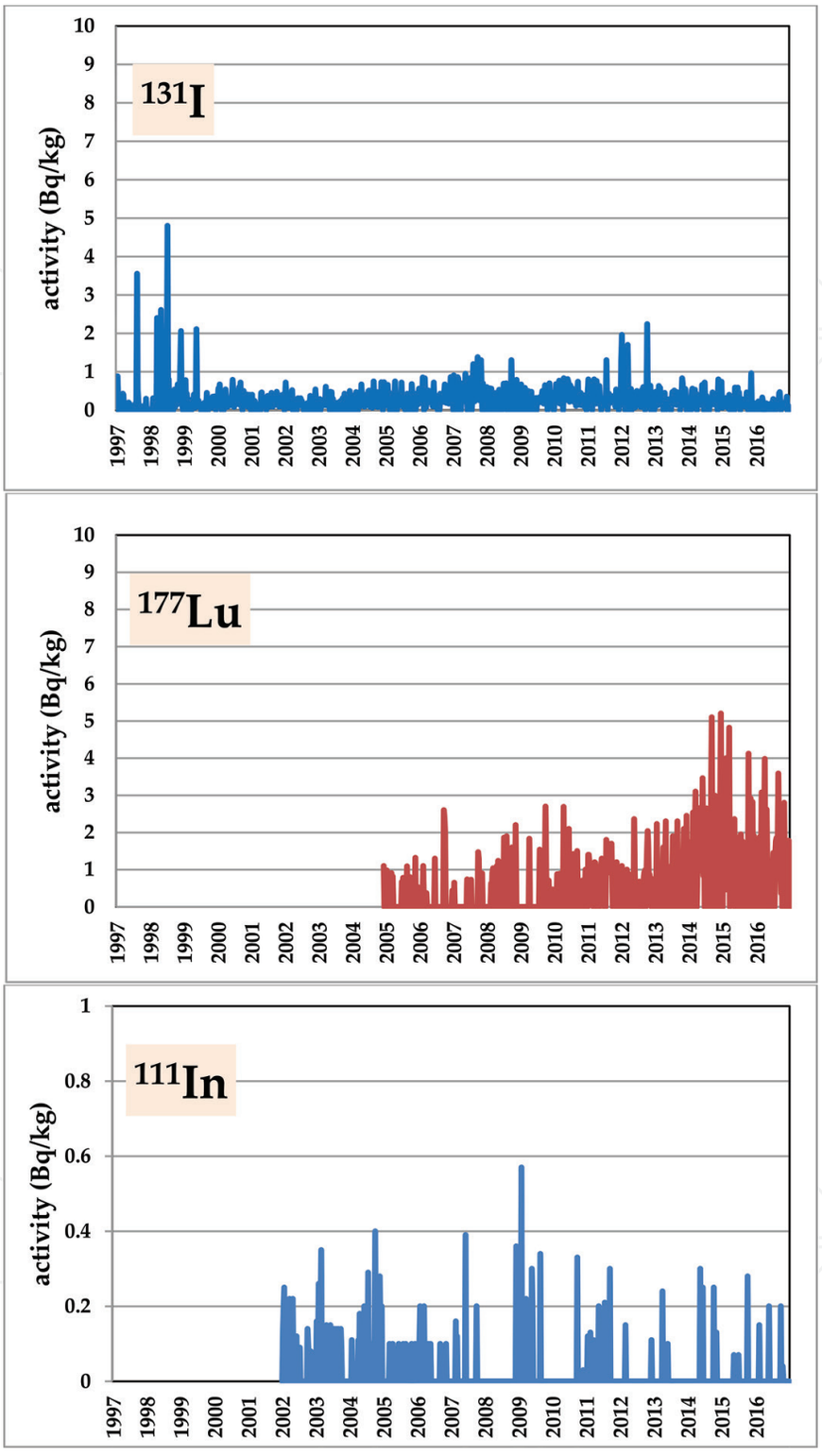


Figure 3. Monitoring of the treated waste water of the WWTP *ProRheno* since 1997.

5.3. Detection of radioactive contamination in the waste net

The investigation of waste water by taking random samples in a waste net does not lead to representative results. This can only be achieved by using automatic water samplers. The installation and use of such samplers in the waste net is a difficult task. Therefore, it is only

Radionuclide	Activity range	Number of positive samples	Mean ± s.d.
^{131}I	<0.1–4.8	1015	0.3 ± 0.3
^{177}Lu	<0.5–5.2	605	0.6 ± 0.9
^{111}In	<0.1–0.6	97	0.2 ± 0.1
^{67}Ga	<0.3–8.4	48	0.5 ± 1.5
^{186}Re	<0.5–23	7	4.4 ± 7.8
^{153}Sm	<0.3–0.72	3	0.5 ± 0.2

All values in Bq/kg. s.d.: standard deviation.

Table 3. Overview of the waste water monitoring at WWTP *ProRheno* from 1999 to 2016.

realised for the monitoring of specific emissions sources, which are under suspicion to violate the law. Another approach is the monitoring of sewer sludge or sewer slime. Sewer sludge is called a biofilm that grows on the interface of the waste water and the concrete of the waste net. Algae, bacteria and fungi build this biofilm, which acts as an excellent sorbent surface for many contaminants, such as heavy metals, polycyclic aromatic hydrocarbons, organochlorine compounds etc. [18, 19]. Radionuclides too, are adsorbed on this biofilms. The substances stay adsorbed until they are washed away from the concrete walls together with the sewer sludge or, in the case of the radionuclides, they have disintegrated. Therefore, sewer sludge can serve as a memory of the load of the run through waste water (**Figure 5**) [20].

Table 5 shows impressively the discrepancy between random sampling of waste water and the sampling of sewer sludge, which memorizes contamination of the waste system for a certain time. Only at two positions, site B and E, were traces of ^{131}I and ^{177}Lu detectable in the waste water on the sampling day, whereas ^{131}I and ^{177}Lu were detectable in the sewer sludge of several sites above and below the emission source. These activities are the result from past discharges of radioactive waste water. The fact that even above the emission source, radionuclides were detected shows that patients at home are also emission sources for a certain time [21]. The sampling of sewer sludge illustrates the contamination of the waste net over a certain time period (some days, depending on the half-life of the analysed radionuclide); but it is not representative enough for the calculation of loads or the release of radionuclides in the waste net. Sewer slime analyses can be very useful to look for specific emission sources in a waste net [20].

5.4. Balance of radiopharmaceuticals at WWTPs

In 2014, Rumpel analysed influents and effluents of the WWTP *ProRheno* for two time periods of a month [20]. During this time, 24 hour samples from the untreated waste water and the cleaned waste water were collected and analysed with gamma ray spectrometry. Samples were collected with automatic samplers at the entrance of the WWTP (untreated waste water) and before the cleaned waste water was discharged to the Rhine River (cleaned waste water). The accumulated sewage sludge was collected and analysed daily before it was burnt. The ashes were collected in containers for transportation to the landfill site. Samples were taken from each container (four samples a month). The activities of the discharges were calculated

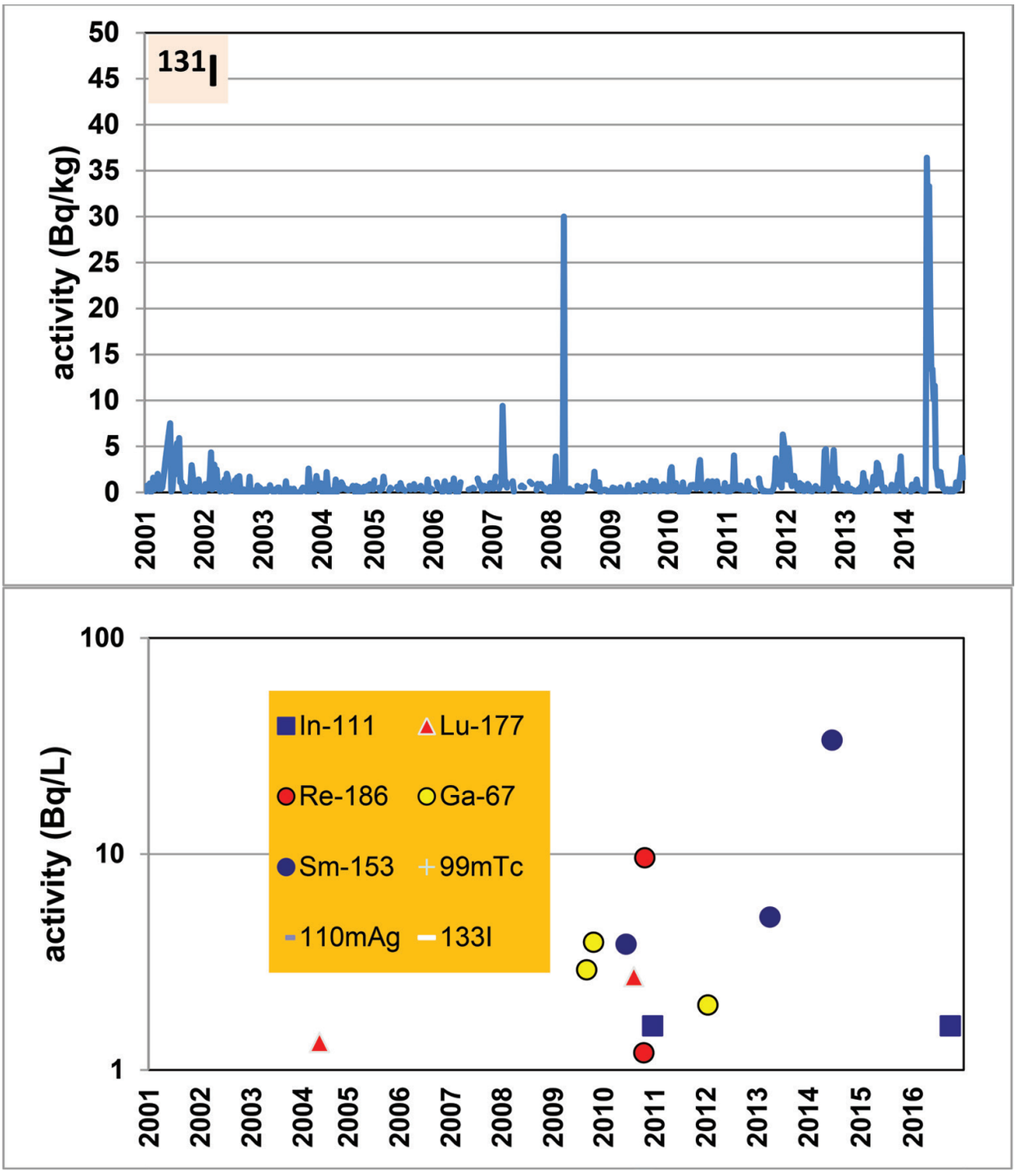


Figure 4. Monitoring of the cleaned effluent from wet scrubbing at the waste incineration plant *KVA Basel* since 2001.

by multiplying the activities with the daily waste water and sewage sludge discharges. **Table 6** shows clearly the bad elimination of ^{131}I. Only 14% are eliminated by the WWT process. Almost 90% of the ^{131}I is dissolved in the water, passes the WWT and is discharged to Rhine River. The 14%, which are taken out of the waste water are lost by the burning of the sewage sludge (the ashes are free of ^{131}I). On the other hand, 42% of ^{177}Lu was eliminated in the WWT. This is not surprising. It corresponds to the elimination rate of heavy metals. The eliminated part

Radionuclide	Activity range	Number of positive samples	Mean ± s.d.
^{131}I	<0.1–36	708	1.0 ± 2.8
^{111}In	<0.1–1.6	7	0.7 ± 0.6
^{177}Lu	<0.5–2.7	6	1.0 ± 0.8
^{153}Sm	<0.3–34	4	11 ± 13
^{110m}Ag	<0.1–0.14	3	0.1 ± 0.03
^{186}Re	<0.5–9.6	2	5.4 ± 4.2

All values in Bq/kg. s.d.: standard deviation.

Table 4. Overview of the waste water monitoring at the waste incineration *KVA Basel* from 2001 to 2016.



Figure 5. Sewer sludge (left) and the sampling of it in the waste net (right).

Sample date: 21.10.2014	Waste water (Bq/L)		Sewer sludge (Bq/kg d.w.)	
Radionuclide analysed	^{131}I	^{177}Lu	^{131}I	^{177}Lu
Above University Hospital	<0.1	<0.3	<1	32
Site A	1.2	<0.3	564	<20
Site B				
Below University Hospital	<0.1	<0.4	<1	282
Site C	<0.1	<0.4	<1	<4
Site D	<0.1	4	115	9.570
Site E				

Table 5. Comparison of waste water and sewer sludge at the same places in the waste net above and below the emission source (university hospital Basel).

Radionuclide MBq/m³	Untreated waste water	Treated waste water	Sewage sludge	Ash from sewage sludge	Elimination rate %
^{131}I	812	701	52	0.2	~14
^{177}Lu	5.500	3.207	1.628	856	~42

Table 6. Balance of radionuclides in the WWTP *ProRheno*.

remains in the ashes from the burning of the sewage sludge, where it disintegrates according to its half-life of 6.7 days [14].

For ^{131}I, similar observations were reported by Rose. The investigations of six WWTP's in USA showed that most of the ^{131}I passed the WWTP's with the treated waste water [22]. In Finland, most of the ^{131}I (up to 94 Bq/L) was found in the water phase, whereas, in the sewage sludge, ^{51}Cr, ^{111}In, $^{201/202}$Tl and other radionuclides were found. Also, sporadically other radionuclides from nuclear power stations were detectable, such as ^{58}Co, ^{60}Co, ^{110m}Ag, or ^{124}Sb [23]. In Kurume City, Japan, four hospitals discharge their waste waters to the local WWTP. The main activities of radiopharmaceuticals were found in the waste water. About 1–4% of the applied activities of ^{99m}Tc, ^{123}I, ^{67}Ga and ^{201}Tl were detected in the WWTP. ^{131}I was only found in the sewage sludge [24]. This is confirmed by others. Investigations in Canada, Italy, France and Sweden showed that the main activities were in the sewage sludge [25–28]. About 1–250 Bq/kg of ^{201}Tl, ^{99m}Tc, ^{131}I were measured in the sewage sludge of French WWTPs [29]. In the WWTP of Valladolid, Spain, 75–1238 Bq/kg d.w. of ^{131}I was found in sewage sludge [30]. Hormann and Fischer investigated the WWTP of Bremen-Seehausen in Germany. They found an overall elimination rate of 50–75% for ^{131}I. Most of the ^{131}I was bound to the sewage sludge. They concluded that ^{131}I was bound to the return sludge and therefore a longer residence time of the waste water resulted. About 30% of the input was organically bound. After the cleaning processes, over 90% was organically bound and therefore could be eliminated from the waste water cycle [31].

Such discrepancies of the fate of radiopharmaceuticals in WWTPs can be explained as follows. The waste water treatment processes, which can vary from WWTP to WWTP, also have influence on the behaviour of the radiopharmaceuticals during the waste water cleaning process. How radiopharmaceuticals are administered (inorganic unbound, or organically bound) is crucial for the elimination behaviour of radiopharmaceuticals in a WWTP.

5.5. Monitoring of suspended matter of Rhine River at Basel

Since 1982, the suspended matter of Rhine River is collected periodically and analysed for radio contamination. This is part of the monitoring programmes of the BAG for the survey of Swiss Nuclear Power Plants (NPP) and WWTPs. From 1982 to 2002, suspended matter was collected in three month periods upstream of the city of Basel. Since 2002, suspended matter was collected monthly by means of a centrifuge at the river monitoring station Weil am Rhein downstream of the city.

In 1982 and 1986, high activities of ^{131}I were found in suspended matter of Rhine River. In 1982, the NPP of Mühleberg discharged radioactive water to Aar River, which is connected

to Rhine River [32]. As a consequence, in 1982, the suspended matter contained 14.8 Bq/kg of ^{131}I and 88 Bq/kg of ^{137}Cs. Additionally, some activation products typically found in emissions from NPPs, such as ^{60}Co (85 Bq/kg) and ^{54}Mn (14.8 Bq/kg), could be detected [33].

In 1986, 2,580 ± 1,680 Bq/kg of ^{131}I were found in the suspended matter of Rhine River, together with 1,720 ± 930 Bq/kg of ^{134}Cs and 3,500 ± 1,740 Bq/kg of ^{137}Cs. These high contaminations originated from the fallout of the reactor fire at Chernobyl in that year [34]. Only after 2006, a regular monitoring for short-lived radionuclides from pharmaceutical use was realised. When short-lived radionuclides have to be monitored, it is important to analyse the collected suspended matter as soon as possible. Before 2006, samples were collected over a year and analysed at the end of the year. Therefore, the short-lived radionuclides were already disintegrated. In suspended matter, the radionuclides ^{131}I and ^{177}Lu are prominent. Since 2009, they are detectable in almost every sample and reflect mainly the local emissions from the WWTP *ProRheno* (**Figure 6, Table 7**). In 2015 and 2016, the radionuclide ^{177m}Lu was found. We suppose

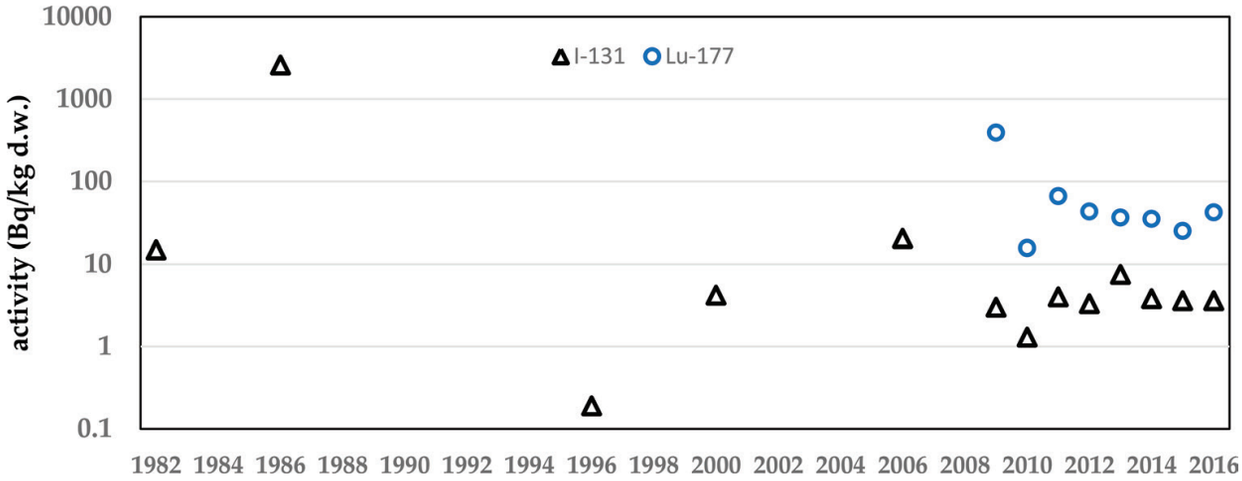


Figure 6. Results from monitoring of suspended matter of Rhine River. All annual average values in Bq/kg dry weight.

Radionuclide	Activity range	Number of positive samples	Mean ± s.d.
^{67}Ga	0–59	7	30 ± 21
^{85}Sr	0–83	21	25 ± 22
^{131}I	0–258	94	5.8 ± 5.6
^{153}Sm	0–183	6	105 ± 65
^{169}Er	0–1,550	1	1,550
^{177}Lu	0–390	92	82 ± 117
^{177m}Lu	0–3	4	3.0 ± 0.1
^{186}Re	0–1,034	1	1,934
^{223}Ra	0–33	8	16 ± 8.2

All values in Bq/kg dry weight.

Table 7. Development of yearly mean activities in suspended matter from 1982 to 2016.

that this nuclide was applied instead of ^{177}Lu, when there were supply difficulties for ^{177}Lu. ^{177m}Lu has a long half-life of 161 days and should therefore not be regularly used for pharmaceutical applications. It remains much longer in the environment, where it can cause damage. Other radionuclides, such as ^{67}Ga, ^{153}Sm, or ^{85}Sr, were found sporadically. Here, different sources (hospitals), connected to the Rhine River catchment, are possible. Since 2015, ^{223}Ra can regularly be found in the suspended matter. Overall, over these years, there were observed no violation of the immission limits for rivers according to the Radioprotection Ordinance. These limits are defined for activities of the river water. In suspended matter, these radionuclides are highly enriched by the collection process of the suspended matter. Supposing a total adsorption of the radionuclides to the suspended particles, the enrichment factor is 1000 and more. Nevertheless, there is only poor knowledge about the low dose effects of radiation on aquatic organisms.

6. Conclusion

Our monitoring programmes for radiopharmaceuticals show that radioactivity is permanently released to the environment despite rigorous treatment and cleaning of the radioactive wastes from hospitals. The limits for radionuclides in rivers and lakes are observed. Nevertheless, little is known about the low dose effects of radiation on aquatic organisms, which may occur well below these limits. Overall, the permanent monitoring of radionuclides in the environment of cities remains an important task.

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