

Anthropogenic ^{129}I concentration and $^{129}\text{I}/^{127}\text{I}$ ratio in rainwater from Seville (Spain) in the period 2005–2008 as affected by airborne releases from Sellafield and La Hague facilities

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A B S T R A C T

^{129}I is a very long-lived radionuclide ($T_{1/2} = 15.7 \times 10^6$ years) that is present in the environment both because of natural and anthropogenic sources. In this work ^{129}I concentration and $^{129}\text{I}/^{127}\text{I}$ ratio have been determined in rainwater samples collected at Seville (south-western Spain) during the period 2005–2008.

Typical ^{129}I concentration range from $(0.26\text{--}8.86) \times 10^8$ atoms/L, while ^{129}I deposition are normally in the order of $10^7\text{--}10^8$ atoms/m²d. Variability in the isotopic ratio $^{129}\text{I}/^{127}\text{I}$ indicates a range of $(0.17\text{--}8.71) \times 10^{-8}$.

Temporal evolution of the ^{129}I deposition seem to be related with the history of the ^{129}I gaseous releases from the European reprocessing facilities at Sellafield and La Hague. The results obtained in this work are lower than the reported in previous works for the same location during the period 1996–1999, probably due to the reduction of the total gaseous ^{129}I releases emitted by Sellafield and La Hague. The study of the dependence of the ^{129}I deposition with some atmospheric parameters suggests that deposition seems to be more important in wet than in dry periods and that also depends in the wind direction, being more important for winds with north to south component. The agreement between the ^{129}I concentration and the $^{129}\text{I}/^{127}\text{I}$ ratio suggest that the gaseous ^{129}I emitted by the reprocessing plants has enough time to equilibrate with the ^{127}I present in the atmosphere before arriving to southern Spain, probably due to the distance between Seville and these reprocessing plants.

Keywords:

AMS
ICP-MS
 ^{129}I
 ^{127}I
Rainwater
Reprocessing plants

1. Introduction

Iodine is an essential micronutrient for animals and human, mainly because it is a constituent of the thyroid hormones. Excessive or deficient iodine intake results in a variety of human thyroid dysfunction and disorder, as hyperthyroidism. The determination of iodine in biological, clinical and environmental samples has received considerable attention during the last few decades as it is considered as essential trace element which plays an important role in human metabolic processes (Gélinas et al., 1998). Whilst ^{127}I

is the only stable isotope, the most hazardous iodine species are the radioactive isotopes such as ^{129}I and ^{131}I .

Because of its biophilic behaviour, iodine can enter the food chain via the air as a result of aerial emissions. This means that ^{129}I ($T_{1/2} = 15.7 \times 10^6$ years), its only long-live isotope, keeps in the food chain, compared to other short-live isotopes (e.g., ^{131}I). Iodine forms compounds (e.g., I_2 , HI, HOI, CH_3I and KI) that are both water-soluble and volatile and thus can easily enter the hydrological cycle too. Hence, ^{129}I is an ideal tracer of water masses.

Iodine-129 is a long-lived cosmogenic radionuclide for which the natural abundances have been altered in a significant way by human actions. In nature, it is produced by cosmic rays interactions with Xe in the atmosphere, by spontaneous fission of ^{238}U and ^{235}U in the lithosphere (Eisenbud and Gesell, 1997) and, to a minor extend, by neutron-induced reactions on ^{128}Te and ^{130}Te in the Earth crust (NCRP, 1983). These processes lead to typical isotopic ratios between 10^{-12} (Kilius et al., 1992) and 6×10^{-13} (Fabryka-Martin et al., 1985). The natural inventory of ^{129}I has been

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estimated to be ~230 kg, most of which resides in the deep oceans (Rao and Fehn, 1999). ^{129}I has also been produced anthropogenically during the last 60 years during fission processes associated with civil and military nuclear activities and accidents, such as Chernobyl (April 1986). An estimated 50–150 kg of ^{129}I were released to the atmosphere during the main period (1945–1964) of nuclear weapons testing (Raisbeck et al., 1995; Wagner et al., 1996) and a further ~6 kg were released due to the Chernobyl accident (Gallagher et al., 2005).

However, the most significant contribution to the mobile ^{129}I inventory in the environment comes from succeeding activities of nuclear fuel reprocessing plants and, in particular, the liquid and gaseous releases from the two major European reprocessing facilities, namely NDA's plant at Sellafield (UK) and AREVA's plant at Cap de La Hague (France), which now account for >90% of the total global releases (Aldahan et al., 2007). These releases have increased dramatically its presence in the different environmental compartments, reaching the background ratios $^{129}\text{I}/^{127}\text{I}$ values between 10^{-10} and 10^{-8} (Handl et al., 1993), with isotope ratio peaks of 10^{-7} or higher in zones directly impacted by such nuclear facilities (Yiou et al., 1994).

Airborne releases from these facilities, and the fraction of their liquid ^{129}I releases volatilised from the ocean surface have been shown to be the main source of ^{129}I deposited over Europe (Persson et al., 2007; Keogh et al., 2010). In this work we present the results

obtained for ^{129}I and $^{129}\text{I}/^{127}\text{I}$ in rainwater collected between 2005 and 2008 from Seville (Spain), continuing the research began in previous works (López-Gutiérrez et al., 2001; López-Gutiérrez et al., 2004). The objectives are to obtain information about the relative impact of the discharges of Sellafield and La Hague on the atmospheric ^{129}I at places relatively far away from them, such as southern Spain, and to compare current levels with previous ones, to confirm its decrease.

2. Sampling and radiochemical method

Rainwater samples were taken on the roof of the Faculty of Physics in Seville (37.5° N, 6° W) during years 2005 to 2008. Samples were carried out monthly (except when rainfall exceeded 25 L m^{-2} , adapting in this case the sampling frequency to rainfall), collected by a circular 1 m^2 surface funnel and stored in 25 L polyethylene bottles. If there is no rain during a certain period, the funnel is washed with double-distilled water in order to recover the particles deposited. So, it is clear that both wet and dry depositions are included in the analysis (dry period samples are marked with "*" in Table 1). Before storage, all samples are slightly acidified to prevent the formation of algae and the hydrolysis of the cations. As reported by Buraglio et al. (2000), these storage conditions do not introduce significant changes in the ^{129}I concentration.

Table 1
 ^{129}I and ^{127}I concentrations, ^{129}I deposition and $^{129}\text{I}/^{127}\text{I}$ ratios in rainwater samples collected in Seville between 2005 and 2008. Samples marked with "*" correspond to only dry deposition periods.

Sampling data		^{129}I ($\times 10^8$ atoms/L) (measured)	^{129}I ($\times 10^8$ atoms/m ² d) (calculated) ^a	^{127}I ($\mu\text{g L}^{-1}$) (measured)	$^{129}\text{I}/^{127}\text{I}$ ($\times 10^{-8}$) (calculated)	
Year	Period					
2005	January*	8.86 ± 1.39	1.48 ± 0.23	2.82 ± 0.18	6.63 ± 1.04	
	February	4.45 ± 0.28	8.33 ± 0.52	2.56 ± 0.17	3.74 ± 0.23	
	March	8.02 ± 1.24	3.72 ± 0.57	1.94 ± 0.04	8.71 ± 1.35	
	April	7.65 ± 1.16	2.02 ± 0.30	2.45 ± 0.14	6.58 ± 1.00	
	May	4.30 ± 0.30	0.66 ± 0.05	4.31 ± 0.15	2.11 ± 0.15	
	July*	0.44 ± 0.12	0.032 ± 0.008	1.86 ± 0.16	0.50 ± 0.13	
	September*	0.26 ± 0.12	0.048 ± 0.009	3.30 ± 0.16	0.17 ± 0.03	
	October	0.95 ± 0.32	5.27 ± 1.75	1.25 ± 0.04	1.61 ± 0.53	
	November	2.36 ± 0.30	1.78 ± 0.23	2.21 ± 0.17	2.25 ± 0.28	
	December	0.74 ± 0.13	0.61 ± 0.11	2.85 ± 0.16	0.54 ± 0.09	
	2006	January	3.13 ± 0.29	4.11 ± 0.51	1.77 ± 0.02	3.73 ± 0.47
		February	2.78 ± 0.27	2.41 ± 0.24	2.37 ± 0.19	2.47 ± 0.24
March		2.01 ± 0.30	1.29 ± 0.19	2.41 ± 0.14	1.76 ± 0.26	
April*		1.20 ± 0.20	0.67 ± 0.11	1.57 ± 0.08	1.62 ± 0.17	
August		2.28 ± 0.29	2.42 ± 0.31	2.69 ± 0.10	1.78 ± 0.22	
September		1.47 ± 0.20	3.15 ± 0.43	2.12 ± 0.21	1.46 ± 0.20	
October		0.65 ± 0.11	3.16 ± 0.53	1.09 ± 0.04	1.26 ± 0.21	
November		1.98 ± 0.28	4.45 ± 0.62	1.72 ± 0.08	2.43 ± 0.34	
December*		1.79 ± 0.25	0.32 ± 0.05	1.14 ± 0.02	3.33 ± 0.47	
2007		January	4.29 ± 0.49	4.83 ± 0.55	2.97 ± 0.04	3.05 ± 0.35
		February	2.04 ± 0.26	4.35 ± 0.54	1.81 ± 0.07	2.38 ± 0.30
		March	1.56 ± 0.20	0.47 ± 0.06	2.31 ± 0.13	1.42 ± 0.18
	April	1.58 ± 0.22	1.26 ± 0.17	1.18 ± 0.03	2.83 ± 0.39	
	May*	0.87 ± 0.16	0.48 ± 0.08	1.32 ± 0.06	1.40 ± 0.25	
	June*	1.50 ± 0.22	0.27 ± 0.03	2.64 ± 0.05	1.20 ± 0.18	
	July	1.74 ± 0.23	0.24 ± 0.03	3.30 ± 0.11	1.11 ± 0.14	
	October	1.14 ± 0.17	0.93 ± 0.14	1.16 ± 0.07	2.07 ± 0.32	
	November	0.73 ± 0.18	4.20 ± 1.02	2.18 ± 0.10	0.71 ± 0.17	
	2008	February	1.44 ± 0.21	6.78 ± 1.01	1.84 ± 0.08	1.64 ± 0.24
		March	0.67 ± 0.13	0.35 ± 0.07	1.77 ± 0.12	0.80 ± 0.15
April*		0.92 ± 0.16	0.38 ± 0.07	1.13 ± 0.13	1.72 ± 0.30	
May		1.61 ± 0.13	1.01 ± 0.08	2.01 ± 0.13	1.69 ± 0.14	
June*		1.21 ± 0.20	0.22 ± 0.04	1.30 ± 0.02	1.96 ± 0.33	
July		1.67 ± 0.29	0.12 ± 0.02	2.15 ± 0.25	1.64 ± 0.28	
August*		0.78 ± 0.17	0.13 ± 0.03	1.71 ± 0.03	0.96 ± 0.21	
September		0.72 ± 0.13	0.94 ± 0.17	2.06 ± 0.15	0.73 ± 0.13	
October		0.55 ± 0.10	0.98 ± 0.17	2.61 ± 0.14	0.45 ± 0.08	
November		1.12 ± 0.19	0.26 ± 0.04	1.99 ± 0.10	1.18 ± 0.21	

^a To calculate these values, precipitation data from the Spanish Meteorological Agency (AEMET, Agencia Estatal de Meteorología) were used.

Iodine was extracted from samples following the method described by Suzuki et al. (2007), adapted to water samples. A 3M Empore™ anion exchange-SR resin disk (diameter: 47 mm, thickness: 0.5 mm, composition: 90 wt. % resin particle and 10 wt. % fiberillated PTFE, surface area of resin: 350 m² g⁻¹, average particle size: 12 μm) was used. The disk was sequentially washed before the extraction to remove any contamination with 10 mL of methanol, 15 mL of double-distilled H₂O, 15 mL of 1M NaOH to convert the resin to OH⁻ form and finally 15 mL of double-distilled H₂O (three times).

All samples in a volume of 500 mL were filtered using a 0.45 μm membrane filter. In order to convert iodate (IO₃⁻) into iodide (I⁻) (IO₃⁻ is the most common form of iodine in precipitation (Aldahan et al., 2009)) 2 mL of 1 M ascorbic acid and 4 mL of 3 M HCl were added to the samples and shaken more than 1 minute with venting. 2 mg of Woodward iodine carrier (¹²⁹I/¹²⁷I ≈ 7 × 10⁻¹⁴ (Roberts et al., 1997)) were added to all samples and these solutions passed through the 3M Empore™ anion exchange resin disk for the adsorption of iodide (I⁻) at a flow rate of 220 mL min⁻¹. After the disk was washed with 20 mL of H₂O, iodide was eluted by 15 mL of 1M HNO₃. After that, AgI was precipitated by the addition of AgNO₃, dry in an oven and mixed with Nb to prepare AMS targets.

3. Experimental

3.1. Measurement of ¹²⁹I by AMS

Determination of ¹²⁹I/¹²⁷I ratios in rainwater samples was conducted at the CNA AMS (Accelerator Mass Spectrometry) tandem accelerator (1 MV Tandetron, High Voltage Engineering Europe, Holland). Details about the measurement and the facility have been previously described (Gómez-Guzmán et al., 2012; Klein et al., 2006; Klein et al., 2007), so only a short description will be given here. A beam of negative iodine ions is extracted from the AgI + Nb target using the Cs⁺ high-intensity sputter source at 35 keV. At the terminal of the tandem (1 MV) negative iodine ions are changed to positive iodine ions by the stripper (pressure at 6 × 10⁻³ mbar of argon, which corresponds to a mass thickness of about 0.15 μg cm⁻²) and they are then accelerated. Following acceleration, selected positive ions (charge state +3) are analysed by mass spectrometer. The ¹²⁷I current beam is measured in a Faraday cup, and ¹²⁹I³⁺ ions are counted in a gas ionization chamber. AMS measurements were performed relative to a standard with known ¹²⁹I/¹²⁷I isotopic ratio which was made by repeated dilutions from NIST SRM 3230 Iodine Isotopic Standard Level I. ¹²⁷I⁻ currents from samples prepared following the radiochemical procedure describe above were generally 250–350 nA before the stripping process. Transmission efficiencies, including selection of charge state +3 after the stripping process, were 9–10%, leading to high energy ¹²⁷I³⁺ currents of 75–100 nA.

The isotopic ratios obtained directly by AMS measurement of the samples (including carrier) were typically of the order of ¹²⁹I/¹²⁷I ~ 10⁻¹¹–10⁻¹². On the other hand, chemical blank to control contamination in the sample preparation process were prepared exactly in the same way as normal samples but using deionised water (18 MΩ cm). The AMS ¹²⁹I/¹²⁷I ratios for the blank were around 3–4 × 10⁻¹³ being, in the worst case, a 10% of the isotopic ¹²⁹I/¹²⁷I ratio measured in the real samples.

3.2. Measurement of ¹²⁷I by ICP-MS

Measurements of ¹²⁷I content in rainwater samples were performed at the ICP-MS Unit of the Servicio de Investigación Agraria (University of Seville, Spain). Details about the measurement and the facility have been previously described (Gómez-Guzmán et al., 2011), so only a short description will be given here. A Quadrupolar

Inductively Coupled Plasma Mass Spectrometer (Thermo X7, Thermo, Madrid, Spain) equipped with a concentric quartz nebulizer (Meinhard Associates, Golden, USA) was used for stable iodine determination. The instrument was used at normal resolution and set to detect the signal intensity at *m/z* 127. The internal standard were composited by indium and terbium diluted (50 μg L⁻¹) in deionised water (18 MΩ cm) produced in a Milli-Q apparatus. This water was used as wash solution, with a 120 s washout time between samples (extended from the normal 50 s to prevent carryover of iodine).

Samples were analysed using some recommendations provided by US EPA 200.8 methodology adapted for iodine. Five samples were made up as standards for calibration (included calibration blank) in the ranges 0.1–20 μg L⁻¹ of iodine. Various data quality tests were used during every instrumental running, such as replicate, matrix matching, memory effects and laboratory reactive blanks checking. Instrumental detection limit of stable iodine calculated as three times the standard deviation of the blank was 0.02 μg L⁻¹.

The methodology used to measure the ¹²⁷I content in rainwater samples by this technique was previously validated by measuring ¹²⁷I content in standard reference materials from the National Institute of Standards and Technology (NIST), the International Atomic Energy Agency (IAEA) and the Community Bureau of Reference (BCR) (Gómez-Guzmán et al., 2011).

4. Results

¹²⁹I and ¹²⁷I concentrations, ¹²⁹I deposition and ¹²⁹I/¹²⁷I ratios in rainwater samples collected between 2005 and 2008 in Seville are shown in Table 1. Concentrations of ¹²⁹I range from (0.26 ± 0.12) × 10⁸ atoms/L (September 2005) to (8.86 ± 1.39) × 10⁸ atoms/L (January 2005). Variability in the isotopic ratio ¹²⁹I/¹²⁷I indicates a range of (0.17–8.71) × 10⁻⁸. These values are typically one order of magnitude lower than others obtained in central and northern Europe, as shown in Table 2. For example, Reithmeier et al. (2005) measured average ¹²⁹I concentrations in rainwater from Bavaria of (4.8–50) × 10⁸ atoms/L and ¹²⁹I/¹²⁷I ratios of (15⁺⁸/₋₃) × 10⁻⁸ during 2003–2004. Also Persson et al. (2007) measured average ¹²⁹I concentrations in rainwater from Sweden of (10–57) × 10⁸ atoms/L and ¹²⁹I/¹²⁷I ratios of (8.3–18) × 10⁻⁸ during 2001–2002. (Hou et al., 2009) reported average ¹²⁹I concentrations in rainwater from Denmark to be (0.28–5.63) × 10⁹ atoms/L and ¹²⁹I/¹²⁷I ratios of (5.04–76.5) × 10⁻⁸ during 2001–2006. With respect to southern locations in Europe, Buraglio et al. (2001) reported ¹²⁹I concentrations in rainwater from Italy of (1.1–9.4) × 10⁸ atoms/L and ¹²⁹I/¹²⁷I ratios of (1.6–17) × 10⁻⁸ during 1998–1999. López-Gutiérrez et al. (2001) measured average ¹²⁹I concentrations in rainwater from Seville of (0.47–50) × 10⁸ atoms/L (with the exception of one sample with a concentration of 600 × 10⁸ atoms/L) during 1996–1997. López-Gutiérrez et al. (2004) also measured average ¹²⁹I concentrations in rainwater from Seville of (0.22–10.78) × 10⁸ atoms/L (with the exception of one sample that presented a specially high concentration of 44.10 × 10⁸ atoms/L) during 1998–1999. It can be seen that the results obtained in this work are lower than these previous results for the same location, and the reasons for such decrease in ¹²⁹I concentrations will be discussed in detail some further. The values reported here are also much lower than other measured close to nuclear reprocessing facilities such as Sellafield. Keogh et al. (2010) reported ¹²⁹I concentrations of (1.9–303) × 10⁸ atoms/L during the period 2005–2006 in Dublin City.

5. Discussion

As we have already commented in the previous section, our ¹²⁹I levels are typically in the order of 10⁷ and 10⁸ atoms/L, in good

Table 2
Concentrations of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ ratios reported in various locations in the Northern Hemisphere.

Location	Sampling period	^{129}I ($\times 10^8$ atoms/L)	$^{129}\text{I}/^{127}\text{I}$ ($\times 10^{-8}$)	Reference	
North and Central Europe	Switzerland (Zurich)	1994–97	2.2–445	–	(Schnabel et al., 2001)
	USA	1995–97	0.07–0.67	0.0002–0.003	(Moran et al., 1999)
	Sweden (Kvidinge)	2001–02	10–57	8.3–18	(Persson et al., 2007)
	Norway (Bergen)	2003	16–41	–	(Persson et al., 2007)
	Germany (Bavaria)	2003–04	4.8–50	15_{-3}^{+8}	(Reithmeier et al., 2005)
	Europe (55° to 68°)	2000–06	0.4–298	1–290	(Aldahan et al., 2009)
	Denmark	2001–06	2.8–56.3	5.04–76.5	(Hou et al., 2009)
	Ireland	2005–06	1.9–303	–	(Keogh et al., 2010)
	South Europe	Italy	1998–99	1.1–9.4	1.6–17
Spain (Seville)		1996–97	0.47–600	–	(López-Gutiérrez et al., 2001)
Spain (Seville)		1998–99	0.22–44.10	–	(López-Gutiérrez et al., 2004)
Spain (Seville)		2005–08	0.26–8.86	0.17–8.71	This work

agreement with the values reported for southern Europe (see Table 2) or even slightly lower than these. This could be due to the fact that an important part of the ^{129}I that is deposited in Central Europe has its origin in the North Sea, which is clearly affected by releases from the large nuclear fuel reprocessing plants: Sellafield (UK) and La Hague (France) (Yiou et al., 1994). This conclusion is supported by all ^{129}I data shown in Table 2 for samples collected in Central and North Europe, which maximum values are, in some cases, orders of magnitude higher than those measured in this work. Spain has been considered a background zone of ^{129}I in Europe (López-Gutiérrez et al., 2001, 2004), although it will be shown that some of the ^{129}I released by these nuclear reprocessing plants arrives to Spain depending on weather conditions.

The analysis of data from Table 1 shows that there were not statistically significant differences at 95% confidence level (CL) among the monthly values of ^{127}I concentration in rainwater in the period 2005–2008. Concerning ^{129}I concentrations in rainwater, the multiple range test with LSD method at 95% CL found statistically significant differences between January and the group from June to December, with the remaining months showing an intermediate behaviour. As it will be seen further, these differences can be linked to the high emissions to the atmosphere by the two European facilities in the period from January to May 2005. Taking into account the whole data set, monthly values of ^{127}I concentrations in rainwater followed a log-normal distribution with mean value 2.10 and standard deviation 0.74 (in units of $\mu\text{g L}^{-1}$). ^{129}I concentrations in rainwater also followed a log-normal distribution

with mean and standard deviations of 2.1 and 2.0 for the whole data set, and 1.48 and 0.98 when excluding the first five months of 2005, respectively (units are $\times 10^8$ atoms/L).

Concentrations of both iodine isotopes in rainwater were correlated with the mean monthly rainfall at 90% CL. In Fig. 1, the ^{129}I deposition and the average precipitation in the sampling periods are compared. There seems to be a clear relationship between both results, showing that the ^{129}I deposition is normally higher for high precipitation rates, as could be expected from previous results. It can also be appreciated that wet deposition is more effective than dry deposition of ^{129}I . This is shown in the fact that for all years, samples collected only due to dry deposition (inside circles in Fig. 1) usually have lower values than others collected from precipitation events. Whether the transport of ^{129}I occurs via wet or dry deposition modes is controversial but recent data on aerosols suggest that dry deposition transport can be less dominant mechanism compared to the wet one (Englund et al., 2010). Precipitation (wet deposition) would also be the major media that brings iodine to the Earth's surface, but whether all the iodine is cloud-bound or partly below cloud wash out is uncertain.

Iodine is released in its gaseous form, but tends to attach to other particles as, e.g. sulphur (Maryon et al., 1991) and its effective dry deposition velocity therefore tends to decrease with time. Dry deposition is usually assumed to take place through three atmospheric resistances: the aerodynamic resistance, the quasi-laminar layer resistance and the canopy resistance, meanwhile the washout of air pollutants by precipitation is basically dependent on the precipitation rate and type of precipitation. Thus, wet deposition

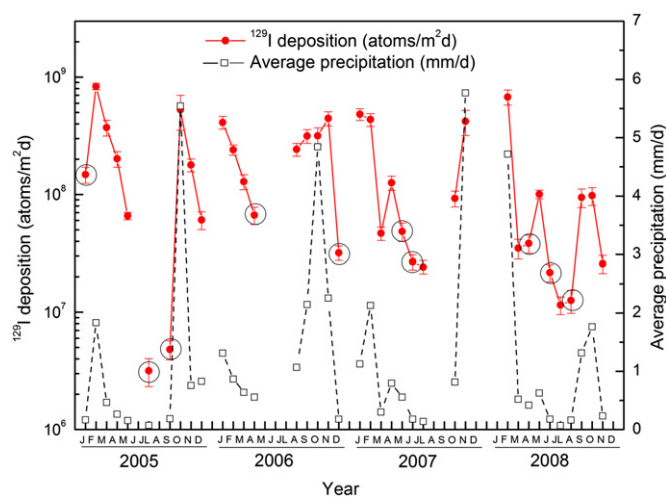


Fig. 1. Comparison between the ^{129}I deposition ($\text{atoms/m}^2\text{d}$) and the average precipitation in each sampling period (mm/d). Samples inside circles correspond to only dry deposition periods.

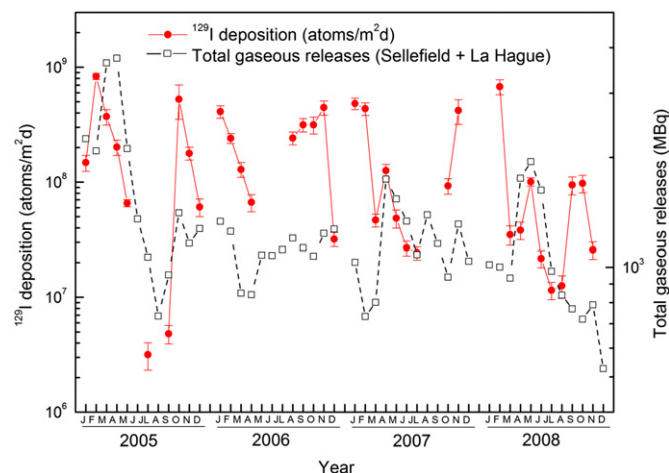


Fig. 2. Comparison between the ^{129}I deposition ($\text{atoms/m}^2\text{d}$) and the gaseous ^{129}I releases from the European reprocessing plants: Sellafield and La Hague.

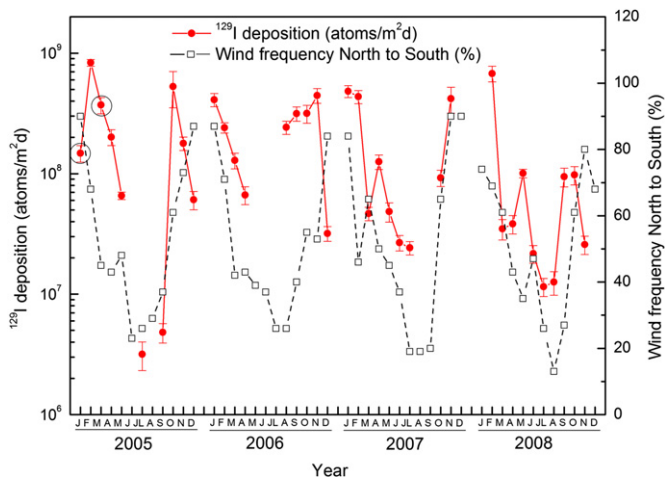


Fig. 3. Comparison between the ^{129}I deposition ($\text{atoms}/\text{m}^2\text{d}$) and the frequency with which the wind is blowing from north to south (fraction of time in %).

has been reported to be the major removal process and to be a large source for radioactive contamination (Brant et al., 2002).

As discussed before, although some of the ^{129}I released by Sellafield and La Hague facilities can arrive to Spain depending on weather conditions, our results reveal that in most of the samples ^{129}I levels were in the order of 10^7 and 10^8 atoms/L, orders of magnitude lower than found in Central and North Europe. Nevertheless, when the results are compared with the temporal evolution of the gaseous ^{129}I emitted by Sellafield and La Hague (Fig. 2) (Sellafield Webmaster, 2011; Cogema Webmaster, 2011), there it can be seen that higher ^{129}I deposition values usually coincide with strong emissions carried out by these two reprocessing facilities. Thus, an statistical analysis reveals a positive linear correlation at 99% CL between the monthly values of ^{129}I concentrations in rainwater in Seville and the monthly gaseous ^{129}I emissions from the two reprocessing plants, which explains 61.5% of the observed variability in ^{129}I concentrations. The correlation still holds at 99% CL when a shift of one month is introduced (to account for transit times), what explained 51% of the variability in ^{129}I concentrations.

Nevertheless, the previous correlations are dominated by the coincidence of high ^{129}I concentrations with the also high emissions in the interval January to May 2005 (the highest values for the whole studied period, 2005–2008). When excluding these data, the statistical correlation disappears (at 90% CL). It is worth to note that there was not statistically significant correlation between ^{127}I concentrations in rainwater and the ^{129}I releases. Another possible explanation for the observed variability in the remaining records of ^{129}I concentrations could be the influence of weather conditions over Spain during the precipitation event.

One important parameter that helps to understand the varying level of ^{129}I in the atmosphere is the origin of the air masses (López-Gutiérrez et al., 2001). In Fig. 3 it is shown the ^{129}I deposition and the mean wind frequency in which the wind is blowing with some north to south component. Specially for some periods, there seems to be correlation between these parameters. It is worth to note that when combining the time series of ^{129}I gaseous releases (Fig. 2) with the wind frequency, the highest values were found for the period January to May 2005. Other events can be identified in which winds and ^{129}I released contribute to the local enhancement of ^{129}I concentrations in rainwater from Seville. Careful scrutiny of meteorological records indicates that the prevailing winds in Seville in these periods of high ^{129}I deposition were generally speaking from the north. This would suggest the possibility that an air-mass labelled with enhanced levels of ^{129}I in gaseous form had travelled from the vicinity of Sellafield and La Hague and that ^{129}I had subsequently been deposited in Seville via precipitation. To test this hypothesis, an air parcel back-trajectory analysis was performed using the National Oceanic and Atmosphere Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) atmospheric transport/dispersion model, together with meteorological data spanning the relevant sampling periods. The model has been designed to support a wide range of simulations related to the atmospheric transport and dispersion of pollutants and hazardous materials to the Earth's surface and it is used to track and forecast the release of radioactive material, volcanic ash, wildfire smoke, etc.

The HYSPLIT backward trajectory shows an aerial view of the path(s) and air parcel(s) took in order to reach its destination at a particular sampling point and date. Detailed description of the

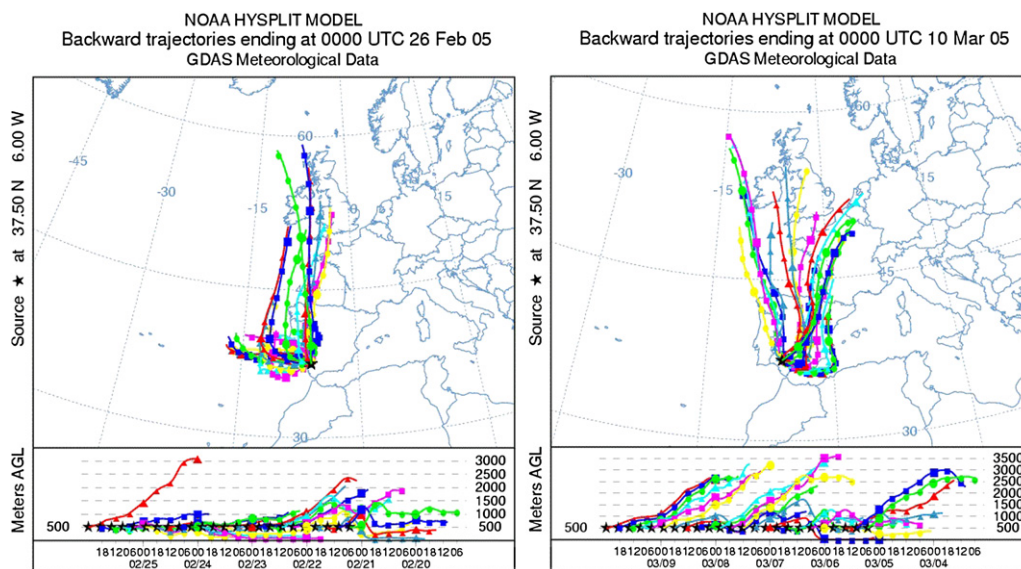


Fig. 4. NOAA HYSPLIT examples of back-trajectories for air parcels arriving at Seville at 26/02/2005 (left) and 10/03/2005 (right) for different altitudes. Note that for both cases back-trajectories are computed at 5-h intervals spanning the 5-d period ending at 00:00 UTC on the date given. Precipitation associated with the air masses has passed through Sellafield and La Hague region. The lower part of the figures shows the changes in the vertical movement of the air mass trajectories.

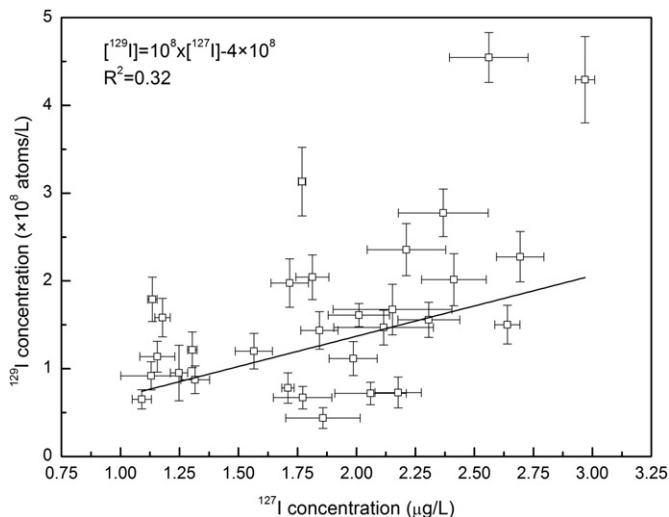


Fig. 5. Comparison between ^{129}I and ^{127}I concentrations in rainwater. Weak positive correlation (0.57) could suggest that both isotopes are partially decoupled due to different source functions and transport modes.

model is published in Draxler and Rolph (2003). We have reconstructed the air mass pathways for all higher ^{129}I wet deposition events that are correlated with the wind coming from the north using the HYSPLIT model. The modelling results confirm that for most of these cases air parcels that were over Seville during periods of rainfall at the time of sampling had previously passed over the vicinity of Sellafield and La Hague plants. Two of these trajectories (February and March 2005, samples inside circles in Fig. 3) are shown in Fig. 4. In contrast, for the periods corresponding to lower measured ^{129}I concentration recorded in Seville, trajectories were mainly from a western direction, and had not traversed the vicinity of either reprocessing facility. As shown before, the results obtained in this work are lower than previous results for the same location (Seville) during the period 1996–1999. This could be explained due to the reduction of the total gaseous ^{129}I releases emitted by Sellafield and La Hague from 9.60 kg in 1996 and 6.08 in 1999 to 3.33 kg in 2005 and 1.97 kg in 2008.

Also the deposition mechanisms of ^{127}I are not clear. Presently, we have no data about anthropogenic sources of ^{127}I within Europe, but fossil fuel and biomass burning may provide insignificant amounts compared with natural sources (ocean, wetlands, soil and

vegetation) (Aldahan et al., 2009). A factor that may cause different distributions of ^{127}I and ^{129}I in precipitation is their respective sources to the atmosphere. Although both isotopes can have marine waters as the main source, ^{129}I has specific point sources related to the discharges from the Sellafield and La Hague facilities. Weak positive correlation (0.57) between ^{127}I and ^{129}I (Fig. 5) could indicate that these two isotopes are partly decoupled mainly due to different source functions and transport modes. This conclusion has also been reported before by Aldahan et al. (2009). Apart from these differences with respect to their origins, if the ^{129}I concentration and the $^{129}\text{I}/^{127}\text{I}$ ratio are plotted together (Fig. 6), there is a good agreement between both curves. This high correlation can be understood from the almost constant levels of ^{127}I concentration in the precipitation (Table 1), while the variation of ^{129}I is big, and therefore the $^{129}\text{I}/^{127}\text{I}$ ratio is dominated by the ^{129}I concentration.

6. Conclusions

^{129}I and $^{129}\text{I}/^{127}\text{I}$ ratios in rainwater samples collected between 2005 and 2008 in Seville (Spain) have been measured. The results show a good agreement with the data reported in the literature for other areas of South Europe considered as ^{129}I background areas, although these results also seem to be related with the history of the ^{129}I gaseous releases from the European reprocessing facilities at Sellafield and La Hague. The study of the dependence of the ^{129}I deposition with some atmospheric parameters suggests that deposition seems to be more important in wet than in dry periods and that also depends in the wind direction, being more important for winds with north to south component, as suggested in previous works. Modelling results using an atmospheric transport/dispersion model support this last interpretation.

The results obtained in this work are lower than the reported in previous works for the same location during the period 1996–1999, probably due to the reduction of the total gaseous ^{129}I releases emitted by Sellafield and La Hague.

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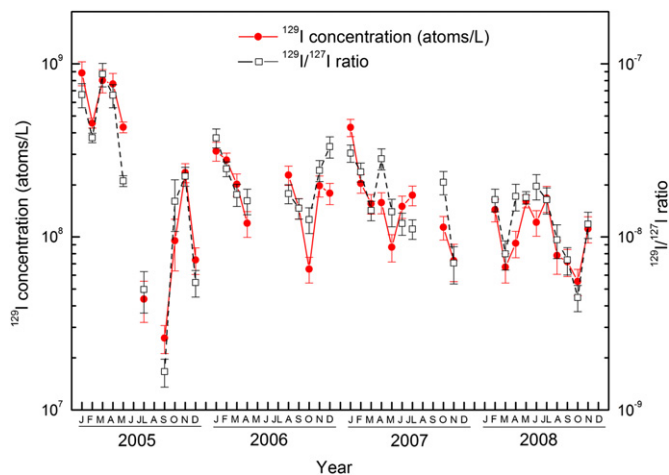


Fig. 6. ^{129}I concentration and $^{129}\text{I}/^{127}\text{I}$ ratio in rainwater samples collected in Seville in the period 2005–2008.

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