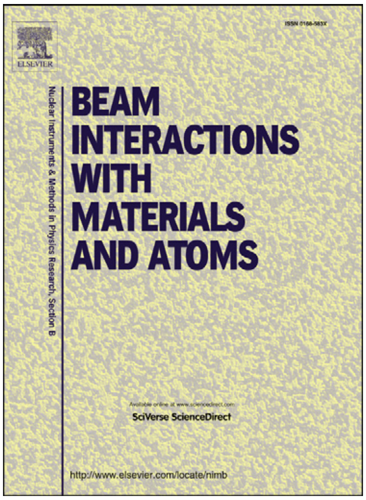

# Relationship between $^{129}$I and $^{127}$I contents in bovine thyroid glands from Argentina

A.E. Negri, J.O. Fernández Niello, A. Wallner, A. Arazi, P. Steier

PII: S0168-583X(12)00397-7
DOI: http://dx.doi.org/10.1016/j.nimb.2012.07.009
Reference: NIMB 58829

To appear in: *Nucl. Instr. and Meth. in Phys. Res. B*

Received Date: 27 June 2011
Revised Date: 7 July 2012
Accepted Date: 8 July 2012

Please cite this article as: A.E. Negri, J.O. Fernández Niello, A. Wallner, A. Arazi, P. Steier, Relationship between $^{129}$I and $^{127}$I contents in bovine thyroid glands from Argentina, *Nucl. Instr. and Meth. in Phys. Res. B* (2012), doi: http://dx.doi.org/10.1016/j.nimb.2012.07.009

# Relationship between $^{129}$I and $^{127}$I contents in bovine thyroid glands from Argentina

A. E. Negri[a], J. O. Fernández Niello[a,b], A. Wallner[c,d], A. Arazi[a], P. Steier[c]

*a Laboratorio TANDAR, CNEA, Av. Gral. Paz 1499, B1650KNA, San Martín, Buenos Aires, Argentina*

*b Universidad Nacional de San Martín, Campus Miguelete, B1650BWA, Buenos Aires, Argentina*

*c VERA-Laboratory, Faculty of Physics, University of Vienna, Waehringer Str. 17, A-1090 Wien, Austria*

*d Department of Nuclear Physics, Research School of Physics and Engineering, The Australian National University, Canberra, Australia*

## Abstract

$^{129}$I/$^{127}$I ratios and iodine concentrations in bovine thyroids stemming from Argentina were determined by accelerator mass spectrometry (AMS) and gas chromatography (GC), respectively. From these measurements, a relationship of the $^{129}$I/$^{127}$I ratio with iodine content in the gland was obtained. A weak correlation between the two isotopes was found, suggesting that $^{129}$I re-emission from the ocean is not the only process for the $^{129}$I deposition in Argentina. Moreover, contributions to the total $^{129}$I inventory in the Southern hemisphere from both natural and anthropogenic sources were theoretically studied. Surface compartments present similar contribution from natural sources and nuclear explosions fallout.

## 1. Introduction

$^{129}$I is a long-lived ($T_{½}$=15.6 My) radioisotope which is naturally formed either from spontaneous fission of uranium or by interaction of cosmic ray particles with xenon in the atmosphere. The natural abundance was estimated in 50,000 kg [1]. Only 263 kg are available in atmosphere, hydrosphere and biosphere compartments and their inventory was increased by nuclear tests by 45 kg approximately [2]. Moreover, since the 1960's nuclear fuel reprocessing plants, placed in the Northern hemisphere, have added another almost 5,000 kg to the total amount of $^{129}$I [3].

For the Southern Hemisphere, a $^{129}$I global deposition pattern recently calculated [4] pointed out that its inventory has a major contribution from atmospheric atomic explosions and is almost unaffected by the emissions from reprocessing plants. In the work of Snyder *et al.* (2010) after analyzing rivers, lakes and shallow seawater samples from the austral hemisphere they conclude that isotopic ratios and concentrations levels range from pre-anthropogenic to a-bombs $^{129}$I values [5].

Thyroids of grazing animals act as sensitive probes to assess the fallout of $^{129}$I in environmental studies such as retrospective dosimetry of the $^{131}$I exposure after the Chernobyl accident [6]. Thyroid hormones require iodine for their synthesis and therefore this element is naturally concentrated in those glands, up to 5 orders of magnitude higher compared to the animal diet. The major intake of iodine in cattle is via the ingestion of fresh pasture. Cattle contain 10 to 30 mg of iodine in their bodies, of which more than 90% is contained in their thyroid gland. Iodine content in thyroids is modulated by its biological half-life, estimated as 100 days, and provides a time-integrated signal [7].

The present work investigates the presence of $^{129}$I in South America by measuring $^{129}$I/$^{127}$I concentration ratios in grazing animal thyroids coming from samples collected at different latitudes in Argentina. These are the first measurements of Southern Hemisphere samples covering a large latitudinal range measured via AMS. Also, we are interested in estimating the origin of $^{129}$I in the Southern Hemisphere. For this reason, natural and anthropogenic contributions to its inventory were analysed.

## 2. Experimental

Between July 2009 and April 2010, thyroids of grazing animals were collected fresh from slaughter houses located at ten different sampling locations ranging between 27ºS and 51ºS (see Fig. 1). From each sampling site adult animals with an age of 3 to 4 years were taken from a herd that grazed fresh pastures at a known location close to the slaughter house for at least one year prior to their thyroid donation. The studied animals did not receive any dietary supplement therefore it is assumed that there is no difference in the diet of the studied animals.

After being lyophilised and homogenised, the collected samples were chemically processed at the TANDAR Laboratory in Buenos Aires. The extraction of iodine for the determination of $^{127}$I and $^{129}$I were based in two methods developed at LLNL [8; 9], and were adapted for this particular matrix where very low $^{129}$I concentration values are expected.

We selected 100 mg of dry-freezed thyroid and applied the following procedure: First, the sample was oxidized in a basic solution of peroxydisulfate. From this solution, we prepared the derivative to determine total iodine by gas chromatography (GC). In a 100 ml separation funnel, we combined 200 µl aliquot of the sample solution with 25 ml of water, 1 ml of 4% pentan-3-one, 1 ml of 30% hydrogen peroxide and 2 ml of 5M sulphuric acid. The derivative was extracted in hexane. The iodo-derivative was measured using a Hewlett-Packard HP5890 Series II gas chromatograph with HP PAS-1701 and Zebron ZB-5 capillary columns and electron-capture detector. Chromatograph and detector operation parameters used were taken from Gu *et al.* (1997). Iodine concentrations were determined as the average of three measurements with each column. For the determination of $^{129}$I, 2 ml of a KI solution (Merck Suprapur®, 1000 μg/ml) were added as carrier into a 250 ml separation funnel with the rest of the sample solution, followed by concentrated nitric acid to adjust pH~1 and then 400 μl of silver nitrate solution (5% m/V), to precipitate silver iodide. The precipitate was thereafter washed and left in the oven to dry overnight, and finally mixed with silver and pressed in a sample holder for AMS measurements.

$^{129}$I/$^{127}$I ratios of the prepared samples were measured at the Vienna Environmental Research Accelerator (VERA) [10]. While the $^{127}$I$^{4+}$ beam was measured at a Faraday cup (currents between 0.1 - 3 μA), the $^{129}$I ions were identified and counted individually by a time-of-flight and a Bragg detector. The $^{129}$I/$^{127}$I ratio of five calibration standards – made from the same material as used in the work of ref. [11], with well-known values ranging from $10^{-9}$ to $10^{-12}$ – were measured along with samples for normalization purposes. Moreover, the concentration in blank samples was also measured to determine the background level to be subtracted. In this way, $^{129}$I/$^{127}$I ratios as low as $(8.3\pm2.4)\times10^{-14}$ were measured. The isotope ratios of thyroid samples were at least one order of magnitude above the chemical blank level, $(3.6\pm0.5)\times10^{-13}$, except for one sample (only a factor 3).

## 3. Results and Discussion

### <u>*Relationship between iodine isotopes*</u>

One way to survey the relationship between iodine and $^{129}$I sources is by plotting the variation of $^{129}$I/$^{127}$I ratios as a function of the iodine content measured (see Fig. 2). The results collected in the present work are listed in Table 1. The solid-line in Figure 2 corresponds to a linear fit of our data, while the dashed-line to a fit reported for bovine thyroids from Taiwan [12]. These fits are described as

$$\log\,(^{129}\mathrm{I}/^{127}\mathrm{I}) = -0.844 \log {}^{127}\mathrm{I} + 8.18 \qquad \text{[present work]}$$

$$\log\,(^{129}\mathrm{I}/^{127}\mathrm{I}) = -0.523 \log {}^{127}\mathrm{I} + 2.46 \qquad \text{[12]}$$

A $d(\log {}^{129}\mathrm{I}/^{127}\mathrm{I})/d\log(^{127}\mathrm{I}) = -1$ corresponds to a complete decorrelation between the sources of both isotopes, while a value close to 0 should be associated to a single relevant source for both isotopes.

Worldwide, the main source of atmospheric $^{127}$I is the ocean volatilization [13]. The principal sources for atmospheric $^{129}$I are the nuclear fuel reprocessing plants (despite that the major part of their $^{129}$I production goes into the sea) and the fallout of this material can occur far away either over land or sea. The fraction falling in the sea is mixed up with $^{127}$I, and both isotopes can be re-emitted giving rise to a correlated component, whereas the fraction falling directly on land is not correlated with any $^{127}$I. Latitudinal variations of both iodine isotopes abundances and isotopic ratio of the samples reflect this behaviour [14].

Fig. 2 also shows measured values from human and bovine thyroids stemming from Chile (**A**), concentration ratio $^{129}$I/$^{127}$I in ovine thyroids from Australia (**B**) [15], and pre-anthropogenic ratio **C** measured from thyroid powder in US in 1930's [2; 16]. Values **A** and **B,** which are the only reported ones from samples collected in the Southern Hemisphere, present $^{129}$I/$^{127}$I ratios larger than the ones obtained in the present work. One should mention that they were measured by Radiochemical Neutron Activation Analysis (RNAA), a technique which does not reach the sensitivity required for the detection of extremely low $^{129}$I concentrations [17], as expected from Southern Hemisphere's samples.

## *$^{129}$I Southern hemisphere's inventory*

To understand the possible sources of the total $^{129}$I inventory in the Southern Hemisphere one needs to study its natural and man-made contributions and the actual ratio between them. The natural contribution of $^{129}$I can be estimated from a dynamic model of the global iodine cycle [18] and a pre-anthropogenic $^{129}$/$^{127}$I ratio for one compartment. The ocean is the principal iodine source for superficial compartments (atmosphere, surface soil and terrestrial biosphere). Taking into account a concentration in sea water of 50 μg/L, the surface of the Southern Hemisphere's ocean of $2\times10^{8}$ km$^{2}$ and an average depth of 4 km, an estimate of the total iodine mass yields $4.1\times10^{13}$ kg. Only 2% of this oceanic iodine remains in the mixed layer (from 0 to 75 m depth). Assuming a pre-anthropogenic $^{129}$I/$^{127}$I ratio of $1.5\times10^{-12}$ for sea water [19], there are 1.2 kg of $^{129}$I in Southern hemisphere ocean mixed layer. According to Kocher [18], there are $8.3\times10^{7}$ kg of iodine in "ocean atmosphere" and $5.7\times10^{6}$ kg in "land atmosphere", and under the assumption of uniform hydrospheric ratio, this corresponds to only $6.2\times10^{-5}$ and $4.3\times10^{-6}$ kg of $^{129}$I, respectively, in the Southern Hemisphere. Terrestrial biosphere and surface soil region have a $^{129}$I pre-anthropogenic inventory of $2.3\times10^{-4}$ and 0.32 kg, respectively.

From 1952 to 1974, a total of 543 nuclear atmospheric tests were detonated, only 61 of them in the Southern Hemisphere, with a total fission yield estimated in 189 Megatons [20; 21]. From these, about 160 Mt equivalent are estimated to have been widely dispersed, contributing to global fallout. Based on worldwide integrated deposition $^{90}$Sr measurements around 40 Mt equivalent were deposited in Southern hemisphere. Assuming a yield of 280 mg

$^{129}$I (50 μCi) per kiloton [3], these tests added 11 kg to the atmosphere. This is 60% of the integrated deposition estimated made by Reithmeier *et al.* [4; 22].

A hint about how this material has changed present day inventories for the different compartments can be obtained simulating its evolution among them. Figure 3 shows the evolution of the $^{129}$I yield of a 50 kiloton device detonated in ocean atmosphere based on Kocher's geochemical model cycle for iodine [18]. The peak of the atmospheric a-bomb tests in the Southern Hemisphere was 45 years ago and if one assumes that all the radioactive material was injected at that time, about 85% of the $^{129}$I injected amount is now in the deep ocean compartment. The other 15% increased the inventories of the atmosphere and the ocean mixed layer by 100% (which is related with re-emission). In this way, the $^{129}$I content in surface soil and terrestrial biosphere increased by 160% in its $^{129}$I content. From this, it seems that nowadays there are similar contribution in surface compartment inventories from nuclear tests and natural sources.

In the Northern Hemisphere the main source of atmospheric $^{129}$I is the nuclear fuel reprocessing plants by means of direct airborne releases (750 kg), from which 60% mixes with air and is available for long transport processes [4]. A minor, but not negligible, proportion of the re-emission to the atmosphere is due to the liquid discharges of these plants. Inter-hemispheric transport of $^{129}$I is usually neglected or not taken into account [23]. However, if only 1% of this long transport available material crosses the equator, the injected material into the Southern inventory would be close to half of the material deposited due to atmospheric nuclear tests.

Fehn *et al.* (2000) [24] pointed out that the reprocessing plants placed in the Northern Hemisphere are the main $^{129}$I source for the Southern Hemisphere. On the other hand, Reithmeier *et al.* (2010) estimated that nuclear atmospheric tests are the main anthropogenic supplier. Snyder *et al.* (2010) points out that samples from the Southern hemisphere generally range from pre-anthropogenic to bomb $^{129}$I values. They came to this conclusion after analysing data from 35 samples from the Southern Hemisphere hydrosphere. This is in agreement with our estimation of a similar contribution from natural and nuclear tests fallout for the $^{129}$I inventory.

## 4. Conclusions

We measured $^{129}$I/$^{127}$I ratios and iodine concentrations in animal thyroids stemming from Argentina using the AMS and GC techniques, respectively. A relationship of the $^{129}$I/$^{127}$I ratio with iodine content in the thyroid gland of bovine animals was found. The low correlation between sources implies a low impact of the $^{129}$I re-emission process in Argentina.$^{129}$I concentrations and isotopic ratio levels obtained in this work are significantly lower than those reported previously for samples stemming from the Southern Hemisphere measured via RNAA, being our values significantly lower than those found previously.

Natural and anthropogenic contributions to the $^{129}$I inventory in the Southern Hemisphere were analysed. It can be concluded that natural sources and nuclear tests have similar contributions.

## Acknowledgment

A. Arazi and A. E. Negri want to express their gratitude to the staff of the VERA laboratory for their kind hospitality during their visits. This work was partially supported by a grant PICT 32757 from Agencia Nacional de Promoción Científica y Técnica (Argentina). The authors want to thank P.F.F. Carnelli for his collaboration during the work.

## References

[1] J. Fabryka-Martin, H. Bentley, D. Elmore, and P.L. Airey, “Natural iodine-129 as an environmental tracer”. Geochim. et Cosmochim. Acta, 49 (1985) 337.

[2] A. Schmidt, C. Schnabel, J. Handl, D. Jakob, R. Michel, H.A. Synal, J.M. Lopez, and M. Suter, “On the analysis of iodine-129 and iodine-127 in environmental materials by accelerator mass spectrometry and ion chromatography”. Sci. Total Environ., 223 (1998) 131.

[3] H. Reithmeier, V. Lazarev, W. Rühm, and M. Schwikowski , H.W. Gäggeler, and E. Nolte, “Estimate of European $^{129}$I releases supported by $^{129}$I analysis in an Alpine Ice Core”. Environ. Sci. Technol., 40 (2006) 5891.

[4] H. Reithmeier, V. Lazarev, W. Rühm, and E. Nolte, “Anthropogenic $^{129}$I in the atmosphere: Overview over major sources, transport processes and deposition pattern”. Sci. Total Environ., 408 (2010) 5052.

[5] G. Snyder, A. Aldahan, and G. Possnert, “Global distribution and long-term fate of anthropogenic 129I in marine and surface water reservoirs”. Geochem. Geophys. Geosyst., 11 (2010) 1.

[6] L. Van Middlesworth, J. Handl, and P. Johns, “Iodine-129 in thyroid glands: A sensitive biological marker of fission product exposure”. J. Radioanal. and Nuc. Chem., 245 (2000) 447.

[7] National Council on Radiation Protection and Measurements, “Iodine-129: Evaluation of releases from nuclear power generation”. NCRP Report No. 75, 1983.

[8] F. Gu, A. Marchetti, and T. Straume, “Determination of Iodine in Milk and Oyster Tissue samples Using Combustion and Peroxydisulfate Oxidation”. Analyst, 122 (1997) 535.

[9] A. Marchetti, F. Gu, R. Robl, and T. Straume, “Determination of total iodine and sample preparation for AMS measurement of $^{129}$I in environmental matrices”. Nucl. Instr. and Meth. B, 123 (1997) 352.

[10] P. Steier, R. Golser, W. Kutschera, A. Priller, C. Vockenhuber, and S. Winkler, “VERA, an AMS facility for “all” isotopes”. Nucl. Instr. and Meth. B, 223-224 (2004) 67.

[11] H. Reithmeier, V. Lazarev, F. Kubo, W. Rühm, and E. Nolte, “129I in precipitation using a new TOF system for AMS measurements”. Nucl. Instr. and Meth. B, 239 (2005) 273.

[12] J.H. Chao, and C.L. Tseng, “$^{129}$I concentrations of mammalian thyroids in Taiwan”. Sci. Total Environ., 193 (1996) 111.

[13] D.C. Whitehead, “The distribution and transformations of iodine in the environment”. Environ. Int., 10 (1984) 321.

[14] A.E. Negri, J.O. Fernández Niello, A. Wallner, A. Arazi, and P. Steier, “Iodine-129 in animal thyroids from Argentina”. Sci. Total Environ., 430 (2012) 231.

[15] J. Handl, “Concentrations of $^{129}$I in the Biosphere”. Radiochim. Acta, 72 (1996) 33.

[16] S. Szidat, A. Schmidt, J. Handl, D. Jakob, W. Botsch, R. Michel, H.A. Synal, C. Schnabel, M. Suter, J.M. López-Gutierrez, and W. Städe, “Iodine-129: Sample preparation, quality and analyses of pre-nuclear materials and of natural waters from Lower Saxony, Germany”. Nucl. Instr. and Meth. B, 172 (2000) 699.

[17] X. Hou, V. Hansen, A. Aldahan, G. Possnert, O.C. Lind, and G. Lujaniene. “A review on speciation of iodine-129 in the environmental and biological samples”. Anal. Chim. Acta, 632 (2009) 181.

[18] D.C. Kocher, “Dynamic model of the global iodine cycle and estimation of dose to the world population from releases of Iodine-129 to the environment”. Health Hazards, 5 (1981) 15.

[19] U. Fehn, J.E. Moran, G.T. Snyder, and Y. Muramatsu, “The initial $^{129}$I/I ratio and the presence of ‘old’ iodine in continental margins”. Nucl. Instr. and Meth. B, 259 (2007) 496.

[20] US Department of Energy, “United States Nuclear Tests July 1945 through September 1992”, DOE/NV—209-REV 15, 2000.

[21] International Atomic Energy Agency, “The Radiological Situation at the atolls of Mururoa And Fangataufa Atolls”. Radiological assessment reports series, 1998.

[22] H. Reithmeier, private communication.

[23] J.E. Moran, S. Oktay, P.H. Santschi, D.R. Schink, “Atmospheric dispersal of $^{129}$I from nuclear fuel reprocessing facilities”. Environ. Sci. Technol., 33 (1999) 2536.

[24] U. Fehn, and G. Snyder, “$^{129}$I in the Southern Hemisphere: Global redistribution of an anthropogenic isotope”. Nucl. Instr. and Meth. B, 172 (2000) 366.

**Table 1.** $^{127}$I and $^{129}$I/$^{127}$I ratios measured in animal thyroid samples from several locations of Argentina. Dry wt means dry weight of thyroid.

**Fig. 1.** Map of South America showing the sampling points locations.

**Fig. 2.** Relationship of $^{129}$I/$^{127}$I ratio with iodine concentration in the thyroid gland. Solid line corresponds to a linear fit of our data. Dashed line corresponds to a linear fit reported by Chao and Tseng (1996) [12] from Taiwanese thyroid samples. **A** represents the plot region where values measured of human and bovine thyroids from Chile (1985/6) are placed. **B** and **C** show reported $^{129}$I/$^{127}$I ratios levels measured in ovine thyroids from Australia (1957 and 1986) [14] and pre-anthropogenic level in thyroid [2; 15], respectively. See text for details.

**Fig. 3.** Contribution to compartment inventories vs. time for a 50 kiloton device detonated in ocean atmosphere in 1965. Nowadays (shown by the arrow) most of the $^{129}$I injected is in the deep ocean.

**Figure 1**

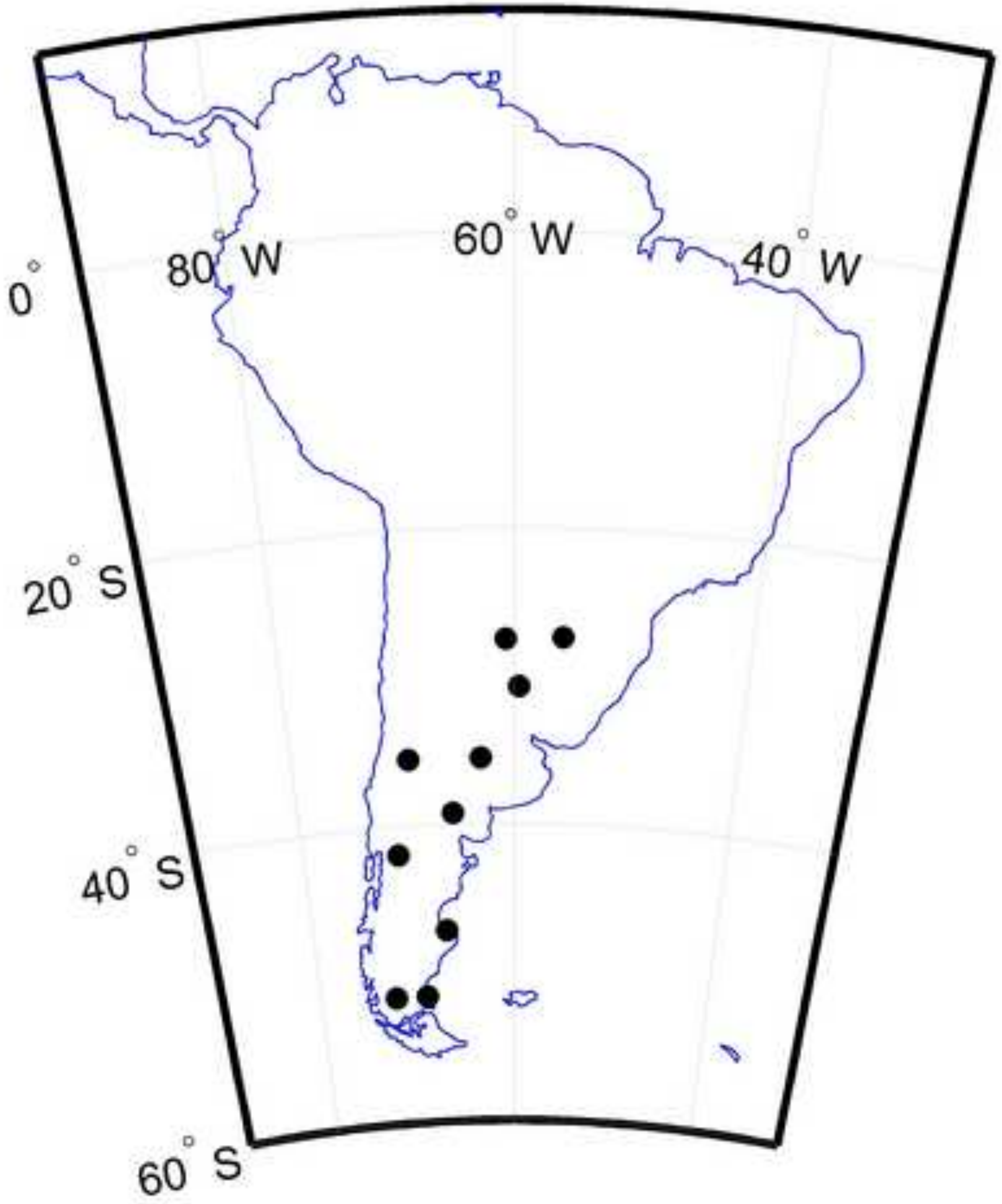

Figure 2

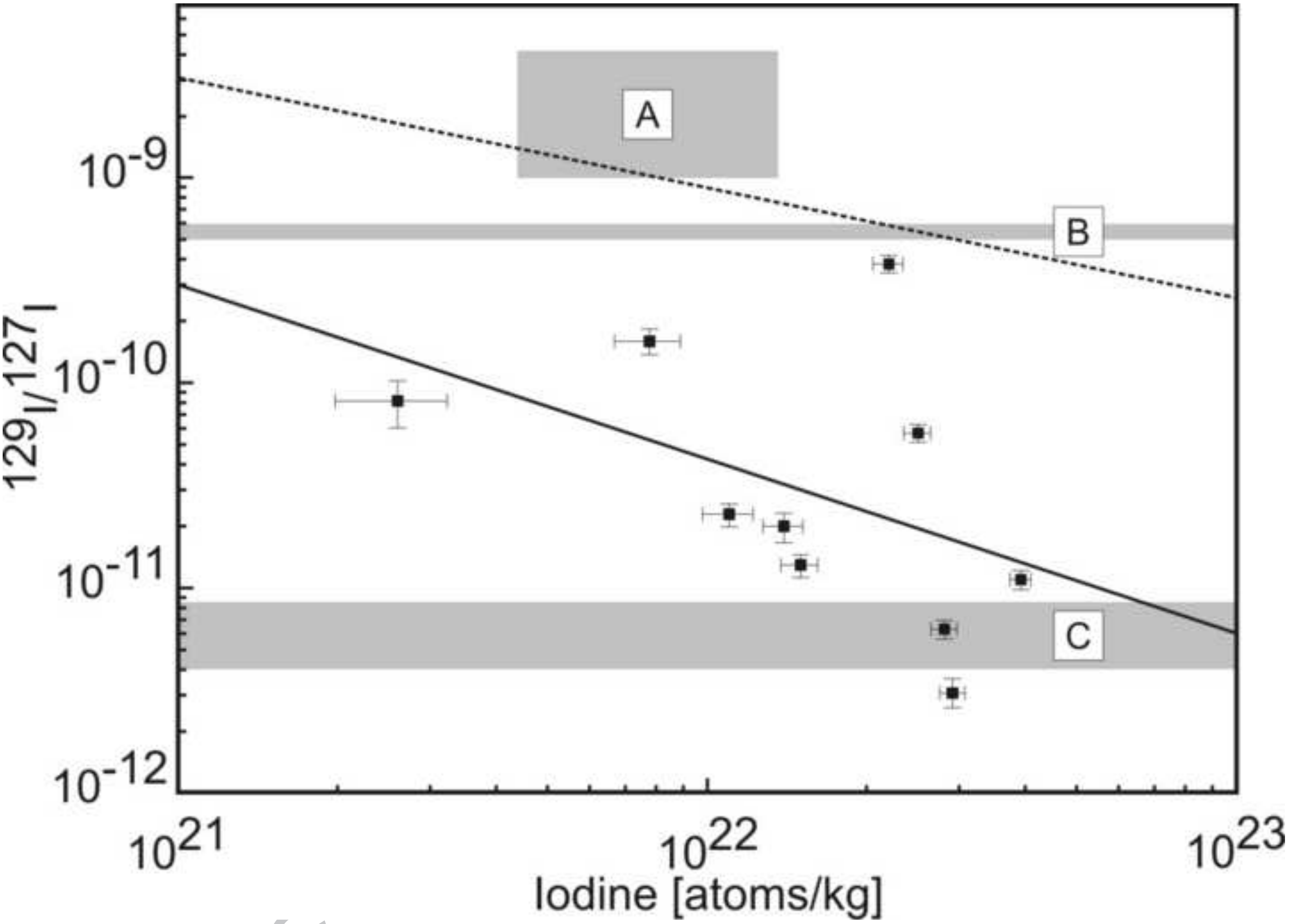
A
B
C
$10^{-9}$
$10^{-10}$
$10^{-11}$
$10^{-12}$
$^{129}I/^{127}I$
$10^{21}$
$10^{22}$
$10^{23}$
Iodine [atoms/kg]

Figure 3

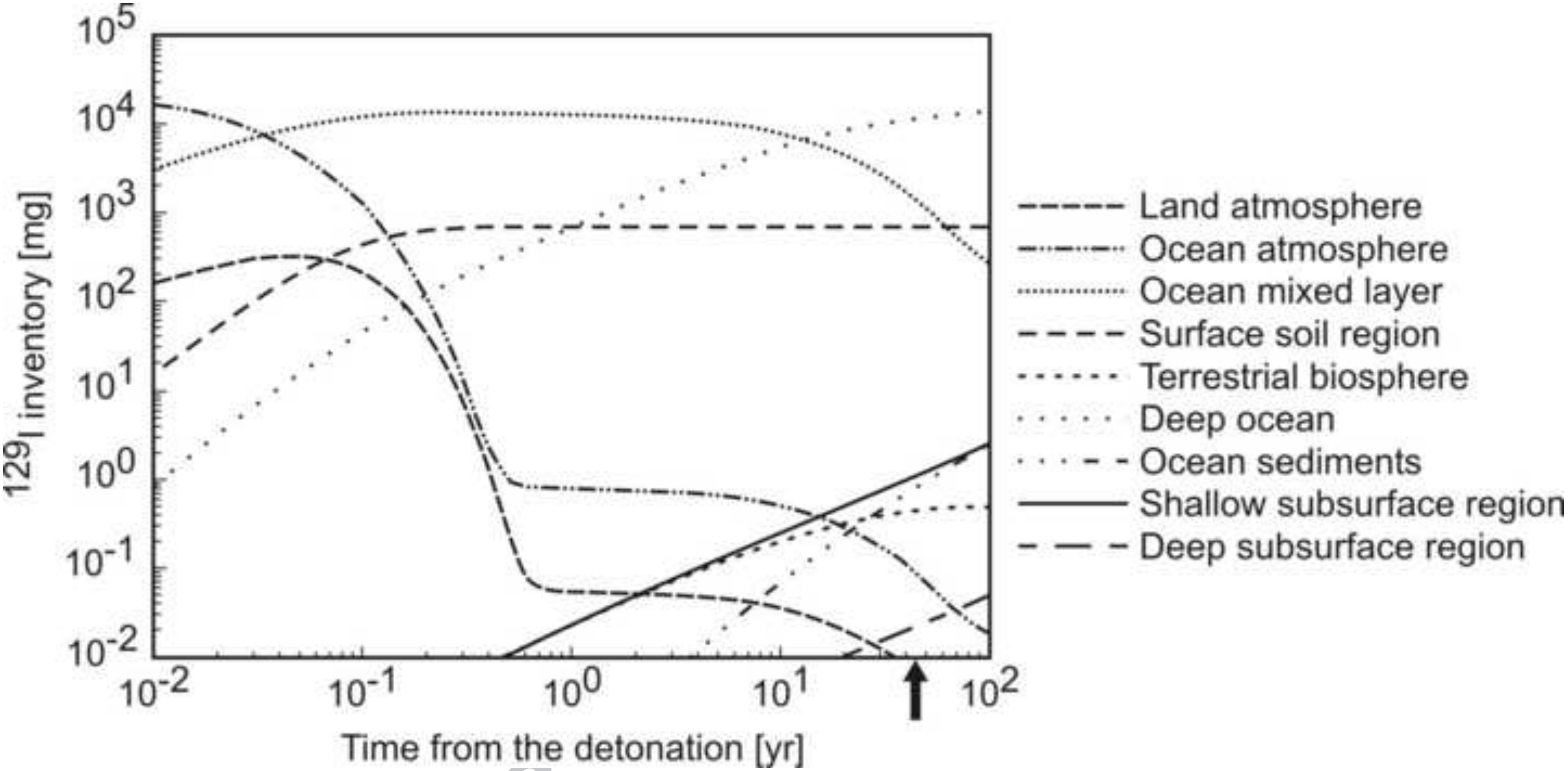
$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
$10^{-1}$
$10^{-2}$
$^{129}$I inventory [mg]
$10^{-2}$
$10^{-1}$
$10^0$
$10^1$
$10^2$
Time from the detonation [yr]
Land atmosphere
Ocean atmosphere
Ocean mixed layer
Surface soil region
Terrestrial biosphere
Deep ocean
Ocean sediments
Shallow subsurface region
Deep subsurface region

Table 1

| Location | Date | Iodine [mg/g dry wt.] | $^{129}I/^{127}I$ ($10^{-11}$) | Lat(S) | Long(W) |
|---|---|---|---|---|---|
| Villa Ángela | Jul-09 | 5.3±0.3 | 5.7±0.4 | 27.5 | 60.7 |
| La Paz | Jul-09 | 3.0±0.3 | 2.0±0.3 | 30.7 | 59.6 |
| Rivadavia | Jul-09 | 3.1±0.3 | 1.2±0.1 | 35.5 | 63 |
| Malargüe | Sep-09 | 2.4±0.3 | 2.3±0.2 | 35.5 | 69.5 |
| Choele Choel | Sep-09 | 0.5±0.3 | 8.2±0.8 | 39.2 | 65.7 |
| Posadas | Apr-10 | 4.6±0.3 | 38±2 | 27.4 | 55.9 |
| Ñorquinco | Apr-10 | 1.6±0.3 | 16±1 | 41.9 | 71 |
| B. Mazaredo | Apr-10 | 8.1±0.3 | 1.1±0.1 | 47.1 | 66.7 |
| Río Turbio | Apr-10 | 5.8±0.3 | 0.6±0.1 | 51.5 | 72.2 |
| Río Gallegos | Apr-10 | 6.2±0.3 | 0.3±0.1 | 51.5 | 69 |