

Determination of total I and ^{129}I concentrations in freshwater of Argentina

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Abstract. Total iodine and ^{129}I in rivers and lakes of Argentina were measured by means of inductively coupled plasma mass spectrometry and accelerator mass spectrometry respectively. The obtained isotopic ratios, higher than the natural level, are explained as the delayed signal from nuclear weapon atmospheric tests. Besides, deposition fluences in catchment areas of the lakes are analyzed. Their latitudinal dependence, similar to the dependence of annual precipitation rates, favours wet deposition as the main ^{129}I fallout mechanism for this region.

1 Introduction

Iodine is a biophilic element with a single stable isotope, ^{127}I . There is only one long-lived radionuclide of iodine, iodine-129 with a half-life of $T_{1/2}=15.7$ Ma. Both isotopes are presumed to have similar geochemical cycles, although the production and decay of ^{129}I establishes a difference compared to the stable isotope.

Iodine is found in large amounts in the oceans (about $60 \mu\text{g/L}$) and is involved in the ocean-atmosphere cycle. Iodine occurs naturally in water systems predominantly as iodide and iodate, with a content of $1 - 20 \mu\text{g/L}$ for fresh surface waters. Rain typically contains $1 - 10 \mu\text{g/L}$. Soils are also generally rich in iodine ($4 - 8 \text{ mg/kg}$), which is mainly associated with organic matter [1].

^{129}I is naturally produced by spallation reactions of cosmic-rays with xenon in the atmosphere, and by the fission of ^{235}U and ^{238}U inside the Earth crust. Those produce a natural inventory of almost 260 kg [2]. Anthropogenic activity has modified the equilibrium of the ^{129}I cycle by adding a huge and well-defined source of this radioisotope to the surface environment. Since 1945 human activities increased the amount of ^{129}I by $50\text{-}130 \text{ kg}$ due to atmospheric nuclear weapon tests and, much more importantly, by about $6,000 \text{ kg}$ from releases from nuclear fuel reprocessing plants placed in the Northern Hemisphere [3]. In this way, ^{129}I concentrations were enhanced several orders of magnitude.

In the Southern Hemisphere, natural sources and nuclear tests have a similar contribution in every ^{129}I surface compartment inventory [4]. Surface water and biological samples stemming from the austral hemisphere

contain ^{129}I concentration levels ranging between the natural values and the one related with nuclear tests [5-7].

Although ^{129}I does not represent any health hazard at present or future concentration levels [7], its detection in the southern hemisphere allows a retrospective coarse estimation of global radioactive yield released from nuclear atmospheric tests. In the northern hemisphere, however, the ^{129}I emissions of nuclear fuel reprocessing plants overwhelm other sources.

In this contribution we analyze results of total iodine and ^{129}I concentration values in freshwater taken at different latitudes in Argentina. The abundances of ^{129}I in surface water were assessed via accelerator mass spectrometry. Details of these measurements are given in Section 2. In Section 3 we discuss the deposition fluences in the catchment areas of various Patagonian lakes. With the help of these results we will briefly discuss possible transport mechanisms for ^{129}I .

2 Experimental

Samples were collected in plastic bottles during the austral summer and fall 2011 and chemically treated at the TANDAR Laboratory in Buenos Aires (see sampling location in Fig. 1). Particulate matter was removed using a $0.45 \mu\text{m}$ filter. Total iodine (^{127}I) concentrations were determined using ICP-MS (Inductively Coupled Plasma Mass Spectrometry). Since the amount of ^{129}I was expected to be low, high volume water samples (2-6 L) were concentrated to a final volume of 200 mL . Due to its known low isotopic ratio ($^{129}\text{I}/^{127}\text{I} = 2 \cdot 10^{-14}$), Woodward iodine was used as carrier. The sample preparation for

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AMS was done using a method in which oxidized iodine is extracted in chloroform and back-extracted in aqueous solution [3]. Finally iodine was mixed with Ag and pressed into Cu sample holders.

The measurement of isotopic ratios of these samples was performed by means of the AMS technique at the Heavy Ion Accelerator Facility (HIAF) at the Australian National University, which is based on a 14UD pelletron accelerator [8]. We used a 32 sample MC-SNICS ion source and sputtered the samples with a Cs beam. Negative ions (I^-) were extracted and accelerated to 150 keV. The negative ions were deflected 90 degree from the horizontal into the vertical direction and injected into the vertical accelerator. This deflection implies a first mass selection. For the ^{129}I measurements of this work the accelerator was operated at 10.5 - 11 MV terminal voltage. We selected the 7+ charge state with the analyzing magnet which bends the beam back into the horizontal direction. After passing a switching magnet and a Wien velocity filter, the rare radioisotope $^{129}I^{7+}$ is counted in a multi-anode ionization chamber. The beam intensity of stable ^{127}I is measured both at the low energy side and at the high energy side with Faraday cups. The ratio measurements are performed in sequential mode, i.e. we measure ^{127}I currents for 10 s, switch then to ^{129}I counting mode for 2 to 3 min and then back to the ^{127}I current measurement. Such sequences are repeated two times. Switching between the different isotopes is done automatically. This AMS system allows measurements with accuracy between 2 and 4%.

Samples measured gave values at least one order of magnitude above the chemical blanks. Pure Woodward spike samples and chemical blanks were used to quantify the intrinsic ^{129}I contribution of the spike and the ^{129}I background in the chemical procedure, respectively.

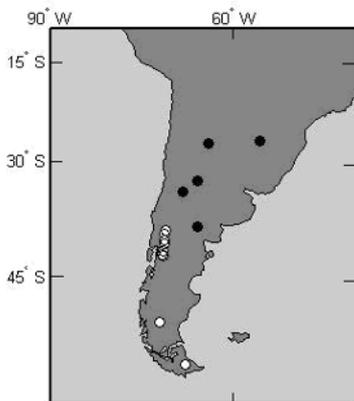


Figure 1. Map of South America showing the various sampling sites. Black circles correspond to rivers while white circles denote water samples taken from lakes.

3 Latitudinal dependence of I and ^{129}I

Iodine latitudinal dependence is shown in Fig. 2. Concentration values decrease with increasing latitude up to around 40°S. South of 50°S higher iodine concentrations were found again. This latitudinal dependency can be explained by considering the main sources of atmospheric iodine for South America [9] and

the regional winds and precipitation patterns [10], which eventually wash out the iodine to the surface. On the one hand, precipitation rates roughly decrease from northern to southern Argentina. On the other hand, in northern and central Argentina the main supply pathway for atmospheric iodine is the Atlantic cyclonic wind system which transports iodine stemming from emissions at the Equatorial Atlantic Ocean and from biomass burning in the Brazilian Amazonia. In the southern part of Argentina, emissions from the South Pacific and South Atlantic are the most relevant sources. The intense westerly airstream brings Pacific air over the southern Andes Mountains (which are much lower at these latitudes than in Central Argentina), with sporadic and local incursions of Atlantic air. The content of total iodine in samples is comparable to values previously reported [11].

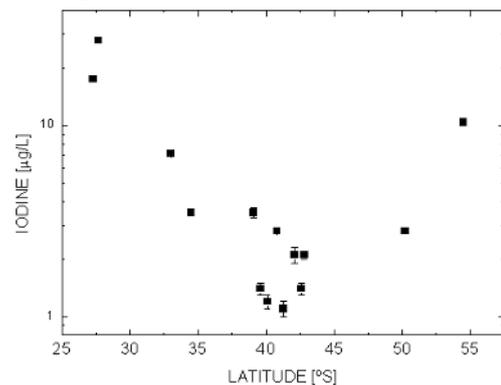


Figure 2. Iodine concentrations measured in freshwater samples.

Concentrations of ^{129}I measured from the freshwater samples vary from $9.7 \cdot 10^4$ to $7.5 \cdot 10^5$ atoms/L [5]. These values are consistently larger than the estimated natural concentration ($3.7 \cdot 10^4$ atoms/L). Indeed, most of them were found close to the value associated with nuclear weapon tests ($1.0 \cdot 10^6$ atoms/L). However, they are more than one order of magnitude lower than the reported values for the Northern Hemisphere, even for locations far away from any reprocessing plants [12]. The latitudinal dependence of ^{129}I is shown in Fig. 3. There is no clear evidence of any latitudinal dependence, in contrast to the case of stable iodine.

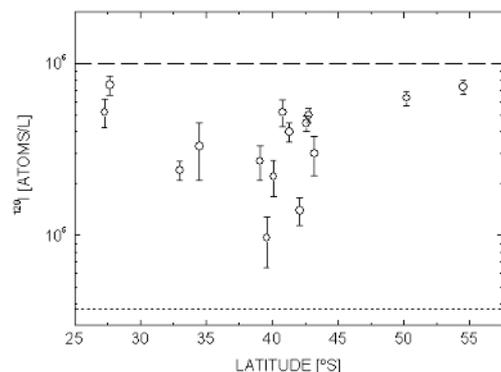


Figure 3. ^{129}I concentrations measured in freshwater samples. The dotted line indicates the natural level ($3.7 \cdot 10^4$ atoms/L).

atoms/L), while the dashed line shows the level associated with nuclear explosions ($1 \cdot 10^6$ atoms/L).

Fig. 4 shows the isotopic ratios of the surface water samples. The measured data range from $6 \cdot 10^{-12}$ to $5 \cdot 10^{-11}$, and are between the natural level ($1.5 \cdot 10^{-12}$) and the one associated with nuclear explosions ($5 \cdot 10^{-11}$), although they are shifted towards the latter one. This can be understood in terms of the buffer effect for the ^{129}I released during the nuclear explosions due to the long iodine residence time in soil, which results in a continuing elevated signal for many years after the cessation of testing. The residence time is likely to be around 4000 y for natural iodine [13] and we recently estimated a value of 1000 y for ^{129}I fallout originating from nuclear explosions [5].

The ^{129}I concentration in lake samples allowed us to estimate the deposition fluences of this radionuclide within their catchment area applying the method described by Reithmeier *et al.* [14]. This model assumes that rain water deposited in the catchment area can be transported to the lake by means of direct deposition on to the lake's surface or by river inflow (which constitutes a delayed signal) and it requires the knowledge of some limnological parameters (lake area and volume, catchment area, etc.) for the calculation of the deposition fluences. All of them (see Fig. 5) are well above the natural deposition fluence level. This level can be roughly estimated by taking into account *i*) the global iodine sinks budget (1000 Gg/y) [15], *ii*) the pre-anthropogenic ratio of $1.5 \cdot 10^{-12}$ [16] and, *iii*) assuming an homogenous fallout onto the surface of the Earth, giving a mean deposition rate of $1.4 \cdot 10^7$ atoms/m²/y. An integration of this deposition rate over a residence time in the lithosphere (4000 y) gives a natural deposition fluence of $5.6 \cdot 10^{10}$ atoms/m². This is comparable with $(6.0 \pm 1.5) \cdot 10^{10}$ atoms/m² reported for a Russian soil sample from 1939 [17].

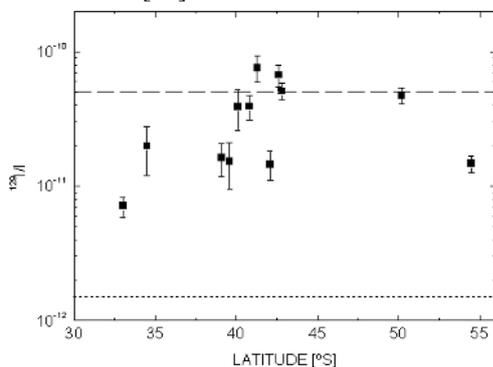


Figure 4. $^{129}\text{I}/^{127}\text{I}$ isotopic ratios measured in freshwater samples taken at different latitudes in Argentina [5]. The dotted line indicates the value of the natural isotopic level ($1.5 \cdot 10^{-12}$). The dashed line shows the isotopic ratio associated to nuclear explosions ($5 \cdot 10^{-11}$).

Latitudinal dependence of the measured fluences for the catchment areas of the lakes studied is plotted as a function of the latitude in Fig. 5. In an attempt to visualize the role of the wet deposition in the ^{129}I fallout associated to atmospheric nuclear tests, we also plot the

annual precipitation rates at each lake location. The figure seems to indicate that the precipitation rates and measured fluences follow the same pattern (with the exception of the sample collected at 50°), although further data is needed to confirm or discard a correlation between both magnitudes.

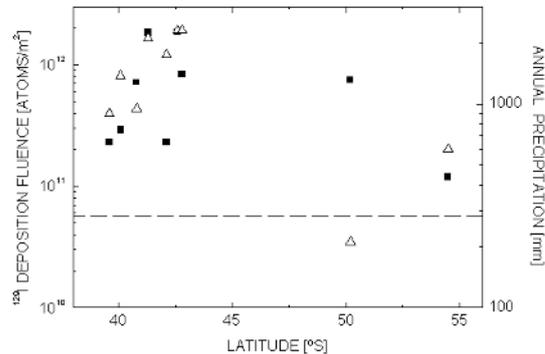


Figure 5. Measured ^{129}I deposition fluences in the catchment areas of the studied lakes (squares) and their respective annual precipitation rates (triangles) as a function of latitude. The dashed line represents the estimated level of the natural deposition fluence ($5.6 \cdot 10^{10}$ atoms/m²).

4 Conclusions

Total iodine and ^{129}I abundances and isotopic ratios in several rivers and lakes of Argentina were analyzed. The ^{129}I concentrations were measured by AMS because it is the only technique with enough sensitivity to measure the low ratios expected in these samples. ^{127}I concentrations present a clear latitudinal dependence that can be comprehended taking into account regional atmospheric iodine sources and the possible transport patterns. On the other hand ^{129}I concentrations range between the natural level ($3.7 \cdot 10^4$ atoms/L) and the one associated to nuclear tests ($1 \cdot 10^6$ atoms/L). The measured $^{129}\text{I}/^{127}\text{I}$ isotope ratios lie between $6 \cdot 10^{-12}$ and $5 \cdot 10^{-11}$. All of them are above the natural level ($1.5 \cdot 10^{-12}$) and close to the reference value associated with nuclear weapon tests ($5 \cdot 10^{-11}$), probably indicating a memory effect in Patagonian lakes.

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