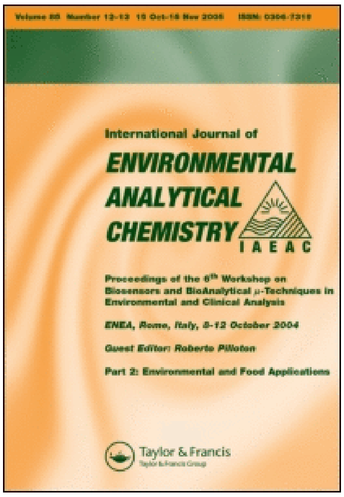

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DISTRIBUTION OF ^{226}Ra IN THE ROSS SEA—ANTARCTICA

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An improved procedure for the determination of ^{222}Rn and ^{226}Ra in seawater developed for easier on-board operations is presented. Data on the radioactive disequilibrium between the mentioned radionuclides as directly determined in the field can be greatly helpful in the study of the gas-exchange processes at the air-sea interface, especially as far as the Antarctic Ocean is concerned. The method employed has been preliminarly tested in laboratory on a set of seawater samples collected in the Ross Sea and ^{226}Ra data collected are discussed and compared to literature data.

KEY WORDS: ^{226}Ra, ^{222}Rn, Antarctic ocean, liquid scintillation counting.

INTRODUCTION

Gas exchange at air-sea interface is a process that plays a key role within the dynamics of global biogeochemical cycles, in particular as regards the evaluation of problems of relevant environmental concern such as the "greenhouse effect", related to the increasing average concentration of reactive gases such as CO_2, CH_4 etc. in the troposphere[1,2].

In order to estimate fluxes between the atmosphere and the ocean, it is necessary to determine the air-sea transfer coefficient. One of the methods employed is based upon the determination of ^{222}Rn deficit in respect to ^{226}Ra along the water column. The inert character of the ^{222}Rn ($t_{1/2} = 3.8$ d) makes it suitable for a study of this important problem. ^{226}Ra in the deep oceans is generally found to be in radioactive equilibrium with the daughter ^{222}Rn, but in near-surface seawater this can escape by diffusion into the atmosphere, due to its lower activity in air than in seawater, causing a disequilibrium with respect to ^{226}Ra[3-6].

In addition, ^{226}Ra itself can be used effectively as a tracer of seawater masses, as was pointed out by Koczy[7]. The presence of ^{226}Ra ($t_{1/2} = 1600$ y) in seawater is due to its primary deep-sea source by ^{230}Th decay in sediments; high inventories of thorium are maintained in the upper sediment column because this isotope is rapidly removed from seawater after its production by ^{234}U decay.

For the large variation of ^{226}Ra on a global scale, this natural radionuclide has been employed, as one of the most important radioactive tracers, in the study of large-scale mixing and ocean circulation, which have been the main effort of the GEOSECS (Geochemical Ocean Sections Study) program between 1970 and 1980[8-14].

In the framework of the Italian Program of Research in Antarctica and taken into account SCAR suggestions for primary scientific requirements[15], an investigation has been recently undertaken with the aim of evaluating the absorption capacity of the Antarctic waters towards the ever increasing concentration of reactive gases as CO_2, CH_4, etc. in the troposphere.

In the present work we describe a new experimental procedure for the determination of ^{226}Ra through ^{222}Rn in seawater. The method described has been set up and tested by processing seawater samples collected in the Ross Sea during the 1988–89, 1989–90 and 1990–91 Italian expeditions in Antarctica.

In spite of the limited number of samples available, some considerations on ^{226}Ra distribution are presented and are compared with those described in the literature.

EXPERIMENTAL

Properties of radon and radium

As a noble gas, radon shares with its homologues reduced chemical reactivity, a remarkable gaseous diffusivity. It is considered as the major source of radioactive disequilibrium in the uranium and thorium decay series and it has an appreciable water solubility (about 0.5 g/l at STP). All radon isotopes are radioactive; the longest-lived ^{222}Rn ($t_{1/2}$ = 3.8 d) tends to behave conservatively in the water column, because its concentration in seawater is supported by that of its radium parent with which it is usually in radioactive equilibrium.

Radium is an alkaline earth element with chemical properties similar to barium, it is an electropositive element and tends to form strong ionic bonds. Most Ra salts are insoluble, particularly sulphates and carbonates. Among the various isotopes of the element, all radioactive, ^{226}Ra, ^{230}Th daughter, has the longest half-life (1600 y).

Analytical procedure

Radium can be determined either directly through its coprecipitation with barium and following α or γ-spectrometry, or mostly by the well-known "radon emanation" technique, in which ^{226}Ra in solution is measured indirectly through its daughter ^{222}Rn once stripped the radon initially present and subsequently reached radioactive equilibrium in a sealed container.

The method employed in this work has been developed in order to be able to determine both radionuclides through ^{222}Rn[16,17]. The improvement of the methods usually described in the literature[4,16], for the quantitative determination of ^{226}Ra in the field, is based on the introduction of two new steps: modified ^{222}Rn desorption[18] and ^{226}Ra preconcentration.

The main steps of the complete experimental procedure are described below.

Sampling

Surface seawater was sampled by a membrane and submersible pumps, while 30 l Niskins bottles were employed for vertical profiles. The samples were stored in polyethylene tanks kept frozen at –30°C. Geographical location of sampling stations are shown in Figure 1.

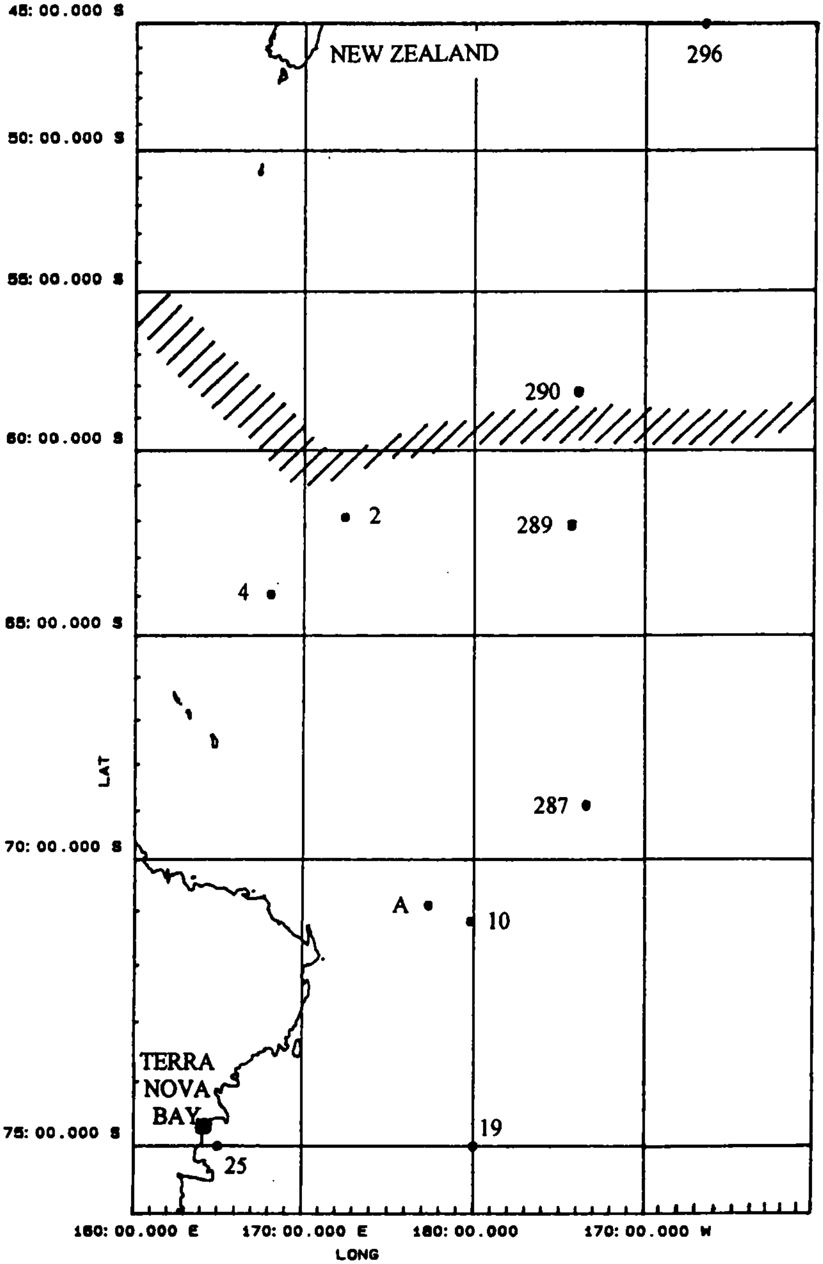

Figure 1 Locations of the ^{226}Ra station reported in this study and those reported previously by Ku *et al.*[9] and by Peng *et al.*[4]. The approximate position of the Antarctic Convergence is indicated (N.B.: station 2SW, is located at 5 km from the coast, near the Italian Base at Terra Nova Ray).

Separation and preconcentration of ^{222}Rn

Water samples were melted and transferred into airtight stainless steel (AISI 316L) 28 l tanks, internally lined with epoxy resin and left for at least one month to allow for the radioactive equilibrium between ^{226}Ra and ^{222}Rn[17].

Radon was then stripped with helium and recirculated for 1 hour in an airtight handling system by means of a membrane pump (flowrate: 2 l/min). Humidity and CO_2 were trapped by ascarite and silica gel and the extracted radon was adsorbed onto a column ($\Phi = 8$ mm; l = 260 mm) filled with 5 g of active coconut charcoal with a low ^{226}Ra activity (< 1 Bq/kg, 10–35 mesh, Fisher Chemical). The column was cooled down to –86°C with an acetone/dried ice mixture. The possible loss of radon is negligible since its boiling and melting points are –65°C and –71°C respectively.

^{222}Rn desorption

The refrigerated column was completely filled with toluene in countercurrent (0.3 ml/min) in respect to previous adsorption flux. It was removed from the refrigerating bath and left reaching room temperature; elution was carried out with 12 ml of toluene in a scintillation counting glass vial after addition of 4 ml of a suitable scintillation fluor (PPO: 4 g/l and POPOP: 0.5 g/l in toluene). Recovery of radon not retained in the first vial was achieved by means of a second vial containing extra 4 ml of toluene. Finally the contents of both vials were combined for subsequent Liquid Scintillation counting.

Liquid Scintillation counting conditions

Scintillation counting was effected at least three hours after sample preparation to allow for further equilibration between radon and its own daughters according to the decay chain, showing that each radon decay is followed by the emission of five particles:

$$^{222}\mathrm{Rn} \xrightarrow[3.82]{\alpha} \underset{\text{Radium A}}{^{218}\mathrm{Po}} \xrightarrow[3.04\ \mathrm{m}]{\alpha} \underset{\text{Radium B}}{^{214}\mathrm{Pb}} \xrightarrow[26.8\ \mathrm{min}]{\beta,\gamma} \underset{\text{Radium C}}{^{214}\mathrm{Bi}} \xrightarrow[19.9\ \mathrm{min}]{\beta,\gamma} \underset{\text{Radium C'}}{^{214}\mathrm{Po}} \xrightarrow[164\ \mu\mathrm{s}]{\alpha}$$

Counting was carried out with a total α–β counter model TriCarb 1000 (Canberra Packard) allowing for spectra acquisition on a portable P.C. by Canberra Packard Datalink and Spectrograph software packages. In order to improve sensitivity in radon measurement, the counting window was optimized so that to obtain a low background and high efficiency; this has allowed to optimize the instrumental figure of merit expressed as the ratio between the square of the counting efficiency and the background.

For given chemical extraction and elution yields (respectively Y_d and Y_e), counting efficiency (E in counts s^{-1} Bq^{-1}), sample volume (V in m^3), sample and background count rate (respectively c_s and c_b in count s^{-1}), constant of decay of radon ($\lambda = 2.1 \cdot 10^{-6}$ s^{-1}), counting sample time (t = 7200 s), time elapsed after radon stripping and time of measurement (Δt), the activity of radon (A in Bq/m^3) was determined according to the following expression:

$$A = \frac{c_s - c_b}{5 \cdot V \cdot Y_d \cdot Y_e \cdot E} \cdot \frac{\lambda \cdot t}{(1 - e^{-\lambda t})} \cdot \frac{1}{(e^{-\lambda \Delta t})}$$

The standard deviation of A was evaluated as:

$$s = \frac{\{[A \cdot 5 \cdot V \cdot Y_d \cdot Y_e \cdot E \cdot e^{-\lambda \Delta t} (1 - e^{-\lambda t})/\lambda t \cdot t] + 2\, c_b \cdot t\}^{0.5}}{5\, V \cdot Y_d \cdot Y_e \cdot E \cdot e^{-\lambda \Delta t} (1 - e^{-\lambda t})/\lambda t \cdot t}$$

which is assumed to be the best estimate for the population standard deviation (σ). The values of A are reported at a confidence limit of 95% (2σ).

Under the experimental conditions adopted, the Lowest Detectable Activity (LDA expressed in Bq/m^3) is evaluated by the expression[19]:

$$\mathrm{LDA} = \frac{1 + (1 + 2\, c_b \cdot t)^{0.5}}{0.5\, V \cdot E \cdot t \cdot 5 \cdot Y_d \cdot Y_e}$$

The suitability of the experimental procedure described was tested both by laboratory and field work. In particular, lab-tests were carried out by means of seawater samples depleted in natural ^{226}Ra by passing through a MnO$_2$-impregnated resin column, subsequently spiked with standard solutions of ^{226}Ra (NBS, 4953D, 147.5 Bq/kg) in order to accurately evaluate the overall recovery efficiency of the method, together with the radiometric efficiency. The total efficiency of this method is 65%.

The values of LDA for the two radionuclides at different volumes of the sample and under different working conditions are reported in Table 1.

^{226}Ra preconcentration method

100 l samples were eluted through a column (ϕ = 25 mm; l = 300 mm) filled with 100 ml of Amberlite XAD – 7 (20–50 mesh, BDH Chemicals LTD.) MnO$_2$ impregnated. After adsorption, the resin was treated with hot 8 M HCl to total dissolution of MnO$_2$. The hydrochloric solution was then allowed to stay for radioactive growth of ^{222}Rn till equilibrium with ^{226}Ra was reached (1 month), using a 250 ml glass bubbler equipped with airtight stopcocks. Radon was finally extracted as previously described.

Table 1 LDA (Bq/m^3) for ^{226}Ra and ^{222}Rn in seawater.

	Volume sample (m^3)	*LDA on board*	*LDA laboratory*
^{226}Ra	0.10	0.05	0.07
^{222}Rn	0.028	0.19	0 25

RESULTS AND DISCUSSION

The validity of the method has been confirmed during oceanographic cruises carried out in the Mediterranean Sea by ENEL (Milano)[16].

The availability of seawater samples from past Antarctic expeditions has offered the opportunity to apply this method for obtaining preliminary results useful for the investigations in the future oceanographic expeditions in Antarctica in sampling stations of the Ross Sea.

Data presented refer to ^{226}Ra activity in Bq/m^3 (1 Bq/m^3 of ^{226}Ra is equivalent to $2.8 \cdot 10^{-13}$ g/l) in surface seawater samples, collected at a depth ranging between 1 and 3 m (Table 2) and in the water column (Table 3). As a matter of comparison GEOSECS data

Table 2 Activities of ^{226}Ra (Bq/m^3) in surface seawater samples in the Ross Sea and comparison with literature data from the same area[4,9].

Station N°	*Lat.*	*Long.*	*Sample size (l)*	*Bottom depth (m)*	*^{226}Ra*
296 Geosecs (1974)	*44°59'S*	*166°42'W*		*5340*	*1.25 ± 0.10*
290 Geosecs (1974)	*58°00'S*	*174°00'W*		*5177*	*2.55 ± 0.10*
2 (1989–90)	61°49'S	172°38'E	100	3850	2.22 ± 0.10
289 Geosecs (1974)	*62°00'S*	*174°00'W*			*2.38 ± 0.10*
4 (1989–90)	63°58'S	168°02'E	100	2980	2.06 ± 0.11
287 Geosecs (1974)	*69°05'S*	*173°30'W*		*4149*	*2.83 ± 0.10*
A (1990–91)	70°53'S	177°21'E	25	1800	2.37 ± 0.25
10 (1989–90)	71°12'S	179°50'E	100	1500	2.40 ± 0.11
19 (1989–90)	75°01'S	179°59'E	25	460	2.99 ± 0.25
25 (1989–90)	75°01'S	170°00'E	100	940	2.98 ± 0.18
2 SW (1988–89)(a)	74°41'S	164°18'E	25	300	3.64 ± 0.29
7 SW (1988–89)(a)	74°41'S	164°18'E	25	300	3.35 ± 0.28

(a) Same station before (2SW) and after (7SW) pack melting.

Table 3 Activities profile of ^{226}Ra (Bq/m^3) and comparison with literature data from the same area[9].

Station 10 (1989–90) (71°12'S, 179°50'E) bottom depth: 1500m		*Station A (1990–91) (70°53'S, 177°21'E) bottom depth: 1800 m*		*Station 287 GEOSECS (1972) (69°05'S, 173°30'W) bottom depth: 4149 m*		*Station 290 GEOSECS (1972) (58°00'S, 174°00'W) bottom depth: 5177 m*	
depth (m)	*^{226}Ra*	*depth (m)*	*^{226}Ra*	*depth (m)*	*^{226}Ra*	*depth (m)*	*^{226}Ra*
3	2.40 ± 0.11	20	2.37 ± 0.25	*5*	*2.83 ± 0.10*	*10*	*2.55 ± 0.10*
100	2.55 ± 0.31	80	2.59 ± 0.30	*66*	*2.90 ± 0.10*	*125*	*2.43 ± 0.14*
200	2.49 ± 0.32	150	2.58 ± 0.29	*183*	*2.81 ± 0.10*	*200*	*2.17 ± 0.10*
400	2.64 ± 0.31	300	2.77 ± 0.32	*318*	*2.90 ± 0.10*	*321*	*2.58 ± 0.10*
600	2.97 ± 0.32	500	2.85 ± 0.33	*537*	*3.25 ± 0.10*	*500*	*2.68 ± 0.10*
800	3.00 ± 0.47	700	3.01 ± 0.33	*780*	*3.43 ± 0.14*	*704*	*2.85 ± 0.14*
1000	3.77 ± 0.57	1000	3.46 ± 0.34	*1004*	*3.38 ± 0.14*	*905*	*2.90 ± 0.10*
		1500	3.73 ± 0.41	*1620*	*3.40 ± 0.10*	*1499*	*3.08 ± 0.14*
					(a)		(b)

(a) approximately constant values reported by the Authors to a depth of 3902 m.
(b) activity values steadily increase to a maximum of 3.76 Bq/m^3 at a depth of 4793 m.

from the same geographical area are included in Table 2. The values obtained, though limited in number, are nevertheless comparable to analogous literature data both for the Ross Sea[9] and for the Weddell Sea[13], collected during the GEOSECS program. It is possible to observe that the values reported range from 1.25 (Station 296, in proximity of New Zealand) to 3.64 (coastal station near the Italian base at Terra Nova Bay). All the other stations, located between 58° and 75° Lat.S, show homogeneous values. This can be attributed to the influence exerted by the Antarctic Convergence, which gives rise to an important oceanic frontal zone, due to the confluence of two different water masses: a) the warmer Circumpolar Bottom Water (forming in temperate areas) that reaches the surface in the circumpolar zone, where it cools and thereafter sinks; b) the colder Antarctic Surface Water (wind-driven to the north) which in proximity of Circumpolar bottom water sinks[20].

The Antarctic Convergence, limiting the mixing of the cold water masses it includes and the external temperate ones, makes the Antarctic continent practically "isolated" allowing for just a very slow and gradual exchange of heat, oxygen and carbon dioxide between the water masses in contact. The ^{226}Ra contents, which inside the Antarctic Convergence is higher due to the vertical mixing of water masses causing bottom resuspension of the parent ^{230}Th, are in accordance with this.

Data reported in Table 3 reflect what has been mentioned above. Variations along the depth profile reflect the combined effect of deep waters upwelling and mixing with southern waters.

It is to note that surface samples from the 1989–90 expedition available in much larger volumes, showed a correspondingly lower measurement uncertainty.

The higher activity values observed for stations 2SW and 7SW (in proximity of the Italian Base at Terra Nova Bay, 5 km off the coast line) can be attributed to the relatively shallow depth of the sea bottom, where sediment contribution of ^{226}Ra by resuspension can not be excluded. Moreover, a terrigenous contribution from the coast through erosional processes can result significant to the local ^{226}Ra activity observed.

A strong influence of the proximity of the seabed seems to be related as well to the data obtained from the vertical profiles at Station 10 and Station A with a bottom depth of 1500 m and 1800 m, respectively. The increase of ^{226}Ra activity with depth brings to the same higher levels observed in the surface samples previously mentioned, when approaching the bottom. This trend was observed also by Ku *et al.*[9] at the same location, further confirming the importance of bottom sediments influence on ^{226}Ra vertical distribution.

CONCLUSIONS

Data of ^{226}Ra preliminarly obtained from seawater samples collected in the Ross Sea, Pacific sector of the Antarctic Ocean, in past expeditions have allowed to elucidate two different aspects of the problems inherent to the use of ^{222}Rn as a tracer of gas exchange at the air-ocean interface: a) the development of an experimental procedure reliable and sensitive even during an oceanographic cruise, when ^{222}Rn is to be determined; b) the collection of basic information on the expected values of activities of the couple ^{226}Ra/^{222}Rn in the Antarctic marine environment.

As regards point a), it is to remark that although the apparatus so far used does not provide the possibility of instrumental and computational α/β discrimination, nevertheless, the results obtained demonstrate its reliability; in addition it has the suitable characteristics required for on-board operations, such as robustness and compactness. The adoption of resin adsorption of ^{226}Ra step for its preconcentration, though extensively used for the separation of other radionuclides from seawater, is a fairly innovative technique for ^{226}Ra itself, leading to remarkable analytical advantages, such as a higher precision and transport of less bulky sample load. In addition, the combination of recent scintillation counting improvements, allowing for α/β discrimination with a correspondingly lower detection limit (the LDA is in fact far lower even than ^{226}Ra activity in the Mediterranean seawater), further encourages the use of "radon deficit" method in the study of air-sea gas exchange and which is our primary objective as concerns our involvement in the National Program of Research in Antarctica.

Moreover, the uncertainty associated to measurement is greatly reduced when analyses are carried out on board, in the open sea, due to negligible instrumental background far off the high contribution to natural radioactivity of crustal rocks. Obviously, the need for on-board operations is dictated by the short half-life of ^{222}Rn, which is directly involved in the gas-exchange process and that, therefore, requires to be determined at the time of sampling.

As for point b), preliminary, data of ^{226}Ra obtained will be useful to locate the most suitable sites for seawater samplings in the next expeditions: special care will have to be paid where sea bottom is shallow, where sediment contribution to ^{226}Ra/^{222}Rn in the water column could significantly affect a correct deficit evaluation.

In addition, since the application of this method requires to know the vertical distribution of ^{226}Ra activity, it is to emphasize that these data independently can provide useful information, when used as water masses tracer. As reported by Ku *et al.*[9], it is possible, therefore, on the basis of different specific activities of ^{226}Ra (Bq/m^3), to distinguish among the main four ocean water masses circulating in the subantarctic oceans: a) surface water (1.3 ÷ 3.0); b) intermediate Antarctic water (2.3); c) intermediate circumpolar water (3.0); deep water (3.3 ÷ 3.8).

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