# $^{210}Po$ and $^{210}Pb$ in fish and shellfish from Guanabara Bay, Brazil

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**Abstract.** Muscles of forty-four fish of two different species, *Mugil spp and Micropogonia furnieri*, and six composite samples of the shellfisb *Perna perna*, collected in Guanabara Bay, a tropical estuary, were analysed for $^{210}Po$ and $^{210}Pb$ contents. The method for $^{210}Po$ determination consisted of spontaneous deposition on copper disks, followed by alfa counting. The method for $^{210}Pb$ determination was mineralization followed by leaching, ion-exchange separation, precipitation and, finally, beta counting. The average values found for concentration of $^{210}Po$ in fish was 2.6 Bq.kg$^{-1}$, wet basis, while for shellfish the values were higher, reaching 43.8 Bq.kg$^{-1}$, wet basis. For $^{210}Pb$, concentrations were very low, frequently below the detection limit for fish samples. For shellfish this was higher, reaching 1.8 Bq.kg$^{-1}$, wet basis.

## 1. INTRODUCTION

The natural radionuclides of the uranium series, $^{210}Pb$ and $^{210}Po$, are widely spread in the environment. Traces of $^{226}Ra$ ($T_{1/2}$ = 1602 years), the source of such radionuclides, are present in most geological materials. $^{226}Ra$ decays to $^{222}Rn$ and part of this gas is continually released from land surfaces into the atmosphere. $^{222}Rn$ ($T_{1/2}$ = 3.8 days) rapidly decays (through short-lived intermediate radionuclides) to $^{210}Pb$ ($T_{1/2}$ = 22.3 years). Since $^{210}Pb$ half-life is much longer than its mean residence time in the troposphere, a natural fall-out of $^{210}Pb$ and its daughters, $^{210}Bi$ ($T_{1/2}$ = 5 days) and $^{210}Po$ ($T_{1/2}$ = 138 days) takes place [1].

In estuaries and other coastal areas the concentration of these radionuclides can vary largely, since it depends on the geology of the watershed and of the chemical weathering conditions [2]. Moreover this concentration can be increased by industrial waste impact, as in case of disposal of phosphogypsum waste from phosphoric acid plants [2-4].

The seawater $^{210}Po$ / $^{210}Pb$ ratio is less than 1, but in marine organisms this ratio is often higher than 10. This means a much more efficient uptake of the $^{210}Po$ than $^{210}Pb$ [1]. $^{210}Po$ is concentrated in most marine organisms by factors of $10^3$-$10^5$ relative to seawater concentration [5] and is the major source of natural radiation dose to which such organisms are exposed [6]. The accumulation of $^{210}Po$ varies from one tissue to another, according to the capacity to concentrate polonium [5]. $^{210}Po$ concentrations in the hepatopancreas are between two and three orders of magnitude higher than in muscle tissue [7]. There is a remarkable difference between $^{210}Po$ and $^{210}Pb$ behaviour in organisms: $^{210}Po$ accumulates preferentially in soft tissues and $^{210}Pb$ in bones.

$^{210}Pb$, $^{210}Bi$ and $^{210}Po$ accumulated by human body are very important contributors to the total radiation dose received by man. Food is the main source of $^{210}Pb$ and $^{210}Po$ for human body [8]. $^{210}Po$ gives rise to almost 7% of the dose equivalent, through natural radiation intake [9]. About 77% of daily intake of $^{210}Po$ comes from solid food [10], mainly seafood [8].

In this paper edible parts of two different species of fish *(Micropogonia furnieri and Mugil spp)* and mussels *(Perna perna)* of Guanabara Bay, were analysed for $^{210}Po$ and $^{210}Pb$ contents.

## 2. METHODS

### 2.1 Study Area

Guanabara Bay is a tropical estuary of 45 small rivers situated on the eastern coast of Brazil in Rio de Janeiro state. Its area is about 400 $Km^2$ and its drainage region is 4000 $Km^2$. The average depth of this bay is 7.7 m. 80% of the total area has a depth of less than 10 m and the maximum depth is 50 m. Dredging is carried out to keep the bay open to shipping.

Guanabara Bay is heavily polluted due to extensive industrial and residential activities. The official estimates of the number of possible polluting industries around the bay and in the drainage region is 12.500. Besides, there are 2 airports, 8 oil terminals, 2 commercial harbours and several shipyards.

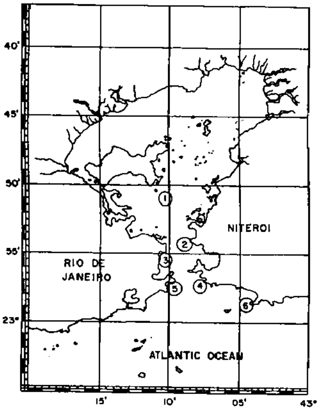


**Figure 1:** Mussel collection stations in Guanabara Bay.

### 2.2 Sampling and Analytical Procedures

Twenty-two organisms of each fish species (*Micropogonia furnieri and Mugil spp*) were studied.

Mussel (*Perna perna)* samples were composed of a different number of organisms for each station, as can be seen in table 3.

Fish was obtained from fishing vessels in winter/98 (dry season) and summer/99 (rainy season) and shellfish was collected in 6 stations shown in figure 1, only in summer/99. All samples were freezing dried before analysis.

To determine $^{210}Po$ concentration, about 2 g of each sample were weighed and spiked with a known activity of $^{208}Po$ as an internal isotopic tracer for radiochemical yield and then digested by concentrated $HNO_3$ and after by $H_2O_2$ 30%. Solution was boiled for 2 hours, cooled and then filtered. Filtrate was evaporated at $80^0$ C until dryness. Residue was dissolved in 0.6 M HCl. 1g was added of hydroxylamine hydrochloride, heated at $90^0$ C and shaken for 4 hours, at the end polonium was spontaneously deposited on copper disks. For determination of $^{210}Po$ activity, an alpha spectrometry system was supplied with a silicon surface barrier detector, ORTEC, model 576, coupled to a computer for spectrum analysis.

5 g of each lyophilised sample was weighed which had been first calcinated at $400^0$ C, for $^{210}Pb$ determination. Ashes were dissolved in 0.5 M HBr. It was added 1 g of hydroxylamine hydrochloride

and 1 ml of lead standard solution (20 $mg.ml^{-1}$) as carrier. Lead was separated in an ion-exchange resin Dowex 1X8, 50-100 mesh, bromide form, and eluted by 1 M $HNO_3$ and precipitated as $PbCrO_4$. Chemical yield was measured by gravimetry. 10 days later $^{210}Pb$ content was measured through beta emission from generated $^{210}Bi$ [11], by a low background alpha-beta proportional counter, BERTHOLD, 10 channels, LB 770WIN-PC model.

Analytical quality control was made by analysis of blank and reference standard (spiked sample) for every 20 analysed samples, according EPA's recommendation [12].

## 3. RESULTS AND DISCUSSION

$^{210}Pb$ content could not be measured in most muscle fish tissue samples, what is in accordance with data from Clulow et al. [13] and Heyraud and Cherry [7]. $^{210}Pb$ concentration values found by these authors in fish muscle samples were under detection limit in first paper, and in the second paper very low concentration of $^{210}Pb$ was measured in only a few organisms. It is due to the fact that $^{210}Pb$ accumulates in bones. On the other hand $^{210}Po$ tends to be accumulated in soft tissues.

Average values of $^{210}Po$ concentration were higher in *Micropogonia furnieri* species than in *Mugil spp*. Other authors found significant variations of $^{210}Po$ and $^{210}Pb$ concentrations between groups of organisms and even between animals from the same species [5,14] and also large variations especially of $^{210}Po$ concentration in muscle tissue [8]. Differences in $^{210}Po$ concentrations in marine organisms are related to the kind of consumed food [15]. It was verified that this radioisotope is almost exclusively absorbed through food [8]. In this way the food chain becomes the major source for $^{210}Po$ accumulation by fish.

Studied species in this paper showed completely different feeding habits. The first species (*Micropogonia furnieri*) feeds on live and dead small fish, some invertebrates, and, since it is detritivorous, it takes in also organic particles settled on the bottom, which have high $^{210}Po$ concentration [5]. On the other hand, *Mugil spp* species eats phytoplankton. Cherry and Shannon [1] showed some typical values for marine organisms and according to such values, *Micropogonia furnieri* species' food is richer in $^{210}Po$ than *Mugil spp*.

In tables 1 and 2 it was verified that there was significant seasonal variation in $^{210}Po$ concentration for the two studied species, being *Micropogonia furnieri* variation the highest one. $^{210}Po$ concentration in both organisms was higher in winter than in summer, what was also verified by Carvalho [8]. It was probably due to weight lost in fish caused by a reduction in food and lower water temperature. Some environmental parameters, mainly temperature of surface water and incidence of sunlight, influence bioproduction [16]. In Brazil bioproduction is higher in summer and spring, when fish population grows on account of ecosystem biomass increase. Therefore $^{210}Po$ can be diluted and its bioavailability can be reduced, and so lower levels of $^{210}Po$ take place in these seasons.

**Table 1:** $^{210}$Pb and $^{210}$Po concentrations and average values (Bq.kg$^{-1}$wet weight) in *Micropogonia furnieri* in winter/98 and summer/99. Size (cm) and weight (kg) are given for each organism.

| Winter 98 | | | | | Summer 99 | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | length | Weight | $^{210}$Pb | $^{210}$Po | Sample | length | Weight | $^{210}$Pb | $^{210}$Po |
| F01 | 44.0 | 0.848 | < 0.8 | 3.8 ± 0.7 | F11 | 57.7 | 1.774 | < 0.5 | 1.9 ± 0.5 |
| F02 | 47.0 | 1.084 | < 0.5 | 12.0 ± 3.2 | F12 | 57.5 | 1.892 | < 0.5 | 1.7 ± 0.3 |
| F03 | 39.0 | 0.728 | < 0.5 | 11.5 ± 3.2 | F13 | 52.0 | 1.450 | < 0.4 | 1.4 ± 0.2 |
| F04 | 35.0 | 0.496 | < 0.4 | 3.9 ± 0.8 | F14 | 55.0 | 1.595 | 0.5 ± 0.2 | 1.8 ± 0.3 |
| F05 | 38.5 | 0.573 | < 0.5 | 3.9 ± 1.3 | F15 | 52.0 | 1.524 | < 0.4 | 1.3 ± 0.3 |
| F06 | 40.0 | 0.568 | < 0.5 | 3.1 ± 1.1 | F16 | 51.0 | 1.196 | < 0.7 | 1.1 ± 0.4 |
| F07 | 47.0 | 0.988 | 0.5 ± 0.2 | 5.3 ± 1.1 | F17 | 45.0 | 0.986 | < 0.4 | 1.3 ± 0.5 |
| F08 | 45.0 | 0.902 | 0.9 ± 0.3 | 0.4 ± 0.5 | F18 | 49.0 | 1.006 | < 0.4 | 1.5 ± 0.2 |
| F09 | 41.5 | 0.723 | < 0.4 | 4.7 ± 1.0 | F19 | 44.0 | 1.192 | < 0.5 | 2.0 ± 0.3 |
| F10 | 39.5 | 0.581 | < 0.4 | 4.3 ± 1.2 | F20 | 48.0 | 1.085 | < 0.5 | 0.9 ± 0.3 |
| | | | | | F21 | 52.0 | 1.414 | < 0.6 | 1.3 ± 0.5 |
| | | | | | F22 | 57.0 | 1.794 | < 0.5 | 2.5 ± 0.7 |
| | | | | **Mean** | | | | | mean |
| | | | | **5.3 ± 1.2** | | | | | 1.56 ± 0.13 |

Other feature was observed in *Micropogonia furnieri* species: $^{210}$Po concentration in smaller fishes was higher and varied widely. On the other hand, $^{210}$Po concentration in bigger fishes was lower and varied little. It probably happened because younger organisms have an active metabolism and therefore higher intake rate. Hence $^{210}$Po accumulation is higher than lost rate (excretion and decay). In older organisms the metabolism is slower and there is equilibrium between accumulation and lost rates.

**Table 2:** $^{210}$Pb and $^{210}$Po concentrations and average values (Bq.kg$^{-1}$wet weight) in *Mugil spp* in winter/98 and summer/99. Size (cm) and weight (kg) are given for each organism.

| Winter 98 | | | | | Summer 99 | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | length | Weight | $^{210}$Pb | $^{210}$Po | Sample | length | Weight | $^{210}$Pb | $^{210}$Po |
| S01 | 42.0 | 0.869 | < 0.4 | 1.5 ± 0.3 | S12 | 39.0 | 0.638 | < 0.5 | 1.3 ± 0.2 |
| S02 | 42.0 | 0.792 | < 0.6 | 3.0 ± 0.8 | S13 | 37.0 | 0.622 | < 0.6 | 1.1 ± 0.3 |
| S03 | 43.0 | 0.849 | < 0.4 | 1.3 ± 0.8 | S14 | 43.0 | 1.026 | < 0.4 | 1.8 ± 0.5 |
| S04 | 41.0 | 0.786 | < 0.4 | 1.6 ± 0.4 | S15 | 38.0 | 0.661 | < 0.4 | 1.0 ± 0.3 |
| S05 | 41.5 | 0.849 | < 0.5 | 2.9 ± 0.8 | S16 | 38.0 | 0.676 | 0.2 ± 0.1 | 0.5 ± 0.2 |
| S06 | 44.0 | 0.892 | < 0.7 | 2.6 ± 0.7 | S17 | 36.0 | 0.551 | < 0.4 | 0.5 ± 0.1 |
| S07 | 42.0 | 0.839 | < 0,4 | 6.9 ± 1.7 | S18 | 42.0 | 0.909 | < 0.6 | 1.7 ± 0.2 |
| S08 | 41.0 | 0.750 | < 0,4 | 1.4 ± 0.4 | S19 | 43.0 | 0.932 | < 0.4 | 0.8 ± 0.3 |
| S09 | 42.0 | 0.854 | 0,3 ± 0,1 | 2.4 ± 0.4 | S20 | 50.0 | 1.622 | < 0.4 | 1.8 ± 0.4 |
| S10 | 37.0 | 0.581 | < 0.3 | 2.6 ± 0.9 | S21 | 44.0 | 1.052 | < 0.4 | 0.8 ± 0.2 |
| S11 | 38.5 | 0.690 | < 0.4 | 1.4 ± 0.4 | S22 | 36.0 | 0.618 | 0.4 ± 0.2 | 3.9 ± 1.2 |
| | | | | Mean | | | | | mean |
| | | | | 2.51 ± 0.48 | | | | | 1.38 ± 0.29 |

The highest $^{210}$Po and $^{210}$Pb concentrations in *Perna perna* (table 3) were close to smallest concentrations found by Germain et al. [4] in analysis of a fairly great amount of *Mytilus edulis* collected in the Seine estuary, from March/90 to November/91.

**Table 3:** $^{210}Pb$ and $^{210}Po$ concentrations (Bq.kg$^{-1}$wet weight) and $^{210}Po/^{210}Pb$ ratios in *Perna perna* mussels in summer/99. Number of organisms (n) for each sample and description of each size range (cm) are given.

| Station | n | Size | $^{210}Pb$ | $^{210}Po$ | $^{210}Po$ / $^{210}Pb$ |
|---|---|---|---|---|---|
| 1 | 25 | 38 – 47 | < 1.0 | 10.8 ± 0.4 | - |
| 2 | 10 | 60 – 88 | 0.7 ± 0.3 | 22.1 ± 0.7 | 31.6 ± 13.6 |
| 3 | 09 | 63 – 75 | 1.6 ± 0.4 | 43.8 ± 1.9 | 27.4 ± 7.0 |
| 4 | 11 | 61 – 73 | < 1.0 | 13.8 ± 0.8 | - |
| 5 | 09 | 49 – 60 | 1.8 ± 0.4 | 43.2 ± 2.2 | 24.0 ± 5.5 |
| 6 | 10 | 54 – 61 | 1.5 ± 0.4 | 14.8 ± 0.9 | 9.9 ± 2.7 |

The values found by Carvalho [5,8] for *Mytilus galloprovincialis* from Portugal coast and Madeira Island were higher, both $^{210}Po$ concentration and $^{210}Pb$. $^{210}Po$ / $^{210}Pb$ ratios varied from 10 to 32, and were within the range of values found by other authors [3,4].

Mussels from 3 and 5 stations showed the highest values; both for $^{210}Po$ and $^{210}Pb$. Intermediate values were found in stations 2, 4, and 6. The lowest concentration stood for mussels collected in station 1. In Fig.1 it can be seen that stations 3 and 5 are diametrically opposite to stations 2, 4, and 6. These verified differences in concentration can be due to the pattern of water circulation in Guanabara Bay, since 3 and 5 stations are more sheltered, which makes water exchange difficult. Station 1 is located in a region where ships pass through, so it is difficult for mussels to settle, mainly due to the constant motion of the waters and to oil pollution that causes their premature death. In this station mussels hardly reach 50 mm, and therefore have less accumulation time than mussels from other stations, whose average size is 64 mm.

Mussels contents were much higher compared to fish, since mussels are filtrating organisms that accumulate $^{210}Po$ and $^{210}Pb$ bound to particulate matter [17], besides their structure is less developed, and they have lower metabolism rate than fish.

As collection was made only in summer, it could not be verified whether or not there was seasonal variation in $^{210}Po$ and $^{210}Pb$ concentrations in mussels.

## 4. CONCLUSIONS

The values found for $^{210}Po$ concentration in fish were in agreement with reported values by other authors.

*Micropogonia furnier* species accumulate more $^{210}Po$ than ***Mugil spp*** and seasonal variations in both were observed.

$^{210}Pb$ concentration was under detection limit in most studied muscle tissue sample.

Studied mussels showed large differences in $^{210}Po$ concentration according to collection point and could be separated in two distinct groups: one from Rio de Janeiro city side and other from Niterói city side.

It is advisable to make a study about $^{210}Po$ concentration in water at many points in Guanabara Bay, to verify if there are differences due to the water circulation pattern. Besides, this study must be carried out in two seasons: summer and winter, so that the influence of both rainy and dry seasons on $^{210}Po$ concentration can be assessed.

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