

EVALUATION OF SEAWATER CONTAMINATION WITH BENZENE, TOLUENE AND XYLENE IN THE UBATUBA REGION AND STUDY OF THEIR DEGRADATION BY IONIZING RADIATION

**Kelly Cristina Santana de Almeida, Vanessa Miguel Cardoso, Manoel Nunes Mori and
Celina Lopes Duarte**

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
kellycsalmeida@ig.com.br
vcardose@usp.br
mnmori@ipen.br
clduarte@ipen.br

ABSTRACT

A major concern with leaking petroleum is the environmental contamination by toxic and low water-soluble components such as benzene, toluene, and xylenes (BTX). These hydrocarbons have relatively high pollution potential because of their significant toxicity. The objective of this study was to evaluate the contamination of seawater by the main pollutants of the output and transport of petroleum, such as benzene, toluene, and xylenes, and their removal by exposure to ionizing radiation. The studied region was Ubatuba region, SP, between 23°26'S and 23°46'S of latitude and 45°02'W and 45°11'W of longitude, area of carry and output of petroleum, and samples were collected from November, 2003 to July, 2005. For BTX in seawater analysis, the Purge and Trap concentrator with FIDGC detector showed significantly higher sensibility than headspace concentrator with MSGC detector. The minimal detected limits (MDL) obtained at FIDGC were of 0.50 µg/L for benzene, 0.70 µg/L for toluene, and 1.54 µg/L for xylenes, and the obtained experimental variability was 15%. While the concentrator type Headspace system with MS detector showed higher MDL, about of 9.30 mg/L for benzene, 8.50 mg/L for toluene, and 9.80 mg/L for xylenes, and 10% of experimental variability. In the studied area the benzene concentration varied from 1.0 µg/L to 2.0 µg/L, the concentration of toluene varied from < 0.70 µg/L to 3.24 µg/L and the maximum value of xylenes observed was of 2.92 µg/L. The seawater samples contaminated with BTX standard were exposed to ionizing radiation using a source of ⁶⁰Co. The results showed a removal from 10% to 40% of benzene at 20kGy absorbed doses and concentration of 35.1 mg/L and 70.2 mg/L, respectively. For toluene the removal were from 20% to 60% with 15kGy and xylenes were removed from 20% to 80% with 15kGy and similar concentrations.

1. INTRODUCTION

Petroleum is constituted of a mixture of hydrocarbons, derived organic and organo-metallic compounds. This material is characterized by the high content of salts and a complex mixture of organic compounds (aliphatic, aromatic, polar and fatty acids) and inorganic (dissolved salts, toxic heavy metals and radionuclides). A major concern with leaking petroleum is the environmental contamination by the toxic and low water-soluble components such as benzene, toluene, and xylenes (BTX). These hydrocarbons have high pollution potential because of their toxicity. All BTX compounds are depressants to the central nervous system. Consequently, BTX are priority pollutants, and their occurrence has led to the development of several physical, chemical and biological methods for their removals [1,2,11].

Benzene, toluene and xylenes, BTX, are known as markers for the exposure to volatile organic compounds and to petroleum compounds, high BTX concentrations can be found close to coal processing plants or refineries and chemical plants [4,10].

The use of ionizing radiation for decomposition of organic compounds has been reported in recent years. The free radical produced by interaction of ionizing radiation with water take to oxidation and reduction of organic pollutants. Depending on the sample origin, the organic compound removal efficiency can vary because of the presence of radical scavengers, such as O₂, bicarbonate/carbonate ions, nitrate ion, methanol. It is therefore, difficult to predict a priori the removal efficiency of the various organic solutes due to irradiation [3,5].

This paper is part of a project that consists of the use of nuclear and isotopic techniques for assessing of conventional and radioactive pollutants in the north coastline of the São Paulo State. The objective was to evaluate seawater hydrocarbon contamination in some bays in Ubatuba City region, São Paulo State, by the output and transport of petroleum, mainly benzene, toluene, and xylenes (BTX), and their removal by the exposition to the ionizing radiation and compare to removal in purified water and underground water. Preliminary results were published, elsewhere [1]. The region is near the most important oil terminal in Brazil, Terminal Marítimo Almirante Barroso, TEBAR. This terminal is in operation since 1969 and operate about 60 petroleum ships per month and is responsible for 50% of petroleum production in Brasil [6].

2. EXPERIMENTAL

2.1 Sampling

The samples were collected in a series of small embayments of Ubatuba, covering latitudes between 23°26'S and 23°46'S and longitudes between 45°02'W and 45°11'W (Table 1). The main studied embayments are Flamengo (Ubatuba Marine Laboratory site), Fortaleza, and Pereque-Mirin. For this study it was made 4 samples collections: in November 2003 (spring), in August 2004 (winter), in February 2005 (summer) and in July 2005 (winter). A total of 84 duplicate samples were collected in four different depths at each site. The samples were collected using a special system for seawater collection and were transferred to dark vials with 250 mL without headspace.

Standard of BTX were prepared in methanol PA – ACS, CAAL, using toluene PA – ACS, Merck, xylenes PA J. T. Baker, and benzene PA, Merck. These standards were employed to calibrate the gas chromatograph and to spike the pool of seawater and purified water.

2.2 Processing

The spiked samples were irradiated with following absorbed doses: 10.0 kGy, 15.0 kGy, 20.0kGy and 50.0 kGy. Irradiation was carried out at room temperature, using an AECL “Gammacell 220” 60Co source in a batch system. The dosimetry research group calibrates this system routinely with Fricke dosimeter to determine the absorbed dose rate. Triplicate 20mL vials were completely filled without headspace.

2.3 Chemical Analysis

The organic analyses before and after irradiation processing were performed, using two different detectors:

- Gas chromatograph associated to mass spectrometry using the Shimadzu, model GCMS QP-5000, with Head Space concentrator using Helium as carrier gas, 20 mL of volume sample and the following condition: capillary column, coated with DB5. J&W Scientific, 30m X 0.25 mm. 0.25 µm film thickness; mass detector operation in electron impact

mode (EI), using 1.50 kV of ionising voltage and temperature 250°C; interface temperature 240°C and continuous operation mode (SCAN);

- Sample concentrator type Purge-and-Trap, O.I.Analytical, model 4560, associates to GC, model 17A, with flame ionization detector, FID, and with capillary column, coated with DB5. J&W Scientific, 30m X 0.25 mm, 0.25 µm film thickness, 5 mL of volume sample.

3. RESULTS AND DISCUSSION

3.1 Evaluation of BTX contamination in the Ubatuba embayments

The result of experiments in chemical analysis of BTX in seawater are discussed elsewhere by the same research group, for BTX in seawater analysis, the Purge and Trap concentrator with FIDGC detector showed significantly higher sensibility than headspace concentrator with MSGC detector. The minimal detected limits (MDL) obtained at FIDGC were of 0.50µg/L for benzene, 0.70 µg/L for toluene, and 1.54 µg/L for xylenes, and the obtained experimental variability was 15%. While the concentrator type Headspace system with MS detector showed higher MDL, about of 9.30 mg/L for benzene, 8.50 mg/L for toluene, and 9.80 mg/L for xylenes, and 10% of experimental variability. [1].

All seawater samples presented benzene concentration about 1.00 µg.L⁻¹. Samples from underground water, collected in February, 2005, presented concentrations higher than 1µg.L⁻¹, but lower than 2 µg.L⁻¹. Most seawater samples presented toluene and xylenes concentrations lower than the detection limit (0.70 µg.L⁻¹). Samples from Fortaleza bay in February, 2005, presented the maximum level of toluene (3.24 µg.L⁻¹) and of xylenes (2.92 µg.L⁻¹).

The obtained BTX concentrations in all samples were lower than the established limits of the Brazilian legislation (CONAMA 357). These results are according to the obtained values of petroleum hydrocarbons in region near these sampling places [11]. However the values are higher when compared those obtained by Huybrechts [7] at regions in the North Sea, where it was found in order to ng.L⁻¹

The BTX concentration variation in water column in depth from 1 to 7 m are showed in the Figures 1a, 1b and, 1c, in different bays and collection periods. Most of them presented variation of concentration according to the salinity, the values increase with the salinity, and the salinity vary in different depth. At summertime the variation were higher, because the evaporation of water increase the salinity near seawater surface.

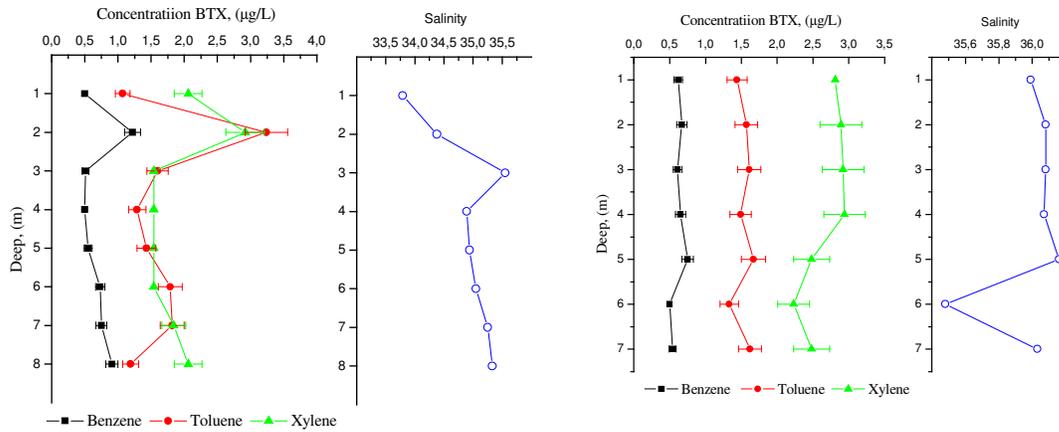


Figure 1a. BTX ($\mu\text{g/L}$) in seawater and salinity versus depth in water column in the Fortaleza bay. Collect date =08/25/2004 and 02/02/2005

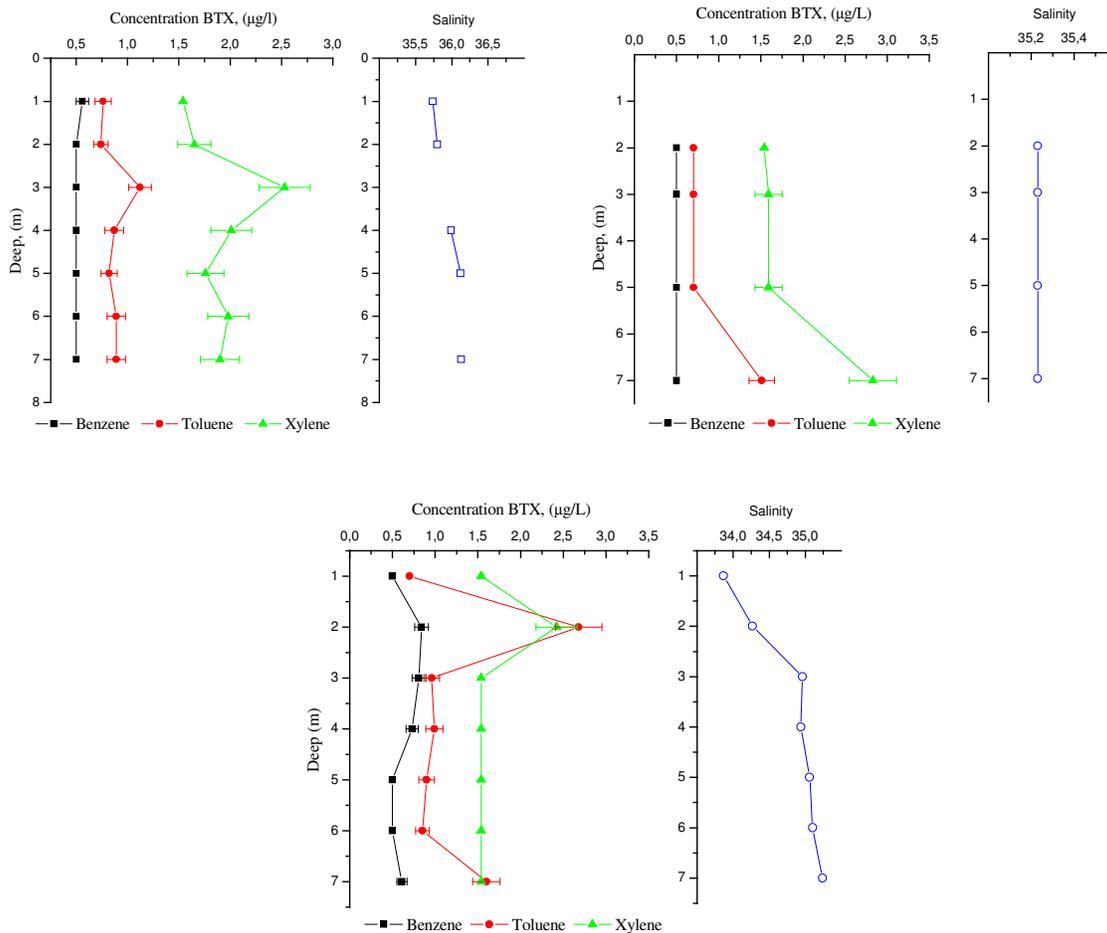


Figure 1b. BTX ($\mu\text{g/L}$) in seawater and salinity versus depth in water column in the Flamengo bay. Collect date =08/25/2004, 02/02/2005 and 06/06/2005.

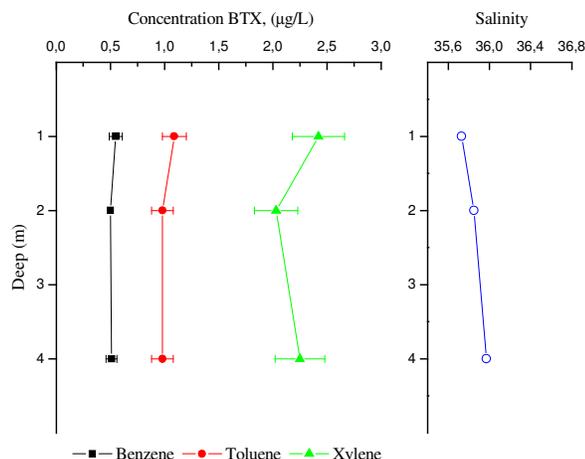


Figure 1c. BTX ($\mu\text{g/L}$) in seawater versus depth in water column in the Pereque Mirim bay. Collect date =08/25/2004

3.2 Gamma radiolytic decomposition of BTX

To study the gamma radiolytic decomposition of BTX and compare the efficiency in different matrices, a pool of seawater and underground water samples from different collected points, were obtained. These samples were spiked with different concentrations of BTX (Table 1) and irradiated with the same absorbed doses.

Seawater samples presented higher total organic carbon (TOC) concentrations, although when the BTX concentration increase TOC does not increase in the same proportion. It happened due to interference of high concentrations of carbonate and bicarbonate in seawater. To decrease this interference, it was necessary to dilute the seawater samples with purified water (1:10) (Table 1).

Table 1. Total Organic Carbon concentration in the three spiked samples with four different concentration of total BTX.

Concentration Mol.L^{-1}	TOTAL ORGANIC CARBON (mg.L^{-1})		
	Ultrapure Water	Underground Water	Seawater
8.8 (C1)	273.1 ± 9.0	266.3 ± 25.0	411.2 ± 39.0
17.6 (C2)	530.6 ± 19.0	514.3 ± 41.0	408.0 ± 41.0
35.2 (C3)	1315.0 ± 35.0	1057.0 ± 99.0	689.0 ± 55.0
70.4 (C4)	2502.0 ± 78.0	2421.0 ± 220.0	1460.0 ± 134.0

As expected, the purified water present higher decomposition yield than seawater, this is due to the interference absence. The removals were approximately 100% of all concentrations and compounds to 20 kGy absorbed doses. However in case of seawater, the removal were 100% to 15 kGy absorbed dose, only for samples with the initial concentration lower than 17.6 mg/L. The removal of benzene, toluene and xylenes from different origin, by ionizing radiation in C3 and C4 concentrations are presented in the Fig.2, the results of the

concentrations C1 and C2 are not showed because it were removed about 100% with the lower applied absorbed dose.

For benzene removal, it was necessary higher dose than the other compounds, considering the same concentration, that can be explained by the necessity of high energy to break the aromatic ring, the removals were 10 to 40% for C3 and C4 respectively and 20 kGy. While toluene presents 20% to 60% in similar concentrations but applying 15 kGy of absorbed doses. Finally xylenes was removed more efficiently, 20% to 80% with 15 kGy.

This paper is distinct from those of the literature [9], that relate that benzene and xylenes should be removed by radiation processing with the same efficiency, while toluene would be removed less efficiently. The OH radicals would be the radicals most responsible for the removal of 93-97% of benzene and xylenes and 83.5% of toluene. However, in the case of toluene, the hydrogen radical could account for up to 16% of the removal.

The conductivity that represents the dissolved salts was about 1.4 μS in purified water and 6000.0 μS in seawater and, 3700 μS in underground water. These salts represent some radical scavengers, such as O_2 , bicarbonate/carbonate ions, nitrate ion, etc, which suppress reactive species and affect their distribution. Nevertheless the behavior of underground samples have to be better investigated, because the low efficiency of BTX removal (Figure 2) is not coherent with its TOC concentration and, mainly its salinity.

4. CONCLUSION

The concentrations of BTX in the studied region are under the Brazilian legislation limits. Salinity and season of year affected the distribution of BTX in the column water in the studied region and samples.

Even in seawater the gamma radiation showed high efficiency to destroy BTX, but due to complexity of that sample (salinity and other inorganic compounds) the yield showed lower than in purified water.

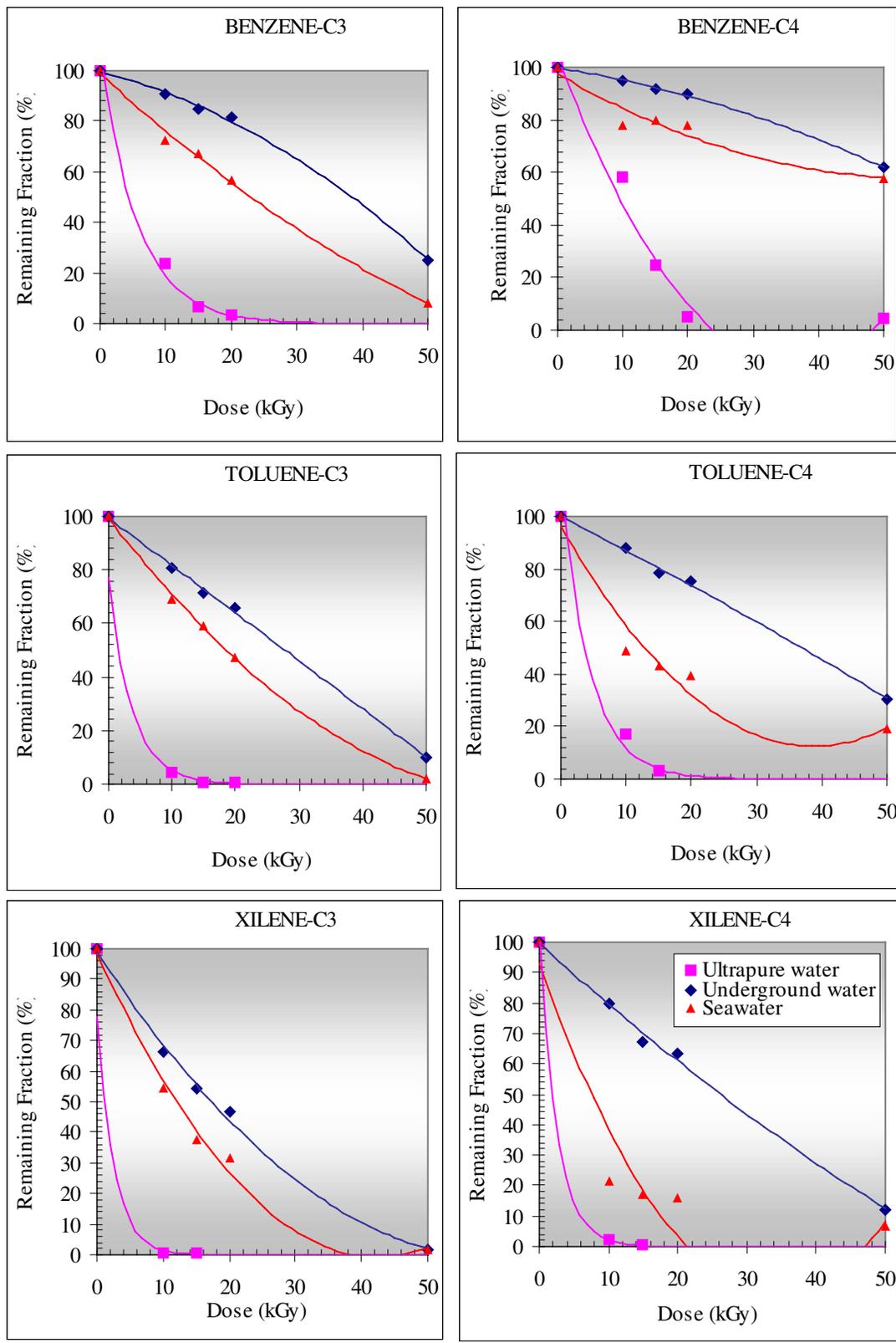


Figure 2. Removal of Benzene, Toluene and Xylenes from different origin, by ionizing radiation in different concentration and absorbed doses.

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