Estimating the impact from Fukushima in Southern Spain by ^{131}I and Accelerator Mass Spectrometry detection of ^{129}I

J.M. Gómez-Guzmán [a], J.M. López-Gutiérrez [b, c, *], R. García-Tenorio [b, d], L. Agulló [b], J.I. Peruchena [b], G. Manjón [d], M. García-León [b, e]

[a] Technische Universität München, Fakultät für Physik, James-Franck-Strasse 1, 85748 Garching, Germany
[b] Centro Nacional de Aceleradores (Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Junta de Andalucía), Thomas Alva Edison 7, 41092 Seville, Spain
[c] Universidad de Sevilla, Departamento de Física Aplicada I, Escuela Universitaria Politécnica, Virgen de África 7, 41011 Seville, Spain
[d] Universidad de Sevilla, Departamento de Física Aplicada II, E.T.S. Arquitectura, Av. Reina Mercedes, 2, 41012 Seville, Spain
[e] Universidad de Sevilla, Departamento de Física Atómica Molecular y Nuclear, Av. Reina Mercedes s/n, Seville, Spain

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ABSTRACT

After the Fukushima accident, large amounts of radionuclides were discharged to the atmosphere. Some of them travelled long distances and were detected in places as far from Japan as Spain a few days after the accident. One of these radionuclides was ^{131}I. Its isotope ^{129}I (T1/2 = 15.7 × 106 years) was also expected to follow the same pathway. In this work, we present the results for the ^{129}I concentration in the same atmospheric samples from Seville (Spain) where ^{131}I activity was measured in 2011 by Baeza et al. (2012). ^{129}I concentrations in aerosol and gaseous samples showed concentrations in the order of 104 and 105 atoms/m^3, typically higher in the gaseous form with respect to the aerosol form. Also ^{129}I in rainwater was measured, showing concentrations in the order of 10^8 atoms/L. The results show a very good agreement with the ^{131}I profile, showing that, if background from other sources is not relevant, it is possible to estimate the impact of similar events years after them thanks to the sensitivity of techniques like Accelerator Mass Spectrometry.

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1. Introduction

One of the most important radionuclides to consider after any nuclear accident is ^{131}I (T$_{1/2}$ = 8.02 days), due to its high radiological toxicity. After the Fukushima accident (2011), relevant amounts of this and other radionuclides were detected in places as far from Japan as Spain during March and April 2011 (Baeza et al., 2012; Piñero García and Ferro García, 2012). However, after very little time, ^{131}I decays and no more analysis can be done to evaluate its impact in a certain zone. An alternative can be the study of its long-lived radioisotope ^{129}I.

^{129}I is a long-lived cosmogenic radionuclide (T$_{1/2}$ = 15.7 × 10^6 years) for which the natural abundances have been altered in a significant way by human actions. Natural production processes lead to typical ^{129}I/^{127}I isotopic ratios between 10^{-12} (Kilius et al.,

1992) and 6 × 10^{-13} (Roberts et al., 1997). The natural inventory of ^{129}I has been 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 (1986). An estimated 50—150 kg of ^{129}I were released to the atmosphere during the main period (1945—1964) of nuclear weapons testing (Wagner et al., 1996) and a further ~6 kg were released due to the Chernobyl accident (1986) (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). 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 (Keogh et al., 2010).

* Corresponding author. Centro Nacional de Aceleradores, c/Thomas Alva Edison, nº 7, 41008 Sevilla, Spain.
E-mail address: lguti@us.es (J.M. López-Gutiérrez).

Several works have shown the possibility of estimating the ^{131}I levels through the measurement of ^{129}I. For example, Mironov et al. (2002) already estimated ^{131}I from ^{129}I in soils from Belarus due to the Chernobyl accident with a reasonable accuracy. Also Michel et al. (2015) have recently used ^{129}I in soils to carry out a retrospective dosimetry of ^{131}I in Northern Ukraine.

In this work, we present the results for ^{129}I and ^{131}I in atmospheric samples taken in Seville (Spain) during March and April 2011, when the radioactive plume from Fukushima arrived to Spain. The measured levels and the origin of the detected ^{129}I are discussed. The results suggest that, in this case, ^{129}I can also be helpful to estimate the ^{131}I in environmental samples.

2. Sampling and radiochemical methods

^{129}I concentrations were measured in three kinds of samples: water (wet and dry deposition), polypropylene filters and activated charcoal filters. The radiochemical methods applied have already been detailed in previous publications, so only a brief description will be given here.

Rainwater samples are usually collected monthly at the roof of the Faculty of Physics at the University of Seville by a rounded 1 m diameter funnel. If no rain is collected for a period, the funnel is washed with 5 L of double-distilled water, so that the deposited particles are collected. However, during the days after the Fukushima accident, samples were taken more often (every two or three days) as a higher concentration of radionuclides was expected. Sample preparation is described in López Gutiérrez et al. (2000) with more detail, being identical for wet and dry deposition. Approximately 500 mL were used for ^{129}I sample preparation. In order to obtain ^{129}I concentrations, 2 mg of Woodward Iodine carrier were added to the sample. After this, NaOH and $NaHSO_3$ were added so that the final concentrations are 0.05 M and 0.025 respectively. The samples were stored for one day and then acidified with 7 M HNO_3. After $NaNO_2$ addition, iodine is oxidized and re-extracted into $CHCl_3$. The sample is then reduced with $NaHSO_3$ and iodine is back-extracted into aqueous solution. Excess of S is eliminated by precipitation of $Ba(SO_3)_2$ by the addition of saturated $Ba(NO_3)_2$. Finally, iodine is precipitated as AgI, mixed with Nb powder and pressed into a Cu cathode for AMS measurement.

Polypropylene filters are expected to trap aerosols. A high flux pump (AEROSOL SAMPLING STATION ASS-500) passes air through a 40×40 cm^2 polypropylene filter (type G3). As for water samples, weekly periodicity was changed to daily for the days after the Fukushima accident. Approximately 1/16 of each filter was used for ^{129}I concentration measurement. Typically, about 15,000 m^3 were filtered per day, so the total amount of ^{129}I extracted was more than enough for ^{129}I measurement by AMS. The portion of polypropylene filter was cut into pieces and introduced into an extraction solution consisting of 0.05 M NAOH and 0.025 $NaHSO_3$ with continuous shaking, following the process described in Santos et al. (2005). At the same time, 2 mg Woodward Iodine carrier are added to the solution. After two days, the solution is filtered and the process is the same as the previously described for water samples.

The pump used for TEDA (Tri-ethylene diamine activated) charcoal filters has a much lower capacity than the one used for polypropylene filters, so samples were taken at least every four or five days after having filtered typically between 150 and 200 m^3. The charcoal is then taken out of the cartridge and introduced in double distilled water together with 2 mL of a 1 mg/mL Woodward Iodine carrier solution as explained in López Gutiérrez et al. (1999). The mix is stirred so that carrier is absorbed into the charcoal. Later, iodine is extracted from the charcoal through an extraction solution similar to the used for polypropylene filters. The following steps are exactly the same as for these ones.

3. Accelerator Mass Spectrometry

Details about the ^{129}I measurement can be found in Gómez-Guzmán et al. (2012a,b). Briefly, ^{129}I is extracted as I$^-$, stripped to I^{3+} at 1 MV terminal voltage with 10% of overall transmission, and counted from the 2-anode signal provided by the gas ionization chamber. The minimum ^{129}I/^{127}I background ratio obtained for the Woodward Iodine (Woodward Iodine Corp., United States) is $(1.887 \pm 0.017) \times 10^{-13}$. Typically, the background ratio is under 5×10^{-13}. For normalisation purposes, it is used a secondary standard named *Q1* with a ^{129}I/^{127}I atom ratio of $(4.667 \pm 0.020) \times 10^{-11}$. It was prepared by dilution of the primary Standard Reference Material coded SRM-3231 supplied by the *National Institute of Standards and Technology* (NIST, United States), and calibrated at the ETH against other primary standards.

4. Results and discussion

^{129}I and ^{131}I concentrations, ^{129}I deposition (wet and dry) and ^{129}I/^{131}I atom ratios in polypropylene filters (for particulate iodine adsorption), wet and dry deposition and activated charcoal filters (for gaseous iodine adsorption) collected in Seville between 03/03/2011 and 28/04/2011 are shown in Table 1 and Fig. 1. Concentrations of ^{129}I in polypropylene filters ranged from $(1.925 \pm 0.099) \times 10^5$ atoms/m^3 obtained on March 3rd, to $(0.140 \pm 0.011) \times 10^5$ atoms/m^3, achieved on April 10th. Activities of ^{131}I had been previously published (Baeza et al., 2012) ranged from (1740 ± 40) μBq/m^3 obtained on March 28th and (2.0 ± 0.2) μBq/m^3 achieved on April 28th.

The concentration of ^{129}I in deposition samples ranged between a minimum of $(0.21 \pm 0.01) \times 10^8$ atoms/L and a maximum of $(1.60 \pm 0.04) \times 10^8$ atoms/L. Wet and dry deposition ranged from $(1.20 \pm 0.06) \times 10^8$ atoms/m^2 on March, 30th and $(0.63 \pm 0.03) \times 10^8$ atoms/m^2 on April 11th to $(7.98 \pm 0.23) \times 10^8$ atoms/m^2 and $(2.8 \pm 0.5) \times 10^8$ atoms/m^2 on April 3rd, respectively.

Finally, ^{129}I concentration in activated charcoal filters ranged from a maximum of $(7.7 \pm 1.1) \times 10^5$ atoms/m^3 obtained on March 24th to a minimum of $(3.23 \pm 0.19) \times 10^5$ atoms/m^3 achieved five days later, on March 29th. In all cases the errors comprise both the errors introduced during the chemistry of the samples (for example, in weighting the samples) plus the errors due to the AMS measurements (statistical). To compare the atmospheric ^{129}I concentrations on a global scale, Table 2 presents a comparison of ^{129}I levels in atmospheric samples from other locations worldwide.

For example, Wershofen and Aumann (1989) reported results obtained in polypropylene filters sampled during 1986 in Karlsruhe (Germany) at different distances from the reprocessing plant WAK (14 km and 0.7 km, respectively), showing a clear relation between nearness and ^{129}I concentration. Results reported by Doshi et al. (1987) and obtained in filters collected in 1987 at 1.8 km away from the reprocessing plant of Trombay (India), also show very high ^{129}I concentration of 1021×10^5 atoms/m^3. This result is comparable with the reported by Wershofen and Aumann (1989). More recently Englund et al. (2010) reported ^{129}I in filters collected between 1983 and 2008 in Sweden, showing concentrations ranging $(0.4–40.4) \times 10^5$ atoms/m^3 for those collected in the North to $(0.07–8.5) \times 10^5$ atoms/m^3 for those collected in the South. Their results indicate variability associated with generally higher values at near coastal sites compared to the inland ones (South sampling station is only 26 km away from the North Sea), and so this concentration is influenced by the ^{129}I transported from the sea to the atmosphere (Michel et al., 2012). Our group has previously reported ^{129}I concentrations in filters collected in Seville between 2001 and 2002 (Santos et al., 2006), ranging those concentrations

Table 1
^{129}I and ^{131}I concentrations (measured), ^{129}I deposition (wet and dry, calculated) and ^{129}I/^{131}I atom ratios (calculated) in polypropylene filters and activated charcoal filters collected in Seville between 03/03/2011 and 28/04/2011. Atomic ratios ^{129}I/^{131}I are decay corrected to 15/03/2011. See the text for explanation.

Polypropylene filters						
Sampling date	^{129}I (10^4 atoms/m^3)	Error (10^4 atoms/m^3)	^{131}I (µBq/m^3)	Error (µBq/m^3)	^{129}I/^{131}I	Error
03/03/2011	19.25	0.99				
10/03/2011	2.74	0.17				
17/03/2011			2.1	0.3		
24/03/2011	4.52	0.27	620	12	48.3	3.0
28/03/2011	8.87	0.56	1740	40	22.9	1.5
29/03/2011	6.21	0.57	766	23	33.4	3.2
30/03/2011	6.13	0.79	644	20	36.0	4.8
31/03/2011	6.39	1.11	819	26	27.0	4.8
01/04/2011	4.13	0.31	857	25	15.3	1.2
02/04/2011	3.36	0.21	359	16	27.3	2.1
03/04/2011	4.01	0.43	401	32	26.7	3.6
04/04/2011	3.44	0.39	254	19	33.2	4.5
05/04/2011	6.00	0.65	446	9	30.3	3.3
06/04/2011	3.69	0.33	274	21	27.7	3.3
07/04/2011	6.47	0.35	239	16	51.2	4.4
08/04/2011	5.86	0.45	206	18	49.3	5.7
10/04/2011	1.40	0.11	40	7	53.6	9.8
12/04/2011	7.25	0.38	61	7	151.5	19.3
14/04/2011	5.56	0.29	38	2	159.4	13.2
16/04/2011	13.48	0.69	35	2	336.1	23.2
21/04/2011	1.57	0.09	4.5	0.9	196.0	41.8
28/04/2011	9.47	0.54	2.0	0.2	1443.0	172.0

Wet and dry deposition					
Sampling date	^{129}I (10^7 atoms/L)	Error (10^7 atoms/L)	Dep wet (10^7 atoms/m^2)	Error (10^7 atoms/m2)	Dep dry (10^7 atoms/m^2)	Error (10^7 atoms/m2)
07/03/2011	8.56	0.46	68.50	3.65		
23/03/2011	2.92	0.06	14.60	0.29		
24/03/2011	5.51	1.06	27.60	5.30		
26/03/2011	7.60	1.90	38.00	9.52		
26/03/2011	2.74	0.54			16.40	3.21
30/03/2011	2.41	0.12	12.00	0.59		
01/04/2011	2.17	0.13			9.76	0.57
03/04/2011	3.49	0.59			27.90	4.72
03/04/2011	15.96	0.46	79.80	2.28		
03/04/2011	3.07	0.15			10.70	0.51
06/04/2011	2.45	0.15			11.00	0.67
07/04/2011	6.07	0.64	30.40	3.19		
08/04/2011	2.58	0.20			10.30	0.79
11/04/2011	2.10	0.11			6.30	0.34
12/04/2011	10.70	2.10	53.70	10.50		
13/04/2011	2.79	0.17			9.76	0.59

Activated charcoal filters	
Sampling date	^{129}I (10^5 atoms/m^3)	Error (10^5 atoms/m^3)
17/03/2011	3.55	0.20
24/03/2011	7.73	1.12
29/03/2011	3.23	0.19
02/04/2011	3.80	0.62
06/04/2011	4.21	0.69

$(0.12–2.46) \times 10^5$ atoms/m^3, and so being in very good agreement with the ones reported in this paper, even in absence of extraordinary impacts as the Fukushima accident.

Regarding deposition samples, Reithmeier et al. (2005) measured average ^{129}I concentrations in rainwater from Bavaria of $(4.8–50) \times 10^8$ atoms/L during 2003–2004. Also Persson et al. (2007) measured average ^{129}I concentrations in rainwater from Sweden of $(10–57) \times 10^8$ atoms/L during 2001–2002. Hou et al. (2009) reported average ^{129}I concentrations in rainwater from Denmark to be $(0.28–5.63) \times 10^9$ atoms/L during 2001–2006. With respect to southern locations in Europe, Buraglio et al. (2001) reported ^{129}I concentrations in rainwater from Italy of $(1.1–9.4) \times 10^8$ atoms/L during 1998–1999. López Gutiérrez et al. (2000) measured average ^{129}I concentrations in rainwater from Seville of $(0.47–50) \times 10^8$ atoms/L during 1996–1997. López-Gutiérrez et al. (2004) also measured average ^{129}I concentrations

in wet and dry deposition samples from Seville of $(0.22–10.78) \times 10^8$ atoms/L during 1998–1999. Finally, Gómez-Guzmán et al. (2012a,b) measured concentrations of ^{129}I ranging $(0.26–8.86) \times 10^8$ atoms/L in wet and dry deposition samples collected in Seville in the period 2005–2008.

Air filter samples show ^{129}I concentrations of 10^5 atoms/m^3, ranging $(3.23–7.73) \times 10^5$, slightly lower than those obtained by Nedveckaite and Filistowicz (1993) in Lithuania in 1982–1984. As reported by those authors, this ^{129}I concentration increased one order of magnitude after the Chernobyl accident. Our group has previously reported ^{129}I concentrations in air samples collected in Seville, ranging $(4.3–61) \times 10^5$ atoms/m^3 for samples collected in 1993–1994 and $(3.5–22) \times 10^5$ atoms/m^3 for samples collected in 1998 (López-Gutiérrez et al., 2000, 2004). Those concentrations from the 90's are slightly higher than the ones obtained in this work.
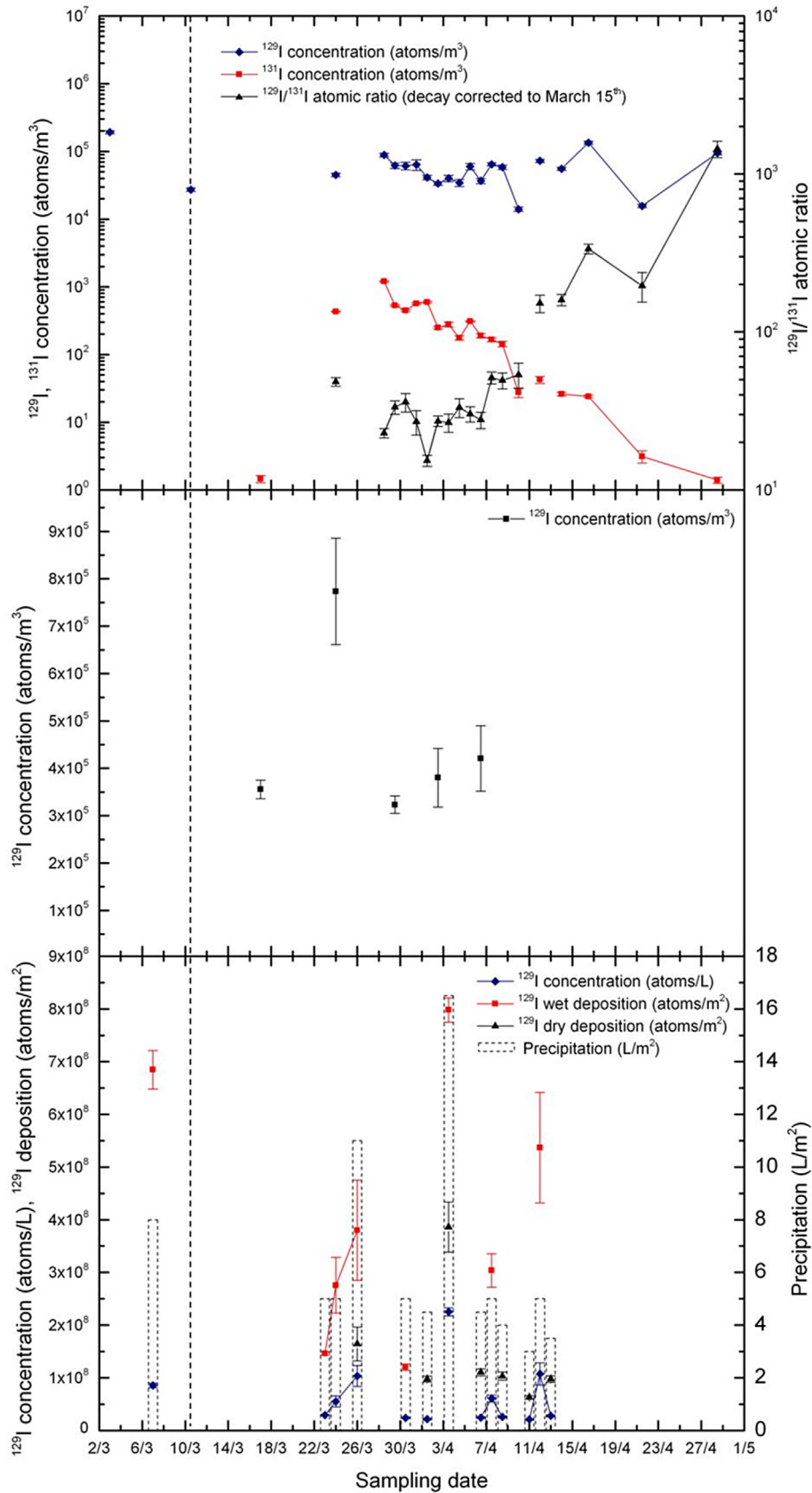
Fig. 1. ^{129}I and ^{131}I concentrations and $^{129}I/^{131}I$ atom ratio in polypropylene filters (top), ^{129}I concentrations in charcoal activated filters (middle) and depositions (wet and dry) in rainwater (bottom). Atomic ratio $^{129}I/^{131}I$ is decay corrected to 15/03/2011. See text for explanation. Vertical black line represents Fukushima accident.

Table 2
^{129}I concentrations reported in various locations worldwide.

Sample	Area	Sampling date	^{129}I concentration	Reference
Gas (atoms/m^3)	Vilnius, Lithuania	1982–1984	14×10^5	Nedveckaite and Filistowicz (1993)
	Seville	1993–1994	$(4.3–61) \times 10^5$	López Gutiérrez et al., 2000
	Seville	1998	$(3.5–22) \times 10^5$	López-Gutiérrez et al., 2004
	Seville	2011	$(3.23–7.7) \times 10^5$	This work
Aerosol (atoms/m^3)	Richland, WA	1965–1968	$(1040 \pm 240) \times 10^5$	Brauer et al., 1974
	Different USA areas	1965–1970	$(27 \pm 12) \times 10^5$	Brauer et al., 1974
	Karlsruhe, 14 km from WAK	1986	1513×10^5	Wershofen and Aumann, 1989
	Karlsruhe, 0.7 km from WAK	1986	8496×10^5	Wershofen and Aumann, 1989
	Yavne (Israel)	1986	$(260 \pm 80) \times 10^5$	Paul et al., 1987
	Trombay, India	1987	1021×10^5	Doshi et al., 1987
	South Sweden	1983–2008	$(0.4–40.4) \times 10^5$	Englund et al., 2010
	North Sweden	1983–2008	$(0.07–8.9) \times 10^5$	Englund et al., 2010
	Vienna, Austria	2001	$(0.4 + 9.3) \times 10^5$	Jabbar et al., 2011
	Seville	2001–2002	$(0.12–2.46) \times 10^5$	Santos et al., 2006
	Seville	2011	$(0.140–1.925) \times 10^5$	This work
Rain water (atoms/L)	Beit Dagan (Israel)	1982	$(0.26 \pm 0.08) \times 10^8$	Paul et al., 1987
	Beit Dagan (Israel)	1986	$(9.1 \pm 2.3) \times 10^8$	Paul et al., 1987
	Heraklion (Greece)	1986	$(44 \pm 4) \times 10^8$	Paul et al., 1987
	Munich (Germany)	1986	$(260 \pm 38) \times 10^8$	Paul et al., 1987
	Japan	1983	0.5×10^8	Muramatsu and Ohmomo, 1986
	Swiss Alps	1985	$(4.2 \pm 0.7) \times 10^8$	Wagner et al., 1996
	Lower Saxony (GE)	1986–1987	$(12.1–62.6) \times 10^8$	Szidat et al., 2000
	Lower Saxony (GE)	1997–1999	$(20–52 \times 10^8$	Szidat et al., 2000
	Dübendorf (Switzerland)	1994–1997	$(26.3–33.1) \times 10^8$	Schnabel et al., 2001
	Bavaria, GE	1988–1989	$(37.5–76.6) \times 10^8$	Bachhuber and Bunzl, 1992
	Germany	1994	$(37–110) \times 10^8$	Krupp and Aumann, 1999
	Germany	1995	$(61–150) \times 10^8$	Krupp and Aumann, 1999
	Sweden	1998–1999	$(4.0–18) \times 10^8$	Buraglio et al., 2001
	Italy	1998–1999	$(1.1–9.4) \times 10^8$	Buraglio et al., 2001
	Bavaria, GE	2003–2004	$(4.8–50) \times 10^8$	Reithmeier et al., 2005
	Sweden	2001–2002	$(10–57) \times 10^8$	Persson et al., 2007
	Denmark	2001–2006	$(2.8–56.3) \times 10^8$	Hou et al., 2009
	Seville	1996–1997	$(0.47–50) \times 10^8$	López Gutiérrez et al., 2000
	Seville	1998–1999	$(0.22–10.78) \times 10^8$	López-Gutiérrez et al., 2004
	Seville	2005–2008	$(0.26–8.86) \times 10^8$	Gómez-Guzmán et al., 2012a,b
	Seville	2011	$(0.21–1.60) \times 10^8$	This work

In general, the comparison of the ^{129}I levels measured in our samples with those present in the literature shows that the amount of ^{129}I in Seville right after the Fukushima accident was not especially high. They are clearly lower than those measurements carried out in zones directly affected by nuclear accidents or nuclear fuel reprocessing plants. Also, when they are compared to Central and Northern Europe, ^{129}I concentrations in Seville are typically similar or lower. Even the ^{129}I levels found in aerosol filters after the Fukushima accident are in very good agreement with those measured in the same place in 2001 and 2002. Then, is possible to assert that the impact of the Fukushima accident was not strong in comparison to the background values in Seville.

The first detection of ^{131}I after the Fukushima accident in Spain was in high-volume filters collected in Seville during the period March 14th–21st (maximum concentration of 1740 atoms/m^3 on March 28th–29th), followed by Cáceres (March 15th–22nd, with a maximum concentration of 3080 atoms/m^3 on March 28th–29th) and Barcelona (March 23rd–28th, with a maximum concentration of 391 atoms/m^3), as reported by Baeza et al. (2012). As is summarized in Table 3, also other authors reported ^{131}I concentrations in different parts of Spain following the Fukushima accident. For example Piñero-García and Ferro-García (2012) measured in Granada a maximum concentration of gaseous ^{131}I of (2630 ± 120) atoms/m^3 between March 23rd–30th using activated charcoal filters, a maximum concentration of (820 ± 80) atoms/m^3 using polypropylene filters in the same dates, and (110 ± 160) atoms/L in rain water samples collected in the period March 30th to April 6th. On the other hand, Lozano et al. (2011) reported a maximum ^{131}I concentration of 3690 atoms/m^3 in Huelva on March 29th. Finally, the Spanish Nuclear Security Council measured a ^{131}I concentration of 1850 atoms/m^3 in La Laguna (Canary Islands) on March 28th (CSN, 2011).

As it is shown in Fig. 1 (bottom) there is an increase of the ^{129}I wet deposition in Seville starting on March 23rd, with a local minimum on March 30th and an absolute maximum on April 3rd. This time evolution is in agreement with Piñero-García and Ferro-García (2012), who detected in Granada (approximately 250 km East of Seville) the highest ^{131}I concentration in rainwater

Table 3
Maximum ^{131}I concentrations measured in activated charcoal filters and polypropylene filters in different sampling stations along Spain after the Fukushima accident.

Area	Sample	First detection date	Maximum concentration period	Maximum concentration ^{131}I (atoms/m^3)	Reference
Cáceres	Polypropylene filter	26th–27th March	28th–29th March	3080	Baeza et al. (2012)
Sevilla	Polypropylene filter	14th–21st March	28th–29th March	1740	Baeza et al. (2012)
Barcelona	Polypropylene filter	25th March	28th–30th March	391	Baeza et al. (2012)
Granada	Polypropylene filter	23rd March	23rd–30th March	2630	Piñero-García and Ferro-García (2012)
Granada	Activated charcoal filter	23rd March	23rd–30th March	820	Piñero-García and Ferro-García (2012)
Granada	Polypropylene filter	28th March	28th–29th March	3690	Lozano et al. (2011)
La Laguna	Polypropylene filter	21st–28th March	21st–28th March	1850	CSN (2011)

(110 ± 160 atoms/L) between March 30th and April 6th. It could be that, after being detected in Granada, the atmospheric conditions transported the clouds West to Seville, originating the rainfall observed between April 3rd and 12th.

The concentrations of ^{129}I measured in polypropylene filters and in activated charcoal filters during the period of influence of the Fukushima accident reached their maximum on March 28th and 24th, respectively. The sampling dates shown in Table 1 and Fig. 1 are the mean dates over each sampling period, taking into account that the ^{129}I deposits in the filters gradually during each sampling period. It is worth to note that usually both kinds of filters are not collected dairy, but with a periodicity of 1—7 days for polypropylene filters and 3—7 days for activated charcoal filters.

In the case of ^{129}I measured in polypropylene filters, the maximum concentration was found on March 28th, what is in agreement with results published by Baeza et al. (2012), who reported maximum ^{131}I concentrations also in Seville around March 28th–29th. In activated charcoal filters the maximum ^{129}I concentration was measured on March 24th. This is also in agreement with Baeza et al. (2012) taking into account that this particular filter was collected on March 28th and March 24th is the mean sampling date.

Regarding the ^{131}I profile, it reaches a maximum of (1740 ± 40) µBq/m^3 on March 28th followed by some other peaks until it disappears due to its short half-life. Both concentration and date agrees well with other data mentioned above (for example Piñero-García and Ferro-García (2012) in Granada and CSN (2011) in La Laguna). It is worth to note that in the absence of events such as the Fukushima accident the ^{131}I concentrations measured in the Faculty of Physics are usually below the detection limit of the measuring equipment.

The similarity between the temporal evolution of ^{129}I and ^{131}I concentrations shown in Fig. 1 (top) between March 24th and April 10th suggests that both isotopes have a common origin, namely the Fukushima accident. This fact can be corroborated by calculating the atomic ratio ^{129}I/^{131}I in those dates and comparing with data published in the literature calculated near Fukushima just after the accident. This work reveals an average ratio for these dates of 34.4 ± 11.7, in very good agreement with the value of (31.6 ± 8.9) reported by Miyake et al. (2012) and (34.1 ± 10.2) reported by Inagawa et al. (2013). In our calculation, ^{131}I activities were decay corrected to March 15th, when the highest rise in the air dose rate was recorded at monitoring posts of the Fukushima Daiichi NPP (TEPCO, 2011). This is supported by the rose wind from March 24th to April 10th (not shown), where a clear SW wind prevailed, probably favouring the arrival to Spain of ^{129}I and ^{131}I released as a consequence of the Fukushima accident.

It is worth to note that in the next three weeks that followed the detection of ^{131}I in Granada, the levels of gaseous ^{131}I (2630—390 atoms/m^3) were always higher than the levels of ^{131}I associated to particles (820—150 atoms/m^3). This fact leaded the authors to conclude that the gaseous phase prevails over the fraction associated to particles, as happens with stable iodine.

Assuming 100% efficiency, the ^{129}I associated to particles in Seville would be between 10.3 and 21.5% (mean value 12.8 ± 4.9%) of total ^{129}I measured in both kinds of filters. This result agrees with values reported by Wershofen and Aumann (1989) for stable iodine, who measured percentages of stable iodine associated to particles ranging 12.9%—24.5% in samples collected near a reprocessing plant located in Karlsruhe (Germany) in 1986. In the other hand, Fuge and Johnson (1986) reported that gaseous stable iodine exceeded the particulate one in a factor between 2 and 6 based on previous results published. Our results show (for ^{129}I) a ratio gaseous/particulate ranging 7.9—8.7, with the exception of one sample that showed a ratio of 3.7, suggesting this last value certain deviation to

the gaseous fraction in the case of ^{129}I. A possible explanation for this issue would be the long distance from the source of ^{129}I to Seville, that would favour the precipitation of iodine associated to particles.

Concentrations of ^{129}I in deposition samples were highly correlated with the mean daily rainfall (correlation factor R = 0.9178). In Fig. 1 bottom, the ^{129}I deposition (wet and dry) 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. 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 dates, samples collected only due to dry deposition (black triangles in Fig. 1) have lower values than others collected from precipitation events (red squares (in the web version) in Fig. 1). 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, mainly as CH_3I and I_2, but tends to attach to other particles (Brant et al., 2002). 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 has been reported to be the major removal process and to be a large source for radioactive contamination (Brant et al., 2002).

It is interesting to mention that ^{129}I concentrations measured in polypropylene filters before the Fukushima accident and after the period of influence of this accident over Spain are in the same order of magnitude than ^{129}I concentrations measured during the period of influence. This would mean that there is little effect of the emissions from the nuclear fuel reprocessing plants of La Hague and Sellafield during that period. If a change in the discharges of these plants is discarded, the effect could have been caused by a wind pattern during this period which did not favour the arrival from Northwestern Europe. This seems to be realistic taking into account the rose wind from March and April 2011 shown in Fig. 2. A clear SW wind prevailed during March 2011, probably favouring the arrival to Spain of ^{129}I and ^{131}I released as a consequence of the Fukushima accident. In April 2011 two wind directions prevailed (SW and NE) favouring the arrival of releases from the Fukushima accident but also releases from Sellafield and La Hague.

This suggests the possibility that an air-mass labelled with enhanced levels of ^{129}I and ^{131}I had travelled from the vicinity of Fukushima Daiichi plant and that both had subsequently been deposited in Seville. 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 (HYSPLIT) atmospheric transport/dispersion model, together with meteorological data spanning the relevant sampling periods (Draxler and Rolph, 2003). 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.

Fig. 3 illustrates the evolution of the air masses from Fukushima after the nuclear accident at three different altitudes (500 m, 1000 m and 1500 m). The 315-h (left) kinematic forward-trajectories starting at 12 UTC March 15th and the 250-h (right)
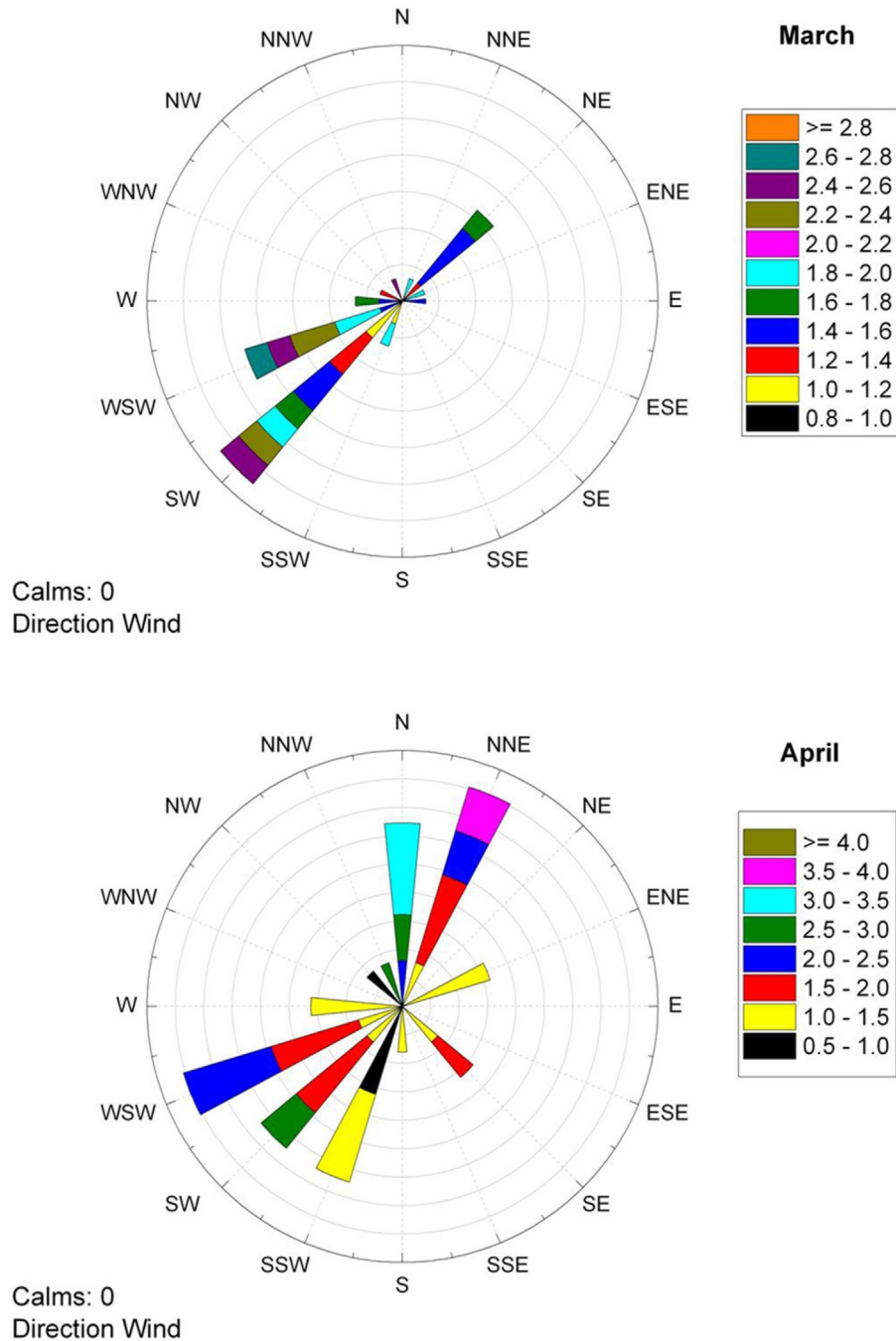
Fig. 2. Wind rose from March and April 2011 obtained in a meteorological station located near the sampling site in Seville.

kinematic forward-trajectories starting at 12 UTC March 22nd were computed with HYSPLIT. This period covers the whole period of maximum influence of the Fukushima accident over Spain, as shown by other authors, like Piñero-García and Ferro-García (2012) and Baeza et al. (2012).

The modelling results show that after the nuclear accident the air masses transported the radioactive cloud from Fukushima toward the Pacific Ocean in the direction of the Arctic Ocean, Canada and northern USA. Subsequently, polar maritime air masses, which had been originated as continental masses over North America, moved the radioactive plume toward the Atlantic Ocean on the way to southeast Spain, where arrived around March 30th, coinciding with the maximum concentration of ^{131}I measured in polypropylene filters.

As a result of this situation, the ^{131}I could be estimated from the ^{129}I concentration in the aerosol samples. In Fig. 4, the evolution of the ^{131}I measured in Sevilla by Baeza et al. (2012) (decay corrected to March 15th) and the one estimated from the ^{129}I concentrations are shown. The average ^{129}I/^{131}I ratio measured in our samples has been (34.4 ± 11.7). If the difference between both curves is minimized, a ratio of 30.1 is obtained. Nishihara et al. (2012) calculated 31.4 in Reactor 1 of the Fukushima Daiichi NPP at the time of the accident by modelling using ORIGEN2 code and the ratios measured by Miyake et al. (2012) and Inagawa et al. (2013) are very close to our values, as commented before. If the correction is done with respect to March 11th, the average ratio in our samples is (24.4 ± 8.3) and the minimum difference ratio would be 21.3. These values agree with the ones
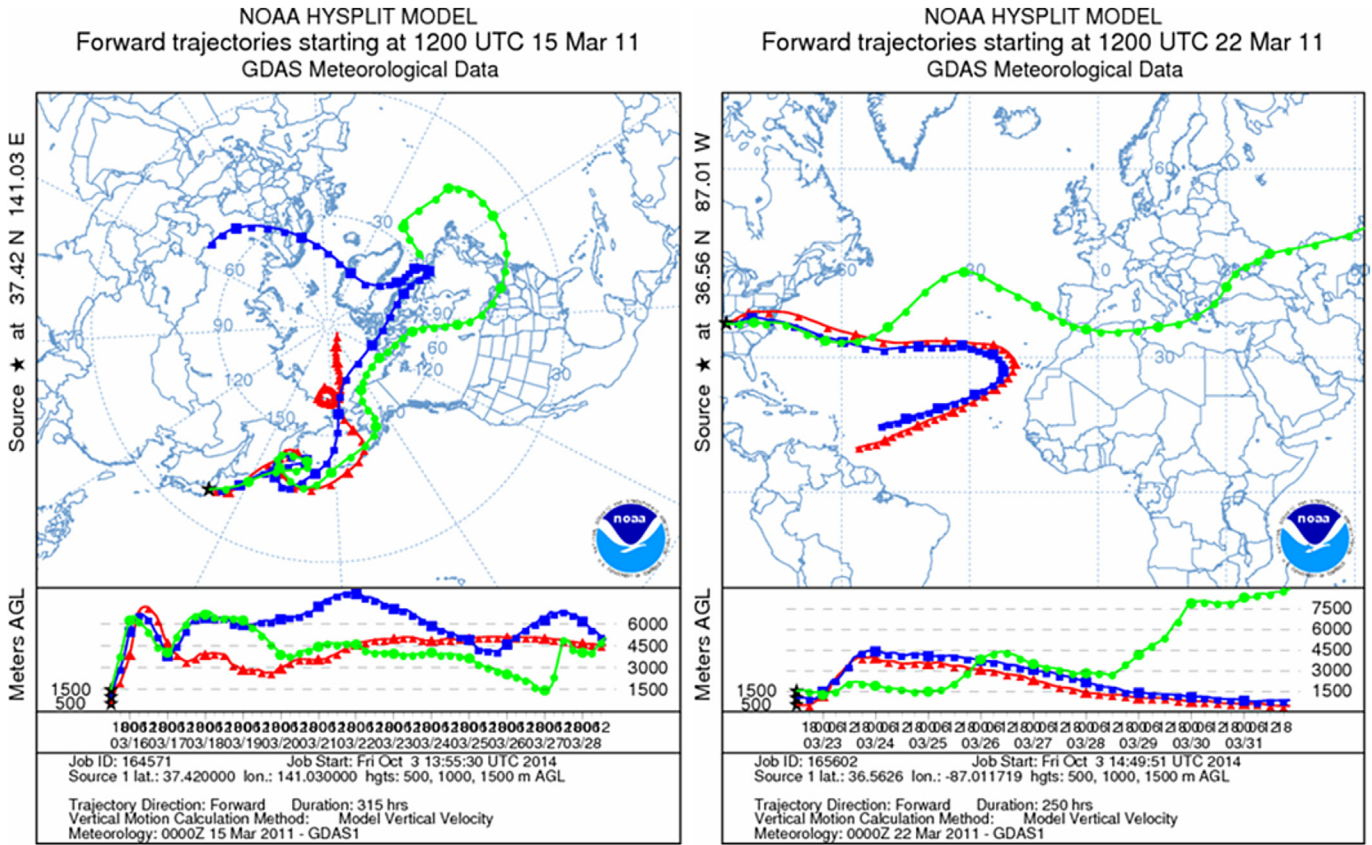
Fig. 3. NOAA HYSPLIT examples of forward trajectories for air parcels starting at Fukushima Daiichi plant at 15/03/2011 (left) and USA at 22/03/2011 for different altitudes (500 m, 1000 m and 1500 m). The lower part of the figures shows the changes in the vertical movement of the air mass trajectories.

calculated by Nishihara et al. (2012) in Reactors 2 (21.9) and 3 (20.8). Also, Muramatsu et al. (2015) found a ratio of 20.8 in soil samples around Fukushima. Then, the isotopic $^{129}I/^{131}I$ ratios would not vary much even far distances from the origin point. Also the variability of this ratio seem no to be higher than the one measured very close to the accident point.
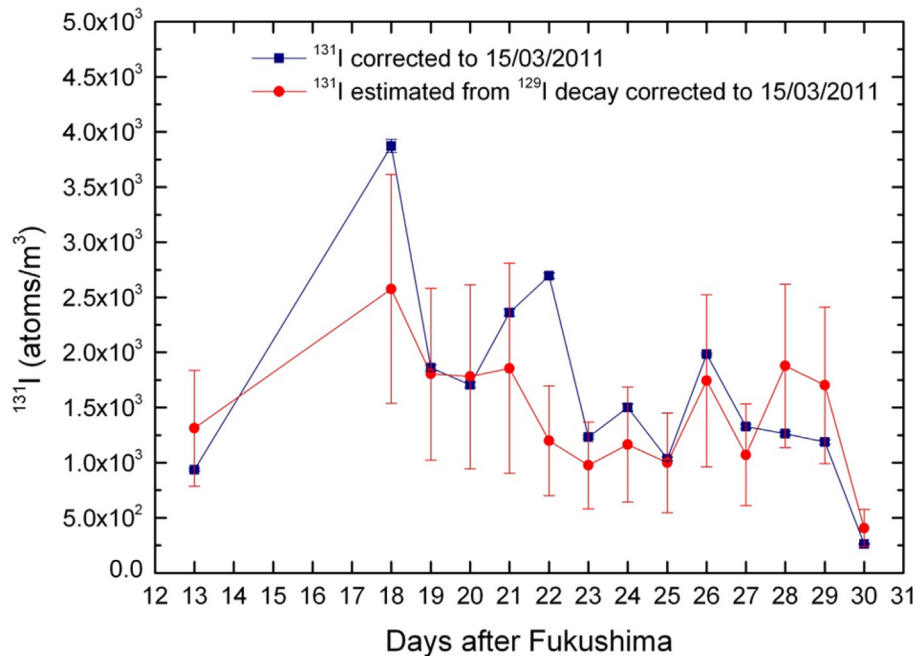

Fig. 4. ^{131}I concentration (decay corrected) measured in aerosol samples and ^{131}I concentration estimated from ^{129}I from the average measured ratio 34.4 ± 11.7.

5. Conclusions

^{129}I emitted in Fukushima during the accident in 2011 has been detected in atmospheric samples taken in Seville (Spain) several years later by Accelerator Mass Spectrometry. The impact in zones as far from the accident as Seville was low. Actually, the measured levels were not higher than the background ones, detected before and after the accident. However, meteorological conditions seemed to providentially reduce the impact of ^{129}I from nuclear fuel reprocessing plants in Seville during those days, letting us to distinguish the signal from Fukushima. In cases like this or in zones with a stronger impact of nuclear accidents, ^{129}I could help estimate the ^{131}I signal many years after them, as the ^{129}I/^{131}I ratio does not seem to change strongly from the original one. Gaseous ^{129}I has shown to be more abundant than particulate ^{129}I, as usually happens with stable iodine. However, the gaseous fraction seems to be even more elevated, maybe due to the more likely precipitation of particulate ^{129}I in the atmosphere during the days after the accident.

Acknowledgements

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