

EVALUATION OF PAHs IN GROUNDWATER AND SURFACE WATERS AT MULTIPURPOSE REACTOR INSTALLATION AREA

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ABSTRACT

Brazil has four research reactors in operation, all old and low power. The IEA-R1 reactor of IPEN/CNEN-SP has only limited radioisotope production capacity, materials irradiation, and neutron beam utilization. This reactor has been operating for fifty-nine years and has prospects of operation for a maximum period of ten years. It is necessary to implement a new reactor, which will support nuclear activities, and the national strategic objectives related to technological development in the areas of energy and defense; scientific and technological development; training of human resources and the growing production of radioisotopes for medical application. The Brazilian Multipurpose Reactor (RMB) will be a nuclear reactor for research and will be built in the state of São Paulo, in the municipality of Iperó. Its construction may involve the release of effluents into the environment. With monitoring before, during and after construction, it will be possible to verify if the construction itself will harm the environment. Several organics compounds are released daily in water bodies collaborating for environmental imbalance. Many of them have carcinogenic and mutagenic properties, receiving more attention by the scientific community. Most of the organic compounds are not included in environmental legislation and many of them present high toxicity, especially those classified as endocrine disrupters, as some Polycyclic Aromatic Hydrocarbons (PAHs). Only seven of the thirteen PAHs studied in this project are contemplated in Brazilian legislation, and just one is contained in international legislation. The PAHs studied in this work present, considered hazardous chemical compounds due to their toxicity, persistence in the environment, their bioaccumulative potential and their tendency to biomagnify. For the determination of the PAHs, the samples were concentrated by solid phase extraction (SPE) followed by quantification by High Performance Liquid Chromatography (HPLC). It was possible to verify values of some PAHs below threshold limit $0.05 \mu\text{g L}^{-1}$ in the water bodies that cross the RMB area.

1. INTRODUCTION

The selected area for this research was an aggregate of infrastructures in the area near the Experimental Center of Aramar, from the Technological Center of the Navy in the state of São Paulo (CTMSP), in the municipality of Iperó. It is located at kilometer 10 of the Municipal Highway Bacaetava - Sorocaba, with distance of approximately 125 km from the city center of São Paulo. The (RMB) is an important project for the country, because it contributes to the reduction of Brazil's dependence on the supply of radioisotopes by foreign countries, besides fundamental importance in the scientific, economic, technological and social area ^[1].

The activities that will be carried out in the area of the RMB enterprise, involve a possible release of effluents into the environment, as any other installation. In this circumstance, to avoid the pollution of water bodies and groundwaters, it is essential a periodical and accurate monitoring of the area ^[2]. Most organic compounds that are released daily into water bodies are not included in the environmental legislation. Many of them show high toxicity, and a group of them are classified as endocrine disrupters, some of them being Polycyclic Aromatic Hydrocarbons (PAHs). Only 7 PAHs present in this work are contemplated at the Brazilian legislation. Only one of them, the benzo[a]pyrene, is included in international legislations, as an example the European Union, Canada and the United States. Nevertheless, all of them are outdated in reference to current knowledge ^[3-7].

The PAHs consist of a group of compounds that present in their molecule two or more condensed aromatic rings ^[8]. They also present ubiquitous behavior, environmentally persistent, different molecular structures and different toxicity levels ^[9]. They are considered hazardous chemical compounds because of their toxicity, persistence in the environment, their bioaccumulative potential and their tendency to biomagnify ^[10].

This work's objective is to evaluate the PAHs' concentration in surface water and groundwater at RMB installation area. To achieve this, 13 PAHs were evaluated: Acenaphthylene, Fluorene, Acenaphthene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[a,h]anthracene and Indene[1,2,3-c,d]pyrene. This basal evaluation will provide guidance on the degree of contamination of water bodies, with respect to the studied compounds, before the beginning of the construction. By monitoring before, during and after construction, it will be possible to verify if the construction work will be responsible for polluting the local environment.

1.1. Applicable legislation

Many laws have been established to protect water resources. For groundwater, there is the Federal Constitution of 1988 ^[11], and the federal law 9.433 ^[12], which establishes the National Water Resources Policy. There is the CONAMA (Environmental National Council) 396 ^[6], which defines classification and environmental guidelines for the groundwater, and N° 045/2014/E/C/I ^[13] law, which provides for the approval of Guidance Values for Soils and Groundwater in the State of São Paulo - 2014. For the water bodies, there is the CONAMA 357/05 ^[5; 13], which establishes the classification of water bodies

and environmental guidelines for their classification and establishing the conditions and standards for effluent disposal. The CONAMA establishes values of some PAHs for class 2 freshwater (water for public supply after conventional treatment). The maximum permissible values of potability are shown in Table 1.

Table 1. Reference values for surface water according to CONAMA 357.

Parameters	*TLV $\mu\text{g L}^{-1}$
Benzo[a]pyrene	0.05
Benzo[b]fluoranthene	0.05
Benzo[k]fluoranthene	0.05
Dibenzo[a,h]anthracene	0.05
Indene[1,2,3-c,d]pyrene	0.05

*TLV: threshold limit value

CONAMA Resolution 396 provides the classification and environmental guidelines for the framing, prevention and control of groundwater pollution. The parameters of threshold limit value (TLV), and limits of quantification (LOQ), considered acceptable by this resolution for the compounds with the highest probability of occurrence in groundwater are presented in Table 2.

Table 2. Reference values for groundwater according to CONAMA 396.

Parameters	CAS number	Predominant uses of water (* TLV) $\mu\text{g L}^{-1}$				
		Human consumption	For thirsty animals	Irrigation	Recreation	PQL Practical
Benzo[a]anthracene	56-55-3	0.05	---	---	---	0.15
Benzo[k]fluoranthene	207-08-9	0.05	---	---	---	0.15
Benzo[a]pyrene	50-32-8	0.05	---	---	0.01	0.15
Chrysene	218-01-9	0.05	---	---	---	0.15
Dibenzo[a, h]anthracene	53-70-3	0.05	---	---	---	0.15
Indene[1,2,3-c,d]pyrene	193-39-005	0.05	---	---	---	0.15

*TLV: threshold limit value

2. MATERIALS AND METHODS

2.1. Sample collection

The water samples were collected according to the recommendation of the CETESB & ANA's collection guide^[14]. The surface water samples were collected with the aid of a polymer vessel, and pumps were used to collect groundwater samples. Four liters of samples were collected from each collection point, 1L was used for analysis and the others for testing and analytical curve elaboration. Previously decontaminated amber glass bottles were used for sample storage. Until the analysis of the PAHs the samples were kept refrigerated. For the accomplishment of the work, the structure of the Chemistry and Environment Center's laboratories from IPEN/CNEN-SP was used for the conservation,

storage and analysis of the samples. The descriptions of collection points and their geographic coordinates are presented in Table 3.

Table 3. Descriptions of collection points.

Collection point identification	Collection point description	Geographic coordinates
PC2	Ribeirão do Ferro, upstream of the RMB - surface water	23°24'17.491"S 47°37'30.187"W
PAS1	Ribeirão do Ferro, downstream of the RMB - surface water	23°23'18.71"S 47°37'0.93"W
PAS3	Rio Sorocaba, upstream of the Ribeirão do Ferro discharge point, after the Ipanema River discharge point in the Sorocaba River - surface water	23°21'55.76"S 47°36'54.27"W
PAS2	Rio Sorocaba, downstream of the Ribeirão do Ferro discharge point - Surface water	23°21'39.40"S 47°36'1.05"W
LAKE	São Benedito Farm (Lake) - surface water	23°22'00.03"S 47°37'24.43"W
IBAMA Stream	Source of Ibama little river - surface water	23°23'25.00"S 47°37'30.59"W
PC3-120m	Ipanema Farm - Lake Well (±120m deep) - groundwater water	23°25'36.55"S 47°35'59.03"W
PC3-130m	Ipanema Farm - water well (± 130m deep) - groundwater water	23°25'40.78"S 47°35'51.46"W
PSU1	São Benedito Farm, downstream of the RMB - groundwater water	23°22'8.56"S 47°37'22.05"W

2.2. Determination of PAHs

The methods used for the preparation and analysis of PAHs in water and particulate material samples was developed and validated by Brito ^[15]. Initially, the samples were vacuum filtrated through PTFE membrane with 0.45 µm porosity, at room temperature, for retention of suspended solids present in the sample, which were also analyzed.

2.2.1. Solid Phase Extraction (SPE) for the determination of PAHs in water.

After filtration, co-solvent (acetone) was added to the sample in the proportion of 4:10, in order to avoid adhesion of PAHs to the walls of the glass vial, thus impairing its quantification. The SPE-C18 cartridge (SUPELCO, filled with octadecyl) was conditioned with 10 mL of purified water followed by 10 mL of purified water/Acetone solution 3:10. The sample with co-solvent added was percolated through the cartridge in a flow of approximately 3 to 4 mL min⁻¹ and the eluate discarded. Cleanup of column was made with 10 mL of purified H₂O, followed by 5 minutes of vacuum drying and subsequent centrifugation of the cartridge for 25 minutes at 3000 rpm to aid in the elimination of water. The elution of the analytes was made twice with 4 mL (4 x 1 mL) of the tetrahydrofuran/Acetone solution (1:1) and then dried in a N₂ smooth flow, taken up to 2 mL of ACN/H₂O (1:1) solution, 0.45 µm membrane filtrate (Millex) and finally analyzed by HPLC.

2.2.2. Extraction of PAHs in particulate material samples

The particulate material retained on the filter membrane was extracted by sonication. Initially, the membranes equivalent to the filtration of 1L of water were placed in an erlenmeyer and 10 mL of the mixture of acetone and tetrahydrofuran (1: 1) was added. Then the sample was subjected to ultrasonic bath for 3 hours ^[15]. The supernatant extract was transferred to a FALCON Polypropylene tube and centrifuged for 15 minutes at 2800 rpm. Purified H₂O was added to the supernatant to reach a concentration of the tetrahydrofuran/acetone solution to about 4:10 of solvent. The diluted extract was percolated in SPE cartridges using the same procedure submitted to the water samples extraction above mentioned. The final extract was then dried in a N₂ smooth flow, taken up to 2 mL of ACN/H₂O (1:1) solution, 0.45 µm membrane filtrate and analyzed by HPLC.

3. RESULTS AND DISCUSSION

Surface and groundwater samples along with their particulate material were collected during days 3, 4 and 5 in October 2016, during the dry season. They were filtered, concentrated and analyzed according to the methodology described above. The results of the concentrations obtained for each analyzed PAH compound were compiled and can be observed in Tables 4 and 5. These results are referent to the collect points described in Table 3.

In order to verify the possible origin of the PAHs, the initial results were compared with the works made during the last decades, regarding the composition and sources of combustion of these compounds ^[16]. One of the forms of diagnosis is the calculated ratios between some PAHs, suggested by several literatures. One of the forms of diagnosis is the calculated ratios between some PAHs, suggested by several literatures. By this rate, it is possible to identify the sources as burned oil or coal, vehicle emissions and atmospheric transport of pollutants ^[17-19].

In this context, the fluoranthene/pyrene (both compounds representatives of the pyrolysis) ratio if inferior to 1 which characterizes a pollution caused by diesel engine exhaustion and, if superior to 1, caused by atmospheric aerosols, being these ^[20; 21].

Table 4: Results of the water samples and particulate material analysis collected in 2016 at points PC2, PAS1, PAS2, PAS3 and PSU1 in the RMB area.

PAHs concentration in $\mu\text{g L}^{-1}$											
Compounds	LOQ $\mu\text{g L}^{-1}$	PC2		PAS1		PAS2		PAS3		PSU1	
		Water	Particulate material	water	Particulate material	water	Particulate material	water	Particulate material	water	Particulate material
Acenaphthylene	0.030	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Fluorene	0.030	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Acenaphthene	0.016	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Phenanthrene	0.026	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Anthracene	0.036	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.015±0.004	< LOQ	< LOQ	< LOQ	< LOQ
Fluoranthene	0.012	< LOQ	0.39±0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Pyrene	0.030	< LOQ	< LOQ	< LOQ	< LOQ	0.32±0.01	< LOQ	< LOQ	< LOQ	< LOQ	0.44±0.05
Benzo[a]anthracene	0.012	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Chrysene	0.012	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.023±0.001	< LOQ	< LOQ	< LOQ	< LOQ
Benzo[b]fluoranthene	0.012	< LOQ	0.08±0.01	< LOQ	0.15±0.03	< LOQ	0.04±0.01	< LOQ	0.04±0.01	< LOQ	0.15±0.03
Benzo[k]fluoranthene	0.016	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.11±0.02	< LOQ	< LOQ	< LOQ	< LOQ
Benzo[a]pyrene	0.012	< LOQ	< LOQ	< LOQ	< LOQ	0.022±0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Dibenzo[a,h]anthracene	0.040	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Indene[1,2,3-c,d]pyrene	0.034	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

LOQ = Limit of Quantification

Table 5: Results of the water samples and particulate material analysis collected in 2016 at points São Benedito Farm LAKE, IBAMA stream, PC3-120m and PC3-130m in the RMB area.

PAHs concentration in $\mu\text{g L}^{-1}$									
Compounds	LOQ $\mu\text{g L}^{-1}$	São Benedito Farm LAKE		IBAMA stream		PC3-120m		PC3-130m	
		water	Particulate material	Water	Particulate material	water	Particulate material	water	Particulate material
Acenaphthylene	0.030	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Fluorene	0.030	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Acenaphthene	0.016	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Phenanthrene	0.026	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Anthracene	0.036	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Fluoranthene	0.012	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Pyrene	0.030	0.54±0.02	0.38±0.05	< LOQ	< LOQ	< LOQ	0.23±0.05	< LOQ	< LOQ
Benzo[a]anthracene	0.012	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Chrysene	0.012	0.045±0.004	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Benzo[b]fluoranthene	0.012	< LOQ	0.10±0.02	< LOQ	0.06±0.01	< LOQ	< LOQ	< LOQ	0.04±0.01
Benzo[k]fluoranthene	0.016	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.04±0.01
Benzo[a]pyrene	0.012	< LOQ	< LOQ	< LOQ	0.17±0.05	< LOQ	< LOQ	< LOQ	< LOQ
Dibenzo[a,h]anthracene	0.040	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Indene[1,2,3-c,d]pyrene	0.034	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

LOQ = Limit of Quantification

The calculation of the diagnostic rates Fluoranthene/pyrene, (Fl/Py), accomplished in samples of surface water and particulate matter at points PC2 ($0.39 \mu\text{g L}^{-1}$), PAS2 ($0.32 \mu\text{g L}^{-1}$), PSU1 ($0.44 \mu\text{g L}^{-1}$), observed in Table 4, and São Benedito Lake ($0.54 \mu\text{g L}^{-1}$), PC3-120m ($0.23 \mu\text{g L}^{-1}$), in Table 5, could be used to calculate the mentioned rates, suggesting that the main source of PAHs studied comes from pyrogenic [22], but there are not sufficient results to do this affirmation.

It was observed Chrysene at points PAS2, $0.023 \mu\text{g L}^{-1}$, in samples of particulate material, showed in Table 4, and São Benedito Lake, $0.045 \mu\text{g L}^{-1}$, in surface water sample, in Table 5. Its occurrence suggests that burning of industrial oil, emission of gasoline combustion gases and incinerators [23; 24].

Association between Chrysene and Benzo (k) Fluoranthene, found at point PAS2, $0.11 \mu\text{g L}^{-1}$ (Table 4) and the point PC3-130, $0.04 \mu\text{g L}^{-1}$ (Table 5), both in samples of particulate material, its occurrence could suggest emissions of vehicles, especially diesel [19].

The benzo[a]pyrene diagnosed at point PAS2, $0.22 \mu\text{g L}^{-1}$ in surface water sample showed in Table 4 and the IBAMA point, $0.17 \mu\text{g L}^{-1}$ in particulate material sample, indicated in Table 5, suggest as font automotive vehicle emission tracers [25; 26].

4. CONCLUSIONS

Due to the construction of the RMB, it is very important to continue the monitoring of the region, and to evaluate a possible contamination by the organic compounds studied in this research. Moreover this monitoring can be evaluable if the construction can/will affect the quality of the waters of the region where the project will be built.

This initial result is an important key to evaluate the concentrations of PAHs, before the enterprise construction, aiming to evaluate the contribution of a big-sized infrastructure, like the RMB, on compromising the quality of the water around the area.

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