



## Tracing the upwelling process in the northern Benguela upwelling system (nBUS) by $^{129}\text{I}$

José María López-Gutiérrez <sup>a,b,\*</sup>, Deon C. Louw <sup>c</sup>, Martina Rožmarić <sup>d</sup>,  
Victoria Lérída-Toro <sup>a</sup>

<sup>a</sup> Centro Nacional de Aceleradores (CNA), Universidad de Sevilla. Junta de Andalucía. Consejo Superior de Investigaciones Científicas, Parque Científico y Tecnológico Cartuja, Thomas Alva Edison 7, 41092, Sevilla, Spain

<sup>b</sup> Universidad de Sevilla. Departamento de Física Aplicada I. Escuela Politécnica Superior, C/ Virgen de África, N° 7, 41011, Sevilla, Spain

<sup>c</sup> National Marine Information and Research Centre (NatMIRC), Ministry of Fisheries and Marine Resources, 1<sup>st</sup> Strand Street, 13000, Swakopmund, Namibia

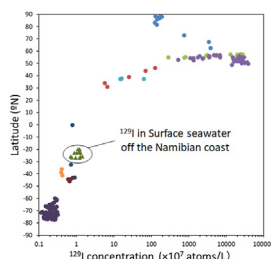
<sup>d</sup> International Atomic Energy Agency, Environment Laboratories, MC 98000, Monaco



### HIGHLIGHTS

- New data on  $^{129}\text{I}$  in seawater from the Southern Hemisphere, where available published data is very limited, is presented.
- Concentrations ( $10^6 - 10^7$  atoms/kg) fit the expected values of the global behaviour of  $^{129}\text{I}$  in the marine environment.
- First set of  $^{129}\text{I}/^{236}\text{U}$  values in the Southern Hemisphere is presented.
- The capacity of  $^{129}\text{I}$  to trace the upwelling process in this zone is shown.

### GRAPHICAL ABSTRACT



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### ABSTRACT

New data on the presence of  $^{129}\text{I}$  in seawater in the Southern Hemisphere measured by Accelerator Mass Spectrometry (AMS) is presented. The samples were collected in 2014 along the Namibian coast during a cruise organised by the National Marine Information and Research Centre (NatMIRC), the national laboratories of the Ministry of Fisheries and Marine Resources (MFMR) in Namibia, and the IAEA Environment Laboratories (IAEA NAEL) in Monaco. The Benguela upwelling system is known as one of the most important marine upwelling regions in the world. Strong winds induce an offshore transport of surface seawater which is substituted by cool subsurface water inshore. As this water is nutrient-rich, which leads to high primary productivity, the Benguela upwelling system has a very important role as a fishing production area. The  $^{129}\text{I}$  concentrations in samples were between  $(0.66 \pm 0.14) \times 10^7$  and  $(1.45 \pm 0.30) \times 10^7$  atoms/kg. The highest  $^{129}\text{I}$  concentrations were found in the offshore surface samples. Deep-sea and inshore samples contained lower  $^{129}\text{I}$  concentrations, possibly as an effect of the upwelling process. A comparison with previously published studies suggests that the presence of  $^{129}\text{I}$  in the northern Benguela upwelling system (nBUS), is mainly due to the impact of nuclear weapons global fallout, without any evident impact of nuclear fuel reprocessing.

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\* Corresponding author. Centro Nacional de Aceleradores (CNA), Universidad de Sevilla. Junta de Andalucía. Consejo Superior de Investigaciones Científicas, Parque Científico y Tecnológico Cartuja, Thomas Alva Edison 7, 41092, Sevilla, Spain.

E-mail address: [lguti@us.es](mailto:lguti@us.es) (J.M. López-Gutiérrez).

### 1. Introduction

The presence of  $^{129}\text{I}$  ( $T_{1/2} = 15.7 \times 10^6$  years) in the environment

has changed significantly since the beginning of the nuclear era. The main anthropogenic activities that have released this radionuclide into the biosphere include atmospheric nuclear weapons tests, nuclear accidents and discharges from nuclear fuel reprocessing plants. Nuclear bomb tests carried out between 1945 and the 1980s were responsible for the presence of approximately 90 kg  $^{129}\text{I}$  in the environment (Hou, 2004; Raisbeck and Yiou, 1999) while nuclear fuel reprocessing plants have discharged more than 6000 kg (He et al., 2013). The impact of nuclear accidents has not been so severe, and it has been estimated that, e.g. between 1 and 6 kg of  $^{129}\text{I}$  were released into the atmosphere after the Chernobyl accident (Aldahan et al., 2007; Paul et al., 1987). The influence of these activities has not been homogeneous on the planet, as the Northern Hemisphere has been especially affected (Reithmeier et al., 2010). The most important nuclear fuel reprocessing plants, Sellafield (United Kingdom) and La Hague (France), release  $^{129}\text{I}$  mainly in liquid form (He et al., 2013), most of which is transported by currents to the North Sea and from there to the Arctic Ocean along the Norwegian coast (Villa et al., 2015; Vivo-Vilches et al., 2018). Atmospheric releases by these reprocessing plants also contain  $^{129}\text{I}$ . However, as  $^{129}\text{I}$  is directly released to the troposphere, the distribution and therefore the impact on the Southern Hemisphere is low (Xing et al., 2015). The distributions of the released radionuclides were more homogeneous with the nuclear bomb tests, the most powerful of which were carried out during the 1950s and 1960s in the Northern Hemisphere. A significant part of the released radioactivity was injected into the stratosphere, distributed in it and slowly deposited on the whole planet surface, having a more homogeneous impact.

Therefore, average  $^{129}\text{I}$  concentrations in the hydrosphere increased from natural levels of  $\sim 4 \times 10^5$  to  $\sim 1.16 \times 10^7$  atoms/kg due to nuclear bomb tests and to  $\sim 10^9$  atoms/kg in the Northern Hemisphere from reprocessing (Snyder et al., 2010). However,  $^{129}\text{I}$  concentrations up to  $10^{11}$ – $10^{12}$  atoms/kg have been measured in certain zones of the Northern Hemisphere (Hou et al., 2007).

A much lower impact on the Southern Hemisphere explains the scarcity of the available data in the literature about the presence of  $^{129}\text{I}$  in this area of the planet. Nevertheless,  $^{129}\text{I}$  conservative behaviour in seawater makes it a very important tracer of environmental processes, especially in the hydrosphere (Edmonds et al., 1998; Raisbeck et al., 1995). Moreover, during recent years, its tracer properties have been enhanced by its combined use with other conservative radionuclides such as  $^{236}\text{U}$  (Castrillejo et al., 2017; Christl et al., 2015). Additionally, its long half-life can help reconstruct the impact of other iodine radioisotopes in the case of nuclear accidents (Gómez-Guzmán et al., 2017). These properties demonstrate the requirement to increase our knowledge about the presence of  $^{129}\text{I}$  and its transport mechanisms, especially in areas in which less information is available.

In this work, the results on the  $^{129}\text{I}$  levels in seawater samples collected in 2014 off the Namibian coast (from 20°S to 27°S) are presented. From a global point of view, the presented data is relevant as no data on seawater systems is available for these latitudes and very little for other latitudes in the Southern Hemisphere. The Namibian coast is part of the Benguela upwelling system (BUS), which is one of the most important upwelling systems in the world with high primary production (Carr and Kearns, 2003; Duncombe Rae, 2005; Shannon and Nelson, 1996). Strong equatorial wind stress induces offshore transport of surface water, which is replaced by cool, nutrient-rich subsurface water, which creates a fishery rich environment. The Benguela upwelling system is divided in the northern and southern Benguela upwelling systems (nBUS and sBUS, respectively) by the Lüderitz upwelling cell, which is the main upwelling cell. Apart from the main upwelling cell smaller

coastal upwelling cells are also found close to Conception Bay, south of Walvis Bay, Cape Frio and Palgrave Point (Boyer et al., 2000) (Fig. 1). During austral spring and summer, the southeasterly winds promote upwelling in the sBUS (south of Hondeklip Bay, about 30°18'S) and during austral winter and spring in the nBUS, from approximately Cape Cross (21°46'S) to north of Cape Frio (18°26'S), however upwelling conditions are almost perennial at the main upwelling cell (from about 26°S to 28°S), (Shannon and Nelson, 1996). It is relevant to study the effect of the upwelling process on  $^{129}\text{I}$  concentration and radioactive impact on this area.

## 2. Material and methods

### 2.1. Sampling

Samples were collected in May 2014 off the Namibian coast. During this period, a sampling campaign was organised by the National Marine Information and Research Centre (NatMIRC) in Namibia, and the IAEA Environment Laboratories (IAEA NAEL) in Monaco. The aim was to establish baseline levels for a series of anthropogenic and natural radionuclides. The sampling points covered a large area from 20°S to 27°S latitudes from (Fig. 1). At each seawater sampling station, samples were taken from the surface ( $\pm 2$  m) by pumping water using a vessel pumping system and at different depths by using Niskin bottles attached to a rosette and a CTD instrument. Samples for  $^{129}\text{I}$  analysis were sent to the Centro Nacional de Aceleradores (CNA) without pre-treatment.

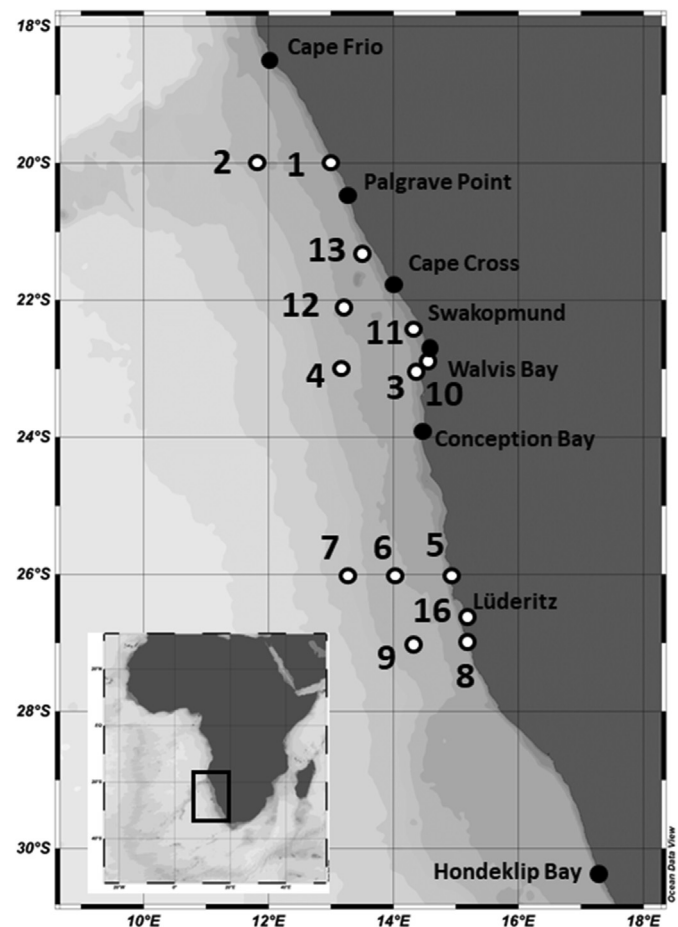


Fig. 1. Sampling locations along the Namibian coast. Plot made with Ocean Data View (Reiner and Schlitzer, 2020).

Results were obtained for 18 seawater samples, 14 surface samples and four deep stations. Oceanographic data (salinity, temperature, and oxygen) was measured during the survey and used for results interpretation.

## 2.2. Sample preparation

The radiochemical method which was used is based on (Muramatsu et al., 2008). Approximately 0.5 L of filtered (Sartorius™ 0.45 μm) seawater was used for  $^{129}\text{I}$  determination. At first, 2 mg of stable iodine carrier was added. As only isotopic ratios  $^{129}\text{I}/\text{I}$  are measured in Accelerator Mass Spectrometry (AMS), the  $^{129}\text{I}$  in the samples was obtained by multiplying the isotopic ratio times the amount of stable iodine added, as the original stable iodine was negligible. Decomposition of organic matter and oxidation of iodine species to iodate ( $\text{IO}_3^-$ ) was carried out by the addition of NaOCl. The sample was kept in an automatic shaker for 30 min at 150–200 rpm and it was stored in darkness for at least 12 h. Then, sodium bisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) and hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) were added for reduction of iodate ( $\text{IO}_3^-$ ) to iodide ( $\text{I}^-$ ) so that all iodine was in the same chemical form. After that, solvent extraction procedure was performed. Sodium nitrite ( $\text{NaNO}_2$ ) 0.45 g/mL and nitric acid were used to oxidize iodide ( $\text{I}^-$ ) to molecular iodine ( $\text{I}_2$ ), as this chemical form is more soluble in the organic dissolvent ( $\text{CHCl}_3$ ) which was used for extraction. Back extraction was done in an aqueous solution of 30 mL  $\text{H}_2\text{O}$ -MQ and 0.5 mL of hydrazine ( $\text{NH}_2\text{-NH}_2$ ) 80%. Hydrazine acts as a powerful reduction agent of iodine into iodide. After these two consecutive extractions, the iodine was purified. We acidified the iodine solution with nitric acid and  $\text{AgNO}_3$  was added in excess in order to precipitate silver iodide ( $\text{AgI}$ ). Finally,  $\text{AgI}$  was dried and mixed with Nb powder (1:1) to increase its thermal and electrical conductivity.

## 2.3. Accelerator Mass Spectrometry measurements

$^{129}\text{I}$  measurement was carried out at the CNA in Seville (Spain) by Accelerator Mass Spectrometry (AMS). Details on the facility and the AMS measurement can be found in (Calvo et al., 2015), although some processes have changed with respect to  $^{129}\text{I}$  measurement. Iodine is extracted from the Cs sputtering ion source as  $\text{I}^-$  and injected into the accelerator through an injector magnet. Typical  $\text{I}^-$  are around 1–2 μA in the low energy side. Terminal voltage is set to 700 kV approximately (instead of a maximum of 1 MV) in order to choose charge state 2+ after stripping. Otherwise, the magnetic rigidity of the  $^{129}\text{I}^{2+}$  ions in the high energy side would be excessive for the magnet. The stripper gas used in this facility is He, which has been shown to give high transmissions for heavy ions in AMS (Vockenhuber et al., 2015). Typical transmission at the accelerator is around 50% for  $^{129}\text{I}^{2+}$  in these conditions. After stripping, a magnetic analyser selects  $^{129}\text{I}^{2+}$  ions and an electrostatic deflector carries the ions to a gas ionization chamber where the energy of the ions is measured.

All samples, standards and blanks were measured for four different cycles in each measurement. One standard is measured for every four or five samples and approximately one blank for every twelve samples. The average raw value of measured blanks is calculated and subtracted to the isotopic ratios obtained for samples and standards. The uncertainty associated to the average blank isotopic ratio was estimated as a maximum between statistical errors and standard deviations of the mean. Then, standard correction is carried out for all sample isotopic ratios. The standard we use at CNA is named Q2 and has a nominal isotopic ratio of  $^{129}\text{I}/^{127}\text{I} = (1.1169 \pm 0.0046) \times 10^{-11}$ . It was obtained from SRM 3231 Iodine-129 Isotopic Standard developed by NIST (NIST Office of Reference Materials, n.d.) and measured at the ETH Laboratory of

Ion Beam Physics (C. Vockenhuber, personal communication). Finally, an average value of the corrected isotopic ratios is calculated. The final uncertainty associated to the isotopic ratio is generally the standard deviation of the mean, as measurement times are chosen so that statistical errors are low enough.

Due to the low amount of  $^{129}\text{I}$  in the Namibian samples, measured isotopic ratios were also low, typically in the order of  $^{129}\text{I}/^{127}\text{I} \sim 10^{-13}$ – $10^{-12}$ . In order to assure the quality of the data, both instrumental and chemical blanks were prepared. Instrumental blank isotopic ratios ( $^{129}\text{I}/^{127}\text{I} \cong 1 \times 10^{-13}$ ) were subtracted from sample measured ratios. A total of five chemical blanks were prepared using the same amount of distilled water as used for the Namibian samples and following the same procedure. The average isotopic ratio after correction was  $(1.83 \pm 0.78) \times 10^{-13}$ . As this value is very similar to the one obtained for the instrumental blanks, the samples were not corrected for hypothetical contamination during sample preparation.

The obtained estimated uncertainties of the results were high due to relatively high amount of carrier added to the original sample to obtain good currents in the AMS measurement. This fact reduces the final isotopic ratio in samples which reach values which are not very different to the instrumental background so the number of counts in the detector is lower and background correction needs to be done. Currently we are carrying out a study on the behaviour of low-current samples in order to reduce background effects. We are also working on the optimization of radiochemical methods to maximise the efficiency of iodine extraction.

## 3. Results and discussion

A compilation of the results of our research is presented in Table 1. The range of  $^{129}\text{I}$  concentrations in seawater samples was between  $(0.66 \pm 0.14) \times 10^7$  and  $(1.45 \pm 0.30) \times 10^7$  atoms/kg. For four stations (2, 4, 6 and 9), surface and deep samples were measured. Results were always lower in deep seawater samples than in surface samples, which we expected because the  $^{129}\text{I}$  source is the atmosphere.

### 3.1. Origin of $^{129}\text{I}$ off the Namibian coast

Most of the available data on  $^{129}\text{I}$  in the marine environment is related to measurements carried out in the Northern Hemisphere. As commented in the introduction, the strong impact of nuclear fuel reprocessing plants, especially at Sellafield and La Hague, has increased the natural levels of  $^{129}\text{I}$  enormously. Measurements in the North Sea and in the English Channel by Hou et al. (2007), showed concentrations in the order of  $10^{11}$  atoms/kg as well as  $^{129}\text{I}/^{127}\text{I}$  isotopic ratios between  $10^{-8}$  and  $10^{-6}$ . This indicates up to six orders of magnitude higher concentrations than the natural level (Snyder et al., 2010). Recently, Castrillejo et al. (2018) measured a transect along the North Atlantic Ocean, and found concentrations between  $7.2 \times 10^7$  atoms/kg near the Portuguese coast and  $77 \times 10^7$  atoms/kg in the Labrador Sea for surface seawater. In the Mediterranean Sea, Castrillejo et al. (2017) measured concentrations in surface seawater between  $4.0 \times 10^7$  and  $13.8 \times 10^7$  atoms/kg, indicating in this case the influence of the Marcoule reprocessing plant.

The limited data available for the Southern Hemisphere shows much lower values of  $^{129}\text{I}$ . Povinec et al. (2011) measured maximum concentrations of  $1.15 \times 10^7$   $^{129}\text{I}$  atoms/kg in the Indian Ocean, which was decreasing to  $0.33 \times 10^7$  atoms/kg in deeper layers. Negri et al. (2013) also measured  $^{129}\text{I}$  in three seawater samples from the Atlantic Ocean near the Argentinian coast, indicating concentrations between  $0.39 \times 10^7$  and  $0.42 \times 10^7$  atoms/L. A more recent study by Xing et al. (2015) reported concentrations between

**Table 1**  
<sup>129</sup>I concentration, <sup>129</sup>I/<sup>236</sup>U ratios and basic oceanographic parameters for seawater samples collected along the Namibian coast.

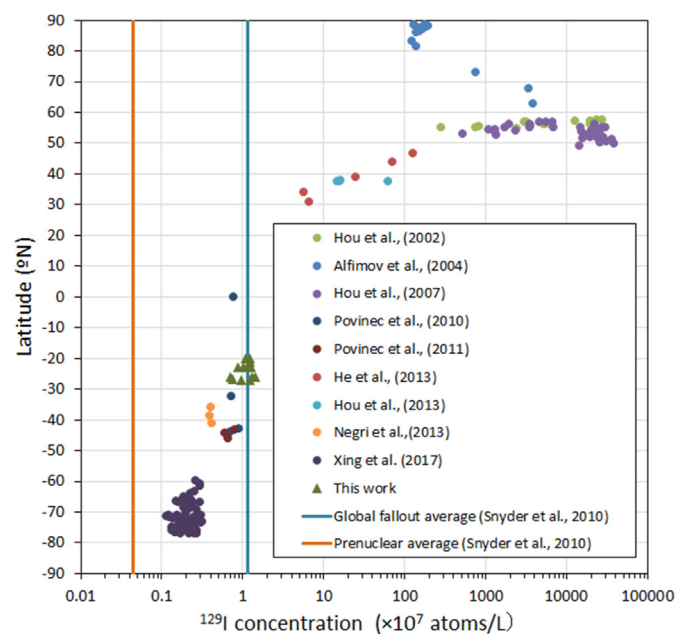
Station code	Station name	Sample	Lat.		Long.	Distance to the shore	Depth	Salinity	Temperature	Oxygen	<sup>129</sup> I concentration		<sup>129</sup> I/ <sup>236</sup> U	
			°N	°E							10 <sup>7</sup> atoms/kg	Error (1σ)	Atom/atom	Error (1σ)
1	20002	1s	-20.0	13.00	3.5	1	35.5	15.2	1.9	1.09	1.09	0.10	2.51	0.24
2	20070	2b	-20.0	11.79	122.6	432	34.7	8.5	1.0	0.782	0.074	—	—	—
		2s				1	35.6	18.0	5.1	1.22	0.11	2.41	0.24	
3	23002	3s	-23.0	14.37	3.4	1	35.3	13.9	1.8	0.87	0.14	1.74	0.43	
4	23070	4b	-23.0	13.14	129.7	342	34.9	9.8	0.9	0.684	0.028	—	—	—
		4s				1	35.3	16.5	4.9	1.28	0.34	2.70	0.73	
5	26002	5s	-26.0	14.92	3.6	1	35.1	11.8	1.7	0.699	0.088	1.61	0.34	
6	26050	6b	-26.0	14.03	89.2	297	34.9	10.0	1.1	0.880	0.050	—	—	—
		6s				1	35.2	15.1	5.8	1.29	0.11	2.28	0.23	
7	26090	7s	-26.0	13.28	166.8	1	35.2	15.6	5.8	1.45	0.30	2.66	0.58	
8	27005	8s	-27.0	15.14	9.7	1	35.2	11.8	2.5	0.95	0.14	2.16	0.33	
9	27050	9b	-27.0	14.30	92.8	363	34.7	8.6	2.4	0.66	0.14	—	—	—
		9s				1	35.1	15.0	5.8	1.217	0.090	2.41	0.21	
10	WBHC	10s	-22.9	14.49	0.1	1	—	—	—	1.005	0.049	2.47	0.20	
11	ZZ1	11s	-22.4	14.30	13.6	1	35.3	13.8	0.0	1.16	0.14	2.37	0.33	
12	ZZ4	12s	-22.1	13.20	34.3	1	35.2	12.2	0.2	1.02	0.26	2.28	0.77	
13	ZZ7	13s	-21.3	13.49	18.4	1	35.4	14.4	1.0	1.218	0.063	2.90	0.22	
16	Lagoon	16s	-26.6	15.14	5.5	1	—	—	—	0.749	0.074	1.90	0.21	

0.141 × 10<sup>7</sup> and 0.25 × 10<sup>7</sup> atoms/L in the Antarctic Ocean. Measured isotopic ratios were between 0.61 × 10<sup>-11</sup> and 1.3 × 10<sup>-11</sup>. In a follow up study in the Antarctic Ocean by the same author <sup>129</sup>I concentrations were in the range of (0.115–0.315) × 10<sup>7</sup> atoms/L and isotopic ratios in the range of (0.61–1.98) × 10<sup>-11</sup> (Xing et al., 2017), so both studies had similar results.

No data has been found in the literature for the South Atlantic eastern coast; however, some data in fresh water from Southern Africa has been published (Snyder and Fehn, 2004). These measurements of <sup>129</sup>I concentrations were typically in the order of 10<sup>6</sup> atoms/L in several locations between 1°S and 25°S with an exceptional value of 6.67 × 10<sup>7</sup> atoms/L at Water Hole (Botswana). Isotopic ratios were between 0.322 × 10<sup>-11</sup> and 106.3 × 10<sup>-11</sup>. Furthermore, Reithmeier (2005) showed measurements of <sup>129</sup>I in Lake Victoria (United Republic of Tanzania, 1.3°S) and Lake Mweru (Democratic Republic of Congo, 9.8°S). He reported concentrations between 0.27 × 10<sup>7</sup> and 0.58 × 10<sup>7</sup> atoms/L and isotopic ratios of 6.060 × 10<sup>-11</sup> and 61.12 × 10<sup>-11</sup>, respectively.

As can be seen in Table 1, the <sup>129</sup>I concentrations along the Namibian coast were approximately 1 × 10<sup>7</sup> atoms/kg or lower for surface samples, which is significantly lower than samples presently measured in the Northern Hemisphere. If an average iodine concentration in the sea of 60 mg/kg is estimated, isotopic ratios would range between 2.3 × 10<sup>-11</sup> and 4.6 × 10<sup>-11</sup>. These ratios show that the influence of discharges from nuclear fuel reprocessing plants is very low. In Fig. 2 a comparison of some results obtained from scientific literature shows <sup>129</sup>I in shallow seawater as a function of latitude. Results presented in this paper are in line with global tendencies and contribute to fill an existing gap regarding studied latitudes. As can also be seen in Fig. 2, the average <sup>129</sup>I concentration in shallow ocean regions calculated by Snyder et al. (2010) is also in good agreement with values measured in this paper. It is likely that the main contribution of the presence of <sup>129</sup>I in the nBUS is mainly due to the effect of global fallout from nuclear weapons tests.

Although <sup>129</sup>I concentrations in lakes from Africa are typically in the order of 10<sup>6</sup> atoms/L, which is up to one order of magnitude lower than the levels in seawater from Namibia, they cannot be directly compared. Snyder et al. (2010) showed that <sup>129</sup>I concentrations in lakes and rivers tend to be one order of magnitude lower than adjacent marine shallow waters but isotopic ratios are much more similar to lakes and rivers. If the expected <sup>129</sup>I/<sup>127</sup>I isotopic ratios which were estimated for Namibian samples,



**Fig. 2.** <sup>129</sup>I concentrations as a function of latitude in surface seawater samples from Namibia (this work) and other data available from literature.

(2.3–4.6) × 10<sup>-11</sup>, are compared with ratios measured in African lakes (Reithmeier, 2005; Snyder and Fehn, 2004), both ratios are similar, as these are typically in the order of 10<sup>-11</sup>. These ratios also coincide with the calculated average isotopic ratio due to nuclear weapons tests calculated by Snyder et al. (2010), which is about 4 × 10<sup>-11</sup>.

It is also possible to estimate the inventory of <sup>129</sup>I in the water column corresponding to the four sampling stations for which deep-sea values were measured (stations 2, 4, 6 and 9). The calculated values are (4.32 ± 0.29), (3.35 ± 0.58), (3.22 ± 0.17) and (3.41 ± 0.31) × 10<sup>12</sup> atoms/m<sup>2</sup>, respectively. These values which were obtained are in line with each other and with the expected average deposition of <sup>129</sup>I due to global fallout, which is in the order of 1 × 10<sup>12</sup> atoms/m<sup>2</sup> (Snyder et al., 2010).

### 3.2. $^{129}\text{I}/^{236}\text{U}$ ratios

The use of the dual tracer  $^{129}\text{I}/^{236}\text{U}$  is very relevant as it has been demonstrated to give additional information in the tracing of environmental processes in comparison to the use of a single radionuclide.  $^{236}\text{U}$  concentrations were previously measured in some of the samples presented in this work (López-Lora et al., 2020). The calculated  $^{129}\text{I}/^{236}\text{U}$  ratios ranged between  $(1.90 \pm 0.21)$  and  $(2.90 \pm 0.22)$  (Table 1). These values can be compared to the samples previously measured in the Arctic Ocean (Casacuberta et al., 2018). A wide range of  $^{129}\text{I}/^{236}\text{U}$  ratios was found in this area: from  $(1 \pm 4)$  in the bottom depths of the Makarov Basin to  $(800 \pm 50)$  in surface samples from the Barents Sea shelf. This difference shows the strong impact of nuclear fuel reprocessing plants again from Sellafield and La Hague. In Casacuberta et al. (2016), the reference  $^{129}\text{I}/^{236}\text{U}$  value for global fallout is estimated to be 0.5, while it increases to 350 for seawater affected by discharges from reprocessing plants. In the case of pre-nuclear levels, the average would also have been higher,  $^{129}\text{I}/^{236}\text{U} = 366$ . The results for the Namibian samples clearly indicate that global fallout is the main component of  $^{129}\text{I}$  presence.

### 3.3. Tracing of water masses in the nBUS using $^{129}\text{I}$

In Table 1 and Fig. 3 the highest  $^{129}\text{I}$  concentrations are typically observed in surface samples collected offshore. Actually, even for samples collected as close as 13.6 km from the coast (sample 11s), the  $^{129}\text{I}$  concentration is already over  $1 \times 10^7$  atoms/kg. On the other hand,  $^{129}\text{I}$  concentrations in deep seawater samples are slightly lower and similar to values found in surface samples taken inshore. Lower concentrations for deep samples are typically expected for regions in which the main input is atmospheric. In the same graph, different colours have been chosen for the four different latitudes for which several samples are available. Inshore samples systematically show lower concentrations of  $^{129}\text{I}$  than surface offshore samples, even if the relatively large errors for some of the measurements are taken into consideration. This could be interpreted as a result of the upwelling processes present in this area. Surface inshore samples could originate from central water samples upwelled near the coast. Then, as this water moves offshore along the surface of the sea, this water mixes with oceanic

surface water and increases its  $^{129}\text{I}$  concentration.

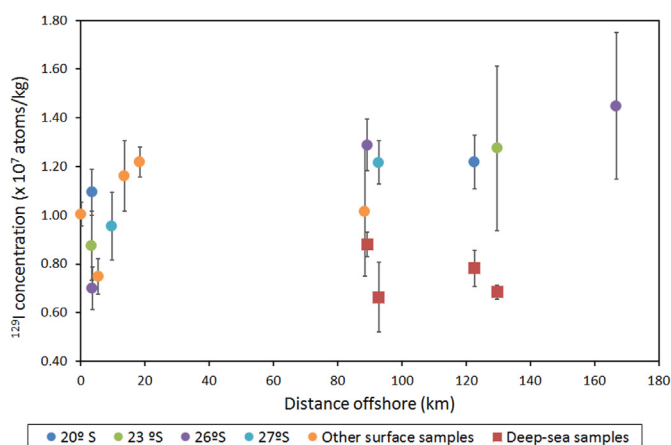
If physicochemical characteristics are analysed for the different samples used in our research (Fig. 4), the distribution is in line with the findings by Duncombe Rae (2005) and Mohrholz et al. (2008). Three water masses can be found: Oceanic Surface Water (OSW), Central Water (CW) and Modified Upwelled Water (MUW). Sample 2s is categorized as OSW, with similar characteristics to the surface water that can be found in the Southern Atlantic outside the tropics. This sample was taken at 20°S and about 120 km offshore. Samples 4s, 6s, 7s, 9s and 12s present typical values which these authors described as MUW. They correspond to surface samples taken offshore and present the highest  $^{129}\text{I}$  concentrations of all the samples. Finally, from their salinity and temperature, the rest of the samples can be considered as CW. This group includes a mixture of deep offshore water and surface inshore water. These results could support the idea that inshore surface samples originate from central waters that emerge close to the shore and would present lower  $^{129}\text{I}$  concentrations than surface samples offshore.

Although  $^{129}\text{I}$  concentration does not present any dependence with latitude when all our samples are included, a certain relationship can be observed if the range is limited to CW samples. In Fig. 5, the  $^{129}\text{I}$  concentration is plotted against latitude. Different colours are used for shallow water samples (<50 m) and deep water samples (>50 m). Despite the large error bars in some cases, shallow water samples present characteristically slightly higher  $^{129}\text{I}$  concentrations in the north than in the south. This effect is not observed in deep water samples. It has been shown that the nBUS is affected by a biannual intrusion of tropical waters, with maxima in October and February (Junker et al., 2017; Mohrholz et al., 2008; Monteiro et al., 2008). The results of our work regarding  $^{129}\text{I}$  distribution could reflect the relative contribution of central waters from the north and south in the region of Namibia. Although the oxygen concentration variability in this region may be modulated by other complex factors (Monteiro et al., 2008), a higher  $^{129}\text{I}$  concentration may be related to a characteristic hypoxia in tropical origin water, caused by the decomposition of sinking organic matter in the Angola gyre (Mohrholz et al., 2008). As iodine plays an important role in organic processes, this phenomenon could enhance the presence of dissolved  $^{129}\text{I}$  in seawater.

If the  $^{129}\text{I}/^{236}\text{U}$  ratio is plotted against the  $^{129}\text{I}$  concentration for the samples belonging to the CW group (Fig. 6), a clear relationship can be observed. The isotopic ratio increases as the  $^{129}\text{I}$  concentration does, so the variability in the  $^{129}\text{I}$  concentrations is not found in  $^{236}\text{U}$ . We have found that both radionuclides have the same origin. So the dependence of  $^{129}\text{I}/^{236}\text{U}$  ratios on  $^{129}\text{I}$  concentration, demonstrates that there is an unknown aspect which affects  $^{129}\text{I}$  and  $^{236}\text{U}$  in a different way to its behaviour in these waters. If the hypothesis given in the previous paragraph about the decomposition of organic matter due to the intrusion of hypoxic water is correct, this means that it would not affect to the presence of dissolved  $^{236}\text{U}$  in the way it affects  $^{129}\text{I}$ .

## 4. Summary and conclusions

A new set of data on the presence of  $^{129}\text{I}$  in the northern Benguela upwelling system presented in this paper increases the scarce amount of data available in literature for the Southern Hemisphere. The  $^{129}\text{I}$  concentrations measured in seawater samples from the Namibian shelf are typically around  $1 \times 10^7$  atom/kg for surface water and lower for deep-sea water. These values suggest that global fallout from the nuclear tests carried out since the 1950's is the main source of  $^{129}\text{I}$  in the northern Benguela ecosystem. This is supported by the calculation of  $^{129}\text{I}/^{236}\text{U}$  ratios, in the order of 1, which are much lower than samples affected by discharges from nuclear fuel reprocessing plants.



**Fig. 3.** Evolution of  $^{129}\text{I}$  concentration in surface water with distance offshore. Different symbols have been chosen for deep water and surface water samples. In addition, different colours have been assigned to the four latitudes for which more than one sample was taken so that the increase of  $^{129}\text{I}$  concentration with the distance offshore can be seen. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

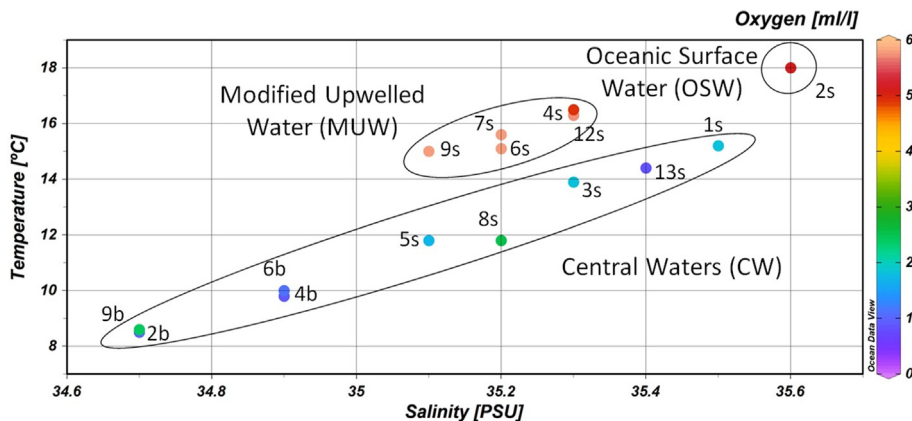


Fig. 4. Physico-chemical parameters of the samples in this work and association to the different water masses present in this region described by Duncombe Rae (2005). Plot made with Ocean Data View (Reiner and Schlitzer, 2020). Samples 10s, 11s and 16s are not included in the plot as their salinity and temperature data were not available.

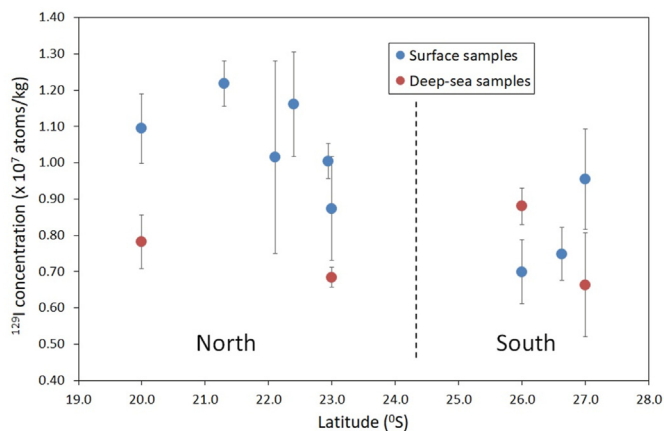


Fig. 5. <sup>129</sup>I concentrations in seawater samples from Namibia classified as Central Waters (CW) as a function of latitude.

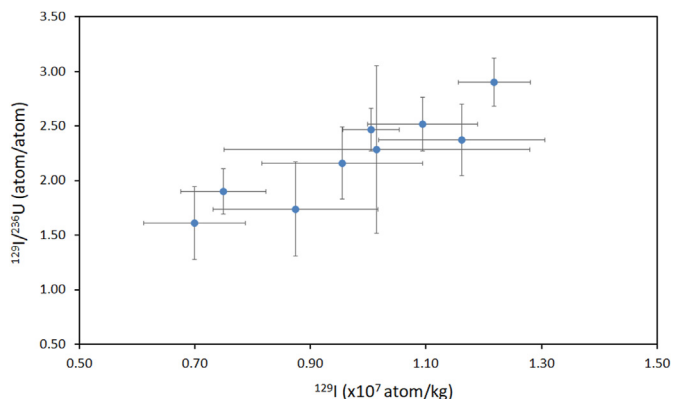


Fig. 6. <sup>129</sup>I/<sup>236</sup>U ratios as a function of <sup>129</sup>I concentration for samples classified as Central Waters (CW).

The role of <sup>129</sup>I as a marine tracer is demonstrated in the case of the Namibian shelf which is part of the nBUS, where coastal upwelling occurs regularly and water is transported offshore due to Ekman transport. The <sup>129</sup>I concentrations in surface water tends to increase with distance from coastlines, which reflects this upwelling effect. Furthermore, the <sup>129</sup>I concentration distribution

with latitude in Central Waters might be related to the intrusion of hypoxic water of tropical origin.

**Credit author statement**

J.M. López-Gutiérrez: Conceptualization, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. Martina Rožmarić: Conceptualization, Validation, Investigation, Resources, Writing – review & editing, Project administration, Funding acquisition. Deon C. Louw: Conceptualization, Validation, Investigation, Resources, Writing – review & editing, Project administration, Funding acquisition. V. Lérída-Toro: Investigation, Resources, Writing – review & editing.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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