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Degradation of petroleum hydrocarbons in seawater by ionizing radiation

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A major concern with leaking petroleum is the environmental contamination by the toxic and water-soluble components such as benzene, toluene and xylenes (BTX). These hydrocarbons have relatively high pollution potential because of their significant 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 removal. The use of nuclear technology for protection and conservation of the environment, by the destruction of toxic organic compounds present in the environmental, drinking water, soils and industrial sewage has been the object of study of several authors in Brazil and in the world. The objective of this paper is to present the preliminary results of the study of contamination of the seawater by the main pollutants of the output and transport of petroleum, such as benzene, toluene and xylene, and their removal by the exposure to the ionizing radiation.

Introduction

The activities of exploitation of petroleum and oil spill accidents resulted in the marine environments and the coast of Brazil a considerable environmental degradation, above all due to the limited capacity of the ecosystems to absorb the resultant impacts.[1]

The petroleum is constituted of a mixture of hydrocarbons, derived organic and organo-metallic compounds. During the petroleum production in offshore areas, large volumes of a waste known as "produced water" are released. This waste is characterized by the high content of salts and a complex mixture of organic (aliphatic, aromatic, polar and grease acids) and inorganic (minerals, metals and radionuclides) compounds.[2]

A major concern with leaking petroleum is the environmental contamination by the toxic and 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 of their removals.[2,3]

BTX are known as markers for the exposure to volatile organic compounds and to petroleum compounds. High BTX concentrations can be found close by coal processing plants or refineries and chemical plants.[2,4,5]

The development of cost effective and clean processes through pollution prevention and waste treatment with enhanced efficiencies is an important chemical task. Destructive methods of the removal of pollutants have been investigated nowadays. The oxidation processes with OH radicals are the most efficient to mineralize organic compounds, and there are various methods to generate OH radicals such as the use of ozone, hydrogen peroxide and ultra-violet radiation entitled Advanced Oxidation Process (AOP). The most efficient method for generating OH radicals in situ is the interaction of ionizing radiation with water. The irradiation of aqueous solutions results in the excitation and ionization of the molecules and rapid (10^{-14}–10^{-9} s) formation of reactive intermediates.[4,5,7–10]

The most reactive species are the reducing radical's solvated electron (e_{aq}), and H· atoms and the oxidizing radical hydroxyl OH. These reactive species will react with the organic pollutants present in liquid effluent inducing their decomposition. The primary products from water irradiation tend to react with the functional groups present in an organic molecule rather than with the molecule as a whole. Depending on the sample origin, the removal efficiency can vary because of the presence of radical scavengers, such as O_2, bicarbonate/carbonate ions, nitrate ion, methanol. Therefore, it is difficult to predict a priori the removal efficiency of the various organic solutes due to irradiation.[7,9,11,12]

The objective of this paper is to present the preliminary results of the evaluation of the seawater contamination in the Ubatuba, SP, region by the output and transport of petroleum, mainly benzene, toluene, and xylene (BTX), and their removal by the exposition to ionizing radiation and compare to removal in purified water.

The work was conducted in collaboration with the Division of Environmental Radiometry of the Institute of Nuclear Research (IPEN), in 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.

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Experimental

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 embayments selected to be studied in this project are Flamengo Bay (Ubatuba Marine Laboratory site), Fortaleza Bay, Mar Virado Bay, and Ubatuba Bay. For this study, 21 duplicate samples were collected in August, 2004 at four different sites and depths. The samples were collected using special system for seawater collection and were transferred to vials of 250-ml without headspace.

BTX standards were prepared in methanol p.a. (ACS, CAAL), using toluene PA (ACS, Merck), xylene (PA J. T. Baker), and benzene (PA, Merck). These standards were employed to the calibration of the gas chromatograph and to spike the pool of seawater and purified water.

Processing

The spiked seawater and purified water samples were irradiated with 10, 15, 20 and 50 kGy absorbed doses. Irradiation were carried out at room temperature, using a ^{60}Co Gammacell-type gamma-irradiator in a batch system. This system is calibrated routinely with Fricke dosimeter to determine the absorbed dose, by the Dosimetry Research Group in a routine way. The vials (20 ml) were completely filled without headspace in triplicate.

Chemical analysis

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

Gas chromatograph associated to mass spectrometry using a Shimadzu GCMS, Model QP-5000, with a 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, 30 m×0.25 mm, 0.25 μm film thickness; mass detector operation in electron impact mode (EI), using 1.50 kV of ionizing voltage and temperature of 250 °C; interface temperature of 240 °C and continuous operation mode (SCAN).

Sample concentrator type Purge and Trap, O. I. Analytical, Model 4560, associate to GC, Model 17A, with flame ionization detector (FID) and with capillary column, coated with DB5, J&W Scientific, 30 m×0.25 mm, 0.25 μm film thickness, 5 ml of volume sample.

Results and discussion

Chemical analysis

To evaluate the BTX sensibility of the two detection systems, a calibration curve was made in water purified by Milli-Q system, and in a pool of seawater with different concentrations, using the concentrator type Purge and Trap with GC-FID detector and Head Space system with MS detector.

Table 1. Samples collected in August 25, 2004 and their localization

Sample	Depth, m	Time	Latitude	Longitude	*T*, °C	Salinity, μg/l
FO-1	7	9:14	S23°31.532	W45°09.288	27	36.40
FO-2	6	9:39	S23°31.532	W45°09.288	24	35.50
FO-3	5	9:57	S23°31.532	W45°09.288	24	36.16
FO–4	4	10:14	S23°31.532	W45°09.288	24	36.07
FO–5	3	10:20	S23°31.532	W45°09.288	24	36.08
FO–6	2	10:33	S23°31.532	W45°09.288	24	36.08
FO–7	1	10:43	S23°31.532	W45°09.288	24	35.99
PE-1	4	13:31	S23°29.513	W45°06.315	24	35.96
PE-3	2	14:09	S23°29.513	W45°06.315	24	35.85
PE–4	1	14:22	S23°29.513	W45°06.315	24	35.73
FPE-1A	1.5	15:08	S23°29.398	W45°06.361	24	36.11
FLA-1A	7	16:11	S23°30.530	W45°05.988	25	36.13
FLA–3	5	16:38	S23°30.530	W45°05.988	24	36.12
FLA-4	4	16:47	S23°30.530	W45°05.988	25	35.99
FLA–6	2	17:07	S23°30.530	W45°05.988	25	35.80
FLA–7	1	17:17	S23°30.530	W45°05.988	26	35.74
PM-01	0.80	11:20	S23°30.009	W45°07.113		–
PM-03	1.50	10:40	S23°30.008	W45°07.105		34.26
PM-04	2.80	10:30	S23°30.013	W45°07.095		34.11
PM-05	3.20	11:00	S23°30.018	W45°07.085		0.361
PM-07	2.90	10:50	S23°30.007	W45°07.093		30.15
PM-08	3.10	10:00	S23°30.012	W45°07.084		31.44

Purge and Trap concentrator with FIDGC detector showed significantly higher sensibility in seawater than Head Space concentrator with GC-MS detector. The minimal detected limits (MDL) obtained at GC-FID were 0.50 µg/l of benzene, 0.70 µg/l of toluene, and 1.54 µg/l of xylene, and the obtained experimental variability ($N = 10$), expressed as relative standard deviation considering 1 sigma of uncertainty (95%), was 10% (Fig. 1). While the concentrator type Head Space system with MS detector showed higher MDL, about 10 mg/l in seawater. The MDL were calculated considering three times the minimal area in the respective peak region.

Due to the very low concentration of BTX expected in seawater, a calibration curve was obtained using the concentrator type Purge and Trap (Fig. 1). The BTX values in the seawater samples are presented in Table 2. The obtained values are preliminary, because represent only one sampling. For more conclusive results, it is necessary to compare the findings with other analysis in the same place. The limits and concentration level (µg/l) are similar with the other petroleum hydrocarbon, nearby the region, according to the literature.[13,14]

Gamma radiolytic decomposition of BTX

To study the gamma radiolytic decomposition of BTX in seawater, a pool of seawater samples were collected from different points. These seawater samples and the samples from purified water (Milli-Q system) were spiked with different concentrations of BTX and irradiated with the same absorbed doses. The results of total organic carbon (TOC) and the concentrations of spiked samples (C1 to C4) are presented in the Table 3.

In all concentrations the purified water presented higher decomposition yield than seawater (Fig. 2). The removals were approximately 100% to all concentrations and compounds at 20 kGy absorbed doses. In seawater the removals were 100% only in concentrations up to 17.6 mg/l at 15 kGy absorbed dose.

To benzene removal the irradiation doses were higher than the other compounds for the same concentration, that can be explained by the necessity of high energy to break the aromatic ring. The removals were 10% to 40% at 20 kGy, to 35.1 mg/l and 70.2 mg/l, respectively. While toluene presents 20% to 60% in similar concentrations but at 15 kGy absorbed doses. Finally, xylene was removed more efficiently, 20% to 80% and 15 kGy absorbed doses.

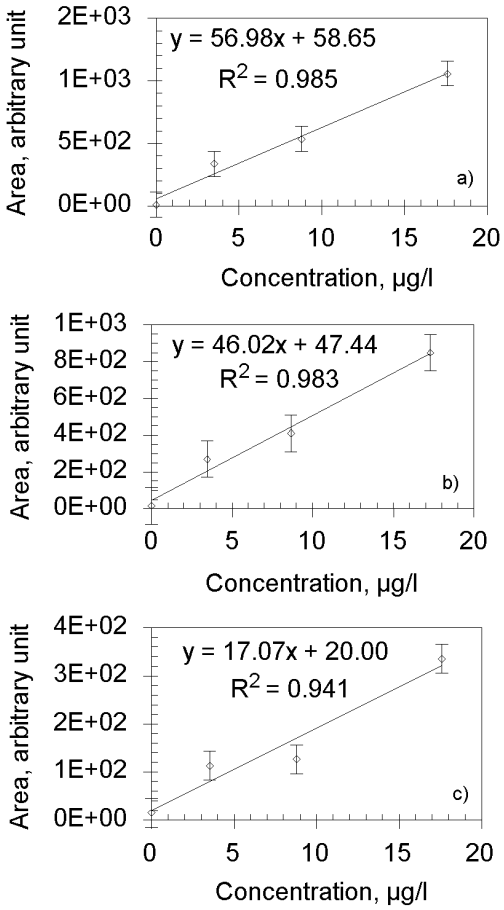

Fig. 1. Calibration curve of benzene (a), toluene (b), and xylene (BTX) (c), using Purge and trap sample concentrator and GC-FID

Table 2. BTX concentration in samples collected in August 25, 2004

Sample	Benzene, µg/l	Toluene, µg/l	Xylene, µg/l
FO-1	2.15 ± 0.21	3.25 ± 0.30	4.12 ± 0.41
FO-2	<2.01	2.96 ± 0.28	3.87 ± 0.38
FO-3	2.36 ± 0.23	3.30 ± 0.30	3.87 ± 0.38
FO–4	2.26 ± 0.22	3.12 ± 0.30	4.59 ± 0.45
FO–5	2.22 ± 0.22	3.24 ± 0.30	4.56 ± 0.45
FO–6	2.28 ± 0.22	3.20 ± 0.30	4.53 ± 0.45
FO–7	2.23 ± 0.22	3.07 ± 0.29	4.45 ± 0.44
PE-1	2.12 ± 0.21	2.62 ± 0.24	3.68 ± 0.36
PE-3	2.07 ± 0.20	2.62 ± 0.24	3.68 ± 0.36
PE–4	2.16 ± 0.21	2.73 ± 0.25	4.06 ± 0.40
FPE-1A	2.10 ± 0.21	2.59 ± 0.23	3.62 ± 0.36
FLA-1A	<2.01	2.53 ± 0.23	3.54 ± 0.35
FLA–3	<2.01	2.47 ± 0.22	3.40 ± 0.34
FLA-4	<2.01	2.52 ± 0.23	3.65 ± 0.36
FLA–6	<2.01	2.38 ± 0.21	3.29 ± 0.32
FLA–7	2.17 ± 0.21	2.41 ± 0.22	2.79 ± 0.27
PM-01	2.12 ± 0.21	2.58 ± 0.23	3.51 ± 0.35
PM-03	<2.01	2.32 ± 0.21	2.77 ± 0.27
PM-04	2.09 ± 0.20	2.49 ± 0.22	3.29 ± 0.32
PM-07	<2.01	2.39 ± 0.21	3.12 ± 0.31
PM-08	2.29 ± 0.22	2.49 ± 0.22	3.37 ± 0.33

Table 3. Total organic carbon in spiked samples of purified water and seawater

Dose, kGy	Purified water	Seawater	Purified water	Seawater	Purified water	Seawater	Purified water	Seawater
	TOC-C1, mg/l		TOC-C2, mg/l		TOC-C3, mg/l		TOC-C4, mg/l	
0.0	273.10	411.20	530.60	408.00	1315.0	689.00	2502.0	1460.0
5.0	282.50	425.70	540.10	437.00	1327.0	737.20	2577.0	1419.0
10.0	281.90	429.40	542.90	454.20	1354.0	753.30	2611.0	1452.0
15.0	285.60	436.40	547.40	560.50	1353.0	739.10	2606.0	1429.0
20.0	286.20	438.50	549.00	554.70	1179.0	751.60	2647.0	1430.0
50.0	283.90	294.60	546.30	560.30	1117.0	742.90	2657.0	1406.0

C1: Benzene 8.80 mg/l, toluene 8.65 mg/l, xylene 8.80 mg/l.
C2: Benzene 17.60 mg/l, toluene 17.30 mg/l, xylene 17.60 mg/l.
C3: Benzene 35.20 mg/l, toluene 34.60 mg/l, xylene 35.20 mg/l.
C4: Benzene 70.40 mg/l, toluene 69.20 mg/l, xylene 70.40 mg/l.

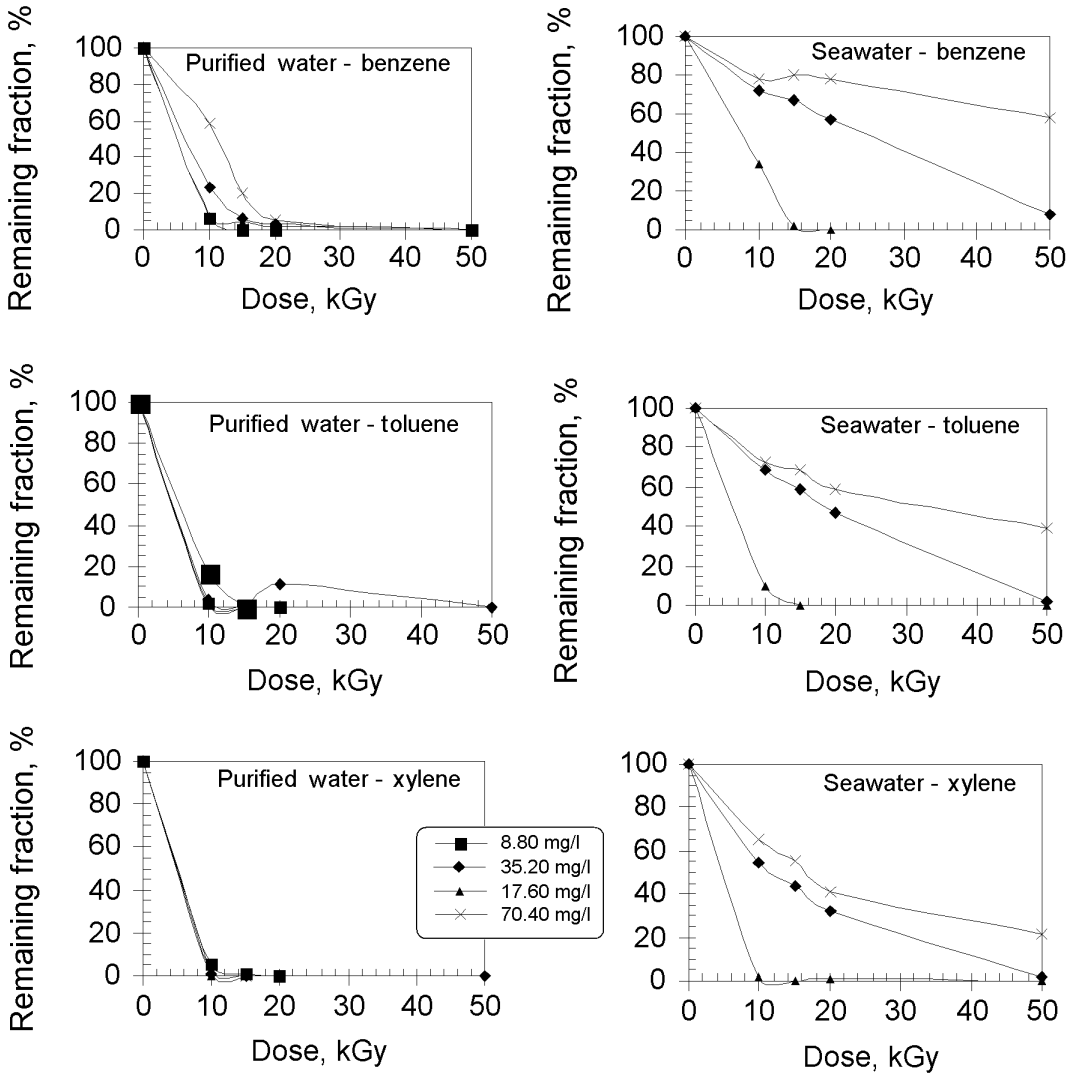

Fig. 2. Radiolytic decomposition of benzene, toluene and xylene, BTX, using spiked seawater and purified water, irradiated to various absorbed doses, using GC-MS and Head Space sample concentrator

These results are different from the assumption of the literature,[9,11] that the benzene and xylene should be removed by radiation processing with the same efficiency, while toluene would be removed less efficiently, and the OH radicals would be the radicals most responsible for the removal of 93–97% of benzene and xylene and 83.5% of toluene. However, in the case of toluene, the hydrogen radical could account for up to 16% removal.

The conductivity that represent the dissolved salts was about 1.4 μS in purified water and 6.0 mS in seawater. These salts represent some radical scavengers, such as O_2, bicarbonate/carbonate ions, nitrate ion, etc., that affect the distribution of the reactive species.

Conclusions

Purge and trap with GC-FID showed high sensibility to measure BTX in seawater. The main advantage of this concentrator system is the elimination of the extraction technique, generating no solvent waste.

Even in seawater the gamma-radiation showed high efficiency to destroy BTX, but due to the complexity of that sample (e.g., salinity) the yield was lower than in purified water.

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