Chapter 3
Evaluation of Produced Water from Brazilian Offshore Platforms

Irene T. Gabardo, Eduardo B. Platte, Antônio S. Araujo, and Fernando H. Pulgatti

Abstract Chemistry and toxicity of produced water (PW) from offshore platforms operated by Petrobras in Brazil were investigated. Three studies – PW monitoring, detailed composition and temporal variability – were conducted during 1996, 2001 and 2006 in the Campos, Santos and Ceara Basins. For approximately 50 samples the median concentrations were ammonia 70 mg L^{-1}, barium 1.3 mg L^{-1}, iron 7.4 mg L^{-1}, BTEX 4.7 mg L^{-1}, PAH 0.53 mg L^{-1}, TPH 28 mg L^{-1}, phenols 1.3 mg L^{-1}, ^{226}Ra 0.15 Bq L^{-1} and ^{228}Ra 0.09 Bq L^{-1}. Acute toxicity median values were $LC50_{96\,h} = 3.57\%$ for *Mysidopsis juniae*, $LC50_{48\,h} = 52.55\%$ for *Artemia sp*., $EC50_{72\,h} = 8.43\%$ for *Skeletonema costatum* and $EC50_{15\,min} = 16.05\%$ for *Vibrio fischeri*. Median chronic toxicity using *Lytechinus variegatus* showed a NOEC = 1.3%. These results for Brazilian PW are similar to those for the North Sea, Gulf of Mexico, Australia and other regions of the world. Dispersion plumes modelled using CORMIX and CHEMMAP predicted that PW can be diluted rapidly after discharge and that permissible levels for all chemical parameters in seawater cited in the Brazilian Resolution CONAMA 357/05 are attained within 500 m of the discharge point. Over 10 years (1998–2010) of monitoring in the vicinity of the Brazilian platforms did not show alterations in sea water quality, supporting the predictions of the dispersion plume modelling. Despite no observed alteration in seawater quality around oil and gas production platforms, the authors recognize the importance of continuous evaluation of the impact of PW discharges from a risk assessment perspective, and studies of bioaccumulation and the use of biomarkers, among other initiatives currently implemented by Petrobras in areas with large volumes of PW discharge. Up to and including 2011, Petrobras remains the major producer of oil and gas in Brazil and the total discharge of produced water by the country is essentially the volume that is discharged by offshore Petrobras operations. In 2005, the average total volume of PW discharged offshore on the Brazilian coast was 73 million m^3/year, representing less than 3% PW discharged onto other oceans worldwide.

I.T. Gabardo (✉)
Department of Environmental Monitoring and Assessment, Petrobras Research Center/CENPES, Rio Janeiro, RJ, Brazil

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1 Introduction

Input of petroleum hydrocarbons to the marine environment can occur from urban outfall, industrial and domestic effluent, navigation, transportation, offshore production and accidental release (Fingas 2001; GESAMP 1993; Bouloubassi et al. 2001; Readman et al. 2002; NRC 2003). Annually 1.3×10^6 tonnes of crude are released from natural seepage, production, transport and consumption, of which offshore oil and gas production activities contribute only 2.9% and >90% of this load is due to produced water (PW) discharge (NRC 2003). Soluble components like aromatics, organic acids and paraffins are degraded by marine bacteria (Stephenson 1992). Other factors that aid hydrocarbon weathering are dispersion, dilution, volatilization, physical—chemical reactions and sedimentation (OGP 2005).

Produced water is the largest volume waste stream in oil and gas production, consisting of natural formation and flood water injected into the formation to maintain well pressure. Initially, PW consists mainly of formation water but as the well matures the proportion of injected seawater or re-injected PW can reach over 10 times the volume of the oil produced for mature fields (OGP 2005; E&P Forum 1994). Oil platforms produce high volumes whereas gas platforms generate less volume but with high concentrations of organic contaminants such as monoaromatics (BTEX), naphthalenes and phenols. Once PW is released into seawater, the distribution of individual compounds into solid (added to particulate matter) or liquid phases depends on their chemical characteristics (Neff et al. 1989; E&P Forum 1994; OLF 2005; OGP 2005, 2002). The major constituents are inorganic salts, dispersed and dissolved hydrocarbons, organic acids and phenols which contribute to its toxicity in addition to the ionic imbalance (Swan et al. 1994) which sometimes cannot be rectified by salinity adjustment (Schiff et al. 1992); hence, toxicity factors are not easily resolved (Fucik 1992). Nevertheless, Rand (1995) considered toxicity testing as a primary approach to evaluate PW effects. Acute and chronic PW toxicity have been documented for Australia (Swan et al. 1994), the North Sea (E&P Forum 1994), Gulf of Mexico and Indonesia (Holdway 2002). There is little evidence of acute PW toxicity beyond the immediate mixing zone (Holdway 2002). Toxicity due to salinity is rapidly reduced by simple dilution in the offshore (Pillard et al. 1996).

Total oil production in Brazil was 596 million bbl in 2005, of which 521 million bbl was produced in the Brazilian offshore area (www.anp.gov.br), constituting 87% of national production. In April 2006 Brazil achieved self-sufficiency, producing 1.8 million bbl per day, implicating an increase in PW discharge. The 107 Brazilian Petrobras offshore facilities are few in comparison with the Gulf of Mexico (~4,000) and North Sea (~500). In 2005 the average annual Brazilian Petrobras offshore facilities PW discharge was 73 million m^3/year (Gabardo 2007), which amounts to less than 3% worldwide (OGP 2005).

World demand for petroleum is expected to increase 47% by the year 2030 as reported by the Energy Information Department (EIA 2006). The supply of crude oil and gas remains an important component of Brazil's current and future energy needs. Most of Brazilian oil and gas production is located in offshore areas in the

States of Rio de Janeiro and Espirito Santo, but in the Santos Basin, Petrobras recently made the biggest oil discovery in Brazil (http://www.petrobras.com.br/minisite/presal/en/questions%2Danswers/).

Prior to 2007 Brazil had no specific criterion for offshore PW discharge. Since then, CONAMA Resolution 393/2007 has established limits for PW oil and grease of 29 mg L^{-1} as a monthly average and a 42 mg L^{-1} daily maximum, besides regulatory monitoring and compliance with the seawater quality criteria of CONAMA Resolution 357/2005 outside a 500 m mixing zone. Also, offshore PW discharge requires detailed monitoring twice a year encompassing several organic and inorganic parameters (Freitas and Mendes 2010).

This chapter deals with surveys conducted in 1996, 2001 and 2005–2006 as well as other samples for PW characterization. The main objectives of this work were (a) to investigate the chemical composition and toxicity of Brazilian PW; (b) to compare Brazilian PW with other regions of the world; (c) to evaluate a single platform for PW temporal variability characteristics; (d) to apply dispersion models to predict environmental effects; (e) to compare modelled predictions in the platform vicinity with field data.

2 Experimental

Figure 3.1 shows the platforms with PW discharge in 2005, and their positions along the Brazilian coast. Table 3.1 presents the detailed platforms data including location, coast distance, water depth, discharge depth and discharge flow. Although there were 107 platforms on the Brazilian coast, only 24 platforms discharged effluents.

2.1 Methods

Study 1 was concerned with monitoring of ammonia (APHA 1995; Standard Method 4500-NH3, colorimetry), Ba, B, Fe, ^{226}Ra and ^{228}Ra (Godoy et al. 1994), BTEX (EPA 5021, headspace, GC-PID), TPH (EPA 1664/8015, GC-FID), PAH (EPA 3510C/3630C/8270D, GC-MS sum of 36 and 38 PAH compounds in 2001 and 2006, respectively), phenols (EPA 3510C/8270D, GC-MS) and toxicity for approximately 55 samples: these data were collected during 1996, 2001 and 2005–2006.

Study 2 consisted of detailed composition profiles from a single sample at each of the 21 platforms in Campos Basin, one in Santos Basin and one in Ceara Basin (Fig. 3.1, Table 3.1), collected from September 2005 to January 2006, and analysed for temperature, salinity (Standard Method 4500, chloride potentiometry), pH, density (densimeter), TSS (Standard Method 2540D, gravimetry), alkalinity (Standard Method 2320, potentiometry), anions (chloride, fluoride, sulphate, nitrate; ion chromatography, electrolytic suppressor/conductivity detector), mercury (UOP 938, auto-analyser NIC SP-3D), metals (Standard Method 3120B, ICP-OES), ^{226}Ra

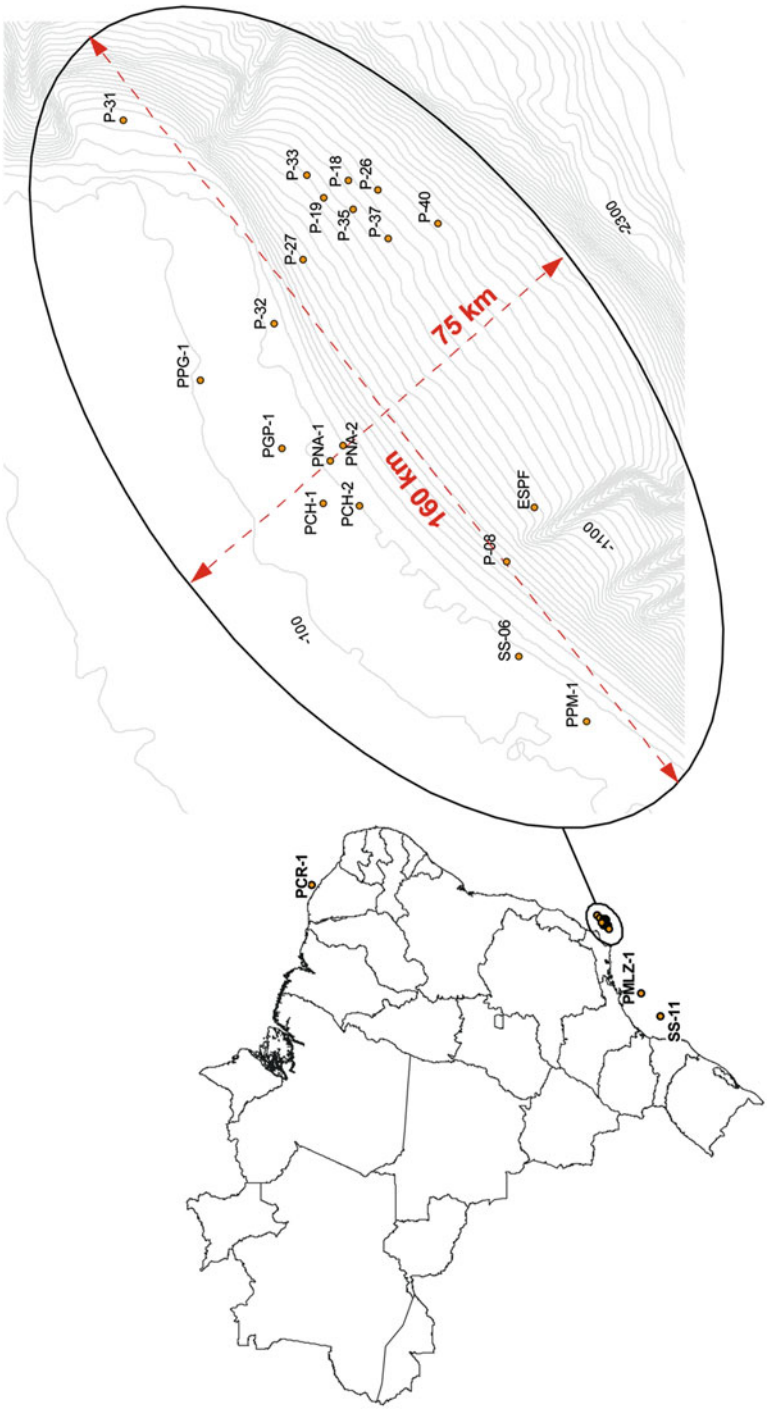

Fig. 3.1 Platforms with produced water discharge along the Brazilian coast (Gabardo 2007, from database 2005)

Table 3.1 Platforms with produced water discharge along the Brazilian coast[a]

Platform	Production	Treatment	Latitude S	Longitude W	Distance (km)	Water depth (m)	Discharge depth (m)	Discharge (m^3/day)
Southeast region – Campos Basin, Rio de Janeiro State, 40 platforms, 21 discharging PW								
PCH-1	Oil and gas	Hydrocyclone, degasser	22°25′ 56.998″	40°28′ 48.309″	71	117	28	845
PCH-2	Oil and gas	Hydrocyclone, degasser	22°27′ 56.030″	40°28′ 06.158″	74	142	–	4,124
PNA-1	Oil and gas	Hydrocyclone, degasser	22°26′ 17.507″	40°25′ 26.815″	76	145	49	2,498
PNA-2	Oil and gas	Hydrocyclone degasser	22°27′ 00.000″	40°24′ 41.000″	77	170	30	5,240
PGP-1	Oil and gas	Oil electrostatic treater, oil/water gravitational separator tank	22°22′ 27.330″	40°25′ 01.440″	72	120	32	4,685
PPM-1	Oil and gas	Oil electrostatic treater, hydrocyclone and dissolved gas flotation	22°47′ 51.010″	40°45′ 43.750″	87	115	63	13,276
PPG-1	Oil and gas	Hydrocyclone, degasser	22°15′ 18.180″	40°19′ 46.425″	72	101	40 or 60	16,823
P-08	Oil and gas	Hydrocyclone, degasser	22°40′ 21.199″	40°32′ 45.618″	87	423	Surface	980
P-18	Oil and gas	Hydrocyclone, degasser	22°25′ 40.887″	40°01′ 41.456″	109	910	Surface	2,650
P-19	Oil and gas	hydrocyclone, degasser	22°23′ 32.058″	40°03′ 15.660″	105	748	Surface	6,162
P-26	Oil and gas	Hydrocyclone, degasser	22°28′ 05.623″	40°01′ 42.174″	110	990	Surface	6,568
P-27	Oil and gas	Hydrocyclone, degasser	22°22′ 49.047″	40°08′ 44.085″	96	540	Surface	2,039
P-31	Oil and gas	Hydrocyclone, degasser	22°07′ 46.640″	39°57′ 58.510″	105	320	Surface	9,538
P-32	Oil	Oil electrostatic treater, hydrocyclone, slop tank	22°20′ 53.801″	40°14′ 24.184″	85	160	Surface	1,535
P-33	Oil and gas	Oil electrostatic treater, hydrocyclone, dissolved gas flotation, slop tank	22°22′ 18.464″	40°01′ 29.933″	107	780	Surface	1,781
P-35	Oil and gas	Oil electrostatic treater, slop tank	22°26′ 11.668″	40°04′ 03.948″	106	850	Surface	8,092
P-37	Oil and gas	Oil electrostatic treater, slop tank	22°29′ 05.010″	40°05′ 43.790″	106	905	Surface	9,586
ESPF	Oil and gas	Oil electrostatic treater, hydrocyclone, slop tank	22°42′ 34.441″	40°27′ 33.918″	96	795	Surface	4,166
SS-06	Oil	Oil electrostatic treater, hydrocyclone, dissolved gas flotation	22°42′ 04.790″	40°40′ 36.180″	80	120	11	11,412
P-40	Oil and gas	Oil electrostatic treater, hydrocyclone, induced gas flotation	22°32′ 48.889″	40°04′ 01.511″	113	1,070	Surface	8,300[b]
FPBR[b]	Oil and gas	Hydrocyclone, slop tank	21°56′ 01.480″	39°49′ 00.090″	120	1,258	Surface	
Northeast Region – 65 platforms in 4 States (SE, AL, CE, RN) but only one discharging PW located in Ceara Basin								
PCR-1	Oil and gas	Oil electrostatic treater	3°05′ 25.568″	38°47′ 34.984″	40	45	21	1,664
South region – Santos Basin, São Paulo State, 2 platforms, 2 discharging PW								
SS-11	Oil and gas	Oil electrostatic treater, hydrocyclone, degasser	26°38′ 51.220″	40°52′ 24.810″	160	150	Surface	330
PMLZ-1[c]	Gas and condensate	Gas treatment & compression	25°15′ 59.304″	45°15′ 08.552″	145	189	Surface	23[c]

[a]Daily discharge (during the year 2005)
[b]Discharge by batches 5′000–15′000 m^3/batch
[c]Sampled only in 2000 due to very small volume of discharge
Datum SAD69 for the geographical coordinates

and ^{228}Ra (Godoy et al. 1994), TOC (Standard Method 5310B, auto-analyser), organic acids (ion chromatography, electrolytic suppressor/conductivity detector) and toxicity. For the southern area, PMLZ-1 was the only platform producing gas and condensate, and was sampled only in 2000 due to the low volume discharged in 2005. In the northeast area of Brazil, PW is pumped to on-shore treatment facilities and only PCR-1 (Curimã platform) discharges PW: this platform was producing a significant amount of gas.

Study 3 on temporal variability at PCR-1 consisted of nine sequential samples collected in 48 h on December 11–12, 2003, with intervals of 3 h, and four individual samples collected in July 2001, June 2003, December 2004 and January 2006. These were analysed for salinity, pH, TOC, TSS, ammonia, sulphide (Standard Method 4500-S-Sulfide, potentiometry), cyanide (Standard Method 4500-CN, voltammetry), anions, BTEX and PAH.

Several laboratories were involved, depending on the campaigns, including CENPES, the Petrobras Research Center (anions, organic acids, BTEX, PAH, phenols); metals and radioisotopes by PUC-Rio Catholic University; PAH, BTEX and phenols by Analytical Solutions and CTGAS, and toxicity by CENPES (Microtox, *Artemia sp.*), LABTOX and University of Itajai Valley.

Samples were collected by laboratory technicians or trained platform operators from Petrobras, who also performed the on-site physical and chemical analysis. Oil and grease, currently are determined gravimetrically according to CONAMA Resolution 393/2007, but this was established after the samples had been analysed. Instead, we used the TPH data from the GC-FID analysis to quantify total oil content in 22 samples from Study 2. Samples were refrigerated during transportation by helicopter from the platforms. As PW is very saline, samples usually have to be diluted 10–1,000 fold, so metals were often below the detection limit.

Acute toxicity tests were done using *Mysidopsis juniae* (96 h survival, with organisms 1–8 d old, CETESB L05.251/1995, ABNT 15308/2005), *Artemia* sp. (48 h survival, CETESB L05.021/1987), *Skeletonema costatum* (72 h growth, ISO 10.253:1995) and *Vibrio fischeri* (Microtox® System, 15 min, CETESB L05.227/2001, ABNT 15411-3/2006), while chronic tests were performed with the sea-urchin *Lytechinus variegatus* (embryo development 24 h after fertilization, CETESB L05.250/1992, ABNT 15350/2006). Salinity was adjusted to normal seawater when necessary, except for brine shrimp (*Artemia* sp.) that tolerates high salinity since it is normally found in salt lakes and inland brackish waters (Veiga and Vital 2002). All organisms used in this study are indigenous to Brazil. The methods were developed by the São Paulo State Environmental Agency (CETESB), but have been recently adapted by the Brazilian Standardization Association as Brazilian Standard Methods (ABNT 2005, 2006a/b). Results for acute toxicity tests are expressed in Effect Concentration to 50% of exposed organisms (EC_{50}) and Lethal Concentration to 50% of exposed organisms (LC_{50}), for chronic toxicity tests; the results are in Lowest Observed Effect Concentration (LOEC) and No Observed Effect Concentration (NOEC).

2.2 Quality Assurance and Quality Control

Daily checks of calibration curves with a second standard, use of blanks, surrogates, percent recoveries, standard spiking for each batch and repeated analysis of some sample extracts were conducted. For the toxicity tests, a minimum of three dilution replicates were analysed for each sample and quality assurance was based on sensitivity tests, variability of the controls and maximum acceptable effect on controls.

2.3 Statistical Analysis

Statistical analysis was performed using SPSS for Windows 10.0 (SPSS, Inc. 1989–1999) and STATISTICA 6.0 (Statsoft, Inc. 1984–2001). Outliers and extreme values were not excluded (except for ANOVA), so we chose medians instead of means as being more representative results. The interquartile range was used as a measure of spread. An outlier is any value that lies more than 1.5 times the interquartile range from either end of the box. An extreme value is one that lies more than 3 times the interquartile range from either end of the box (Barnett and Lewis 1994).

2.4 Modelling

Applied Science Associates (ASA) South America in Sao Paulo, Brazil, used two models: Cornell Mixing Zone Expert System (CORMIX, developed by Cornell University, USA) and Chemical Discharge Model System (CHEMMAP, ASA Inc., USA). The CORMIX model was used for near-field studies where effluent speed and density dominate in the first few minutes and the principal mechanism is dilution. In the initial dilution or jet phase, the plume rapidly entrains ambient sea water.

The CHEMMAP model was used for the far-field modelling where effects due to site dynamics and passive transportation in the plume happen in hours or days. The model uses individual compound density, vapour pressure, solubility, degradation rate, adsorbed and dissolved partition coefficients, viscosity, surface tension and ambient forcing from wind, currents and seawater density and considers mixtures of products. Far-field dilution is only important during the first hours, after which other concentration reduction mechanisms prevail. The model was used in the stochastic mode to predict the trajectory and biogeochemical transformations (fate) of compounds. Spreading, advection, dispersion, evaporation, volatilization, entrainment, dissolution, partitioning, sedimentation, adsorption and degradation were simulated. The mass of the chemical component is transported by three-dimensional currents as determined by the hydrodynamic model that is forced by tides, wind, oceanic currents, buoyancy and dispersion. The plume was simulated as Lagrangian particles of known mass.

In probabilistic mode, simulations covered January to March (summer) and June to August (winter) for the Campos Basin, and May to July (winter) and October to

December (summer) for the Ceara Basin. Each scenario for plume behaviour was composed of 30 simulations in which there was constant PW release over 24 h and variable meteorological and oceanographic data. To determine the area of influence of the plume, multiple trajectories were used to produce contour curves of maximum expected concentrations for each chemical component at each grid point and the average of the highest concentrations was calculated for the 30 simulations. Data on effluent properties and field conditions were used as input data for the modelling studies' predictions of water column concentrations.

The modelling studies occurred in 2004/5 and the PW composition inputs were the median values of real PW compositional data obtained in 2001. To emphasize plume shape and characteristics, a dilution value equivalent to 10,000 times the CONAMA Resolution 357/2005, Class I regulation criteria for seawater was considered as the threshold value to stop the simulation. Also concentrations of each component at the 500 m limit of the mixing zone (established by CONAMA Resolution 393/2007) were predicted.

3 Results

The results of the PW composition and toxicity obtained for all 3 studies are summarized in Table 3.2. Details can be found in the PhD thesis by Gabardo (2007).

3.1 Results of Study 1

In order to verify the variability between different samples and sampling times, the results for approximately 50 samples were compiled using selected PW parameters (Table 3.3).

3.2 Results of Study 2

For the detailed PW study, 23 samples were collected. pH ranged from 6 to 8.2, temperature from 33 to 90°C (median = 59°C) and TSS from 1.9 to 106 mg L^{-1} (median = 10.6 mg L^{-1}). Median concentrations of anions were sulphates 481 mg L^{-1}, bicarbonates 436 mg L^{-1}, nitrates <0.1 mg L^{-1}, fluorides 2.1 mg L^{-1} and chlorides 45,776 mg L^{-1}. In all samples the concentration of cyanide was below the detection limit (<10 μg L^{-1}). Salinity was 38,182–179,766 mg L^{-1} with a median of 75,434 mg L^{-1}. Ammonia concentration ranged from 22 to 91 mg L^{-1}, with a median of 51.7 mg L^{-1}. Radionuclide activity for ^{226}Ra ranged from 0.02 to 10.9 Bq L^{-1} and for ^{228}Ra from 0.04 to 10.5 Bq L^{-1}.

TOC, measured by TOC Automatic Analyser, ranged from 86 to 971 mg L^{-1} (median = 307 mg L^{-1}).

Table 3.2 Median results of PW from Brazilian platforms; n = number of samples

	Study 1 monitoring general parameters 1996–2006		Study 2 monitoring detailed composition 2005/6		Study 3 variability at same platform 1996–2006	
Parameter	n	mg L^{-1}	n	mg L^{-1}	n	mg L^{-1}
Benzene		1.7		1.6		9.1
Toluene		1.9		2.1		5.2
Ethylbenzene	53	0.2	22	0.2	11	0.4
Xylenes		0.9		0.9		1.1
BTEX		4.7		4.9		15.8
TPH	45	28	22	10.0	10	37.4
Phenols	46	1.3	23	0.73	11	2.0
PAH[a]	45	0.53	23	0.44	10	0.61
Ammonia	47	70	23	51.7	4	47
Ba	55	1.3	23	2.0	12	1.0
B	55	31	23	36.4	12	17.5
Fe	53	7.4	23	1.1	12	17
Ra-226 (Bq L^{-1})	36	0.15	23	0.42	–	–
Ra-228 (Bq L^{-1})	36	0.09	23	0.41	–	–
Toxicity tests						
L. variegatus $_{\text{NOEC }\%}$	45	1.3	24	1.97	11	12.5
L. variegatus $_{\text{LOEC }\%}$	45	5	24	3.92	11	25
M. juniae $_{LC_{50}\%}$	36	3.57	24	2.95	2	1.1
Artemia sp. $_{LC_{50}\%}$	44	52.55	23	61.3	3	64.7
S. costatum $_{EC_{50}\%}$	–	–	16	8.43	–	–
V. fischeri $_{EC_{15}\%}$	12	16.05		–	–	–

[a]In 1996 PAH were quantified by UV Fluorescence and were not integrated with the 2001 and 2005 results that were obtained by GC-MS

TPH concentrations ranged from 4 to 66 mg L^{-1} (median = 10 mg L^{-1}). From this analysis, GC-FID fingerprints were obtained and in general, oil profiles were typical (a) for some PW samples, but for others the profile showed an atypical pattern (Fig. 3.2b), that was investigated using GC-MS. Cyclic sulphur compounds in PW extracts were probably generated from the reaction H_2S scavenger and identified alkylbenzene peaks from C8 to C10 were from demulsifier solvents.

BTEX concentrations ranged from 1.39 to 20 mg L^{-1} (median = 4.87 mg L^{-1}). Individual concentration ranges were benzene, 0.6–13.46 mg L^{-1}; toluene, 0.4–5.97 mg L^{-1}, ethylbenzene, 0.05–0.77 mg L^{-1} and xylenes, 0.23–3.90 mg L^{-1}. The highest BTEX concentrations were obtained at platforms P-35 (13.2 mg L^{-1}), SS-11 (20 mg L^{-1}), PPG-1 (9.7 mg L^{-1}) and PCR-1 (7.2 mg L^{-1}).

Total phenols (sum of 14 compounds) ranged from 49.7 to 5,735 μg L^{-1} with a median of 730 μg L^{-1}. The compound concentrations were phenol, 4–450 μg L^{-1}; C1-phenols 0.013–0.99 μg L^{-1}; C2-phenols 0.029–3.68 μg L^{-1}, and C3-phenols, 0.003–0.62 μg L^{-1}.

Table 3.3 Summary of chemical analysis and toxicity of PW samples obtained for Study 1

Parameter	Min	Max	Mean	Median	SD	*n*
Ammonia (mg L^{-1})	22.3	800	85.4	70	111	47
Ba (mg L^{-1})	0.2	45	7.1	1.3	10.0	55
B (mg L^{-1})	6	120.4	34.2	31	19.6	55
Fe (mg L^{-1})	0.04	25	7.5	7.4	6.9	53
^{226}Ra (Bq L^{-1})	0.01	10.9	1.24	0.15	2.5	36
^{228}Ra (Bq L^{-1})	<0.02	10.5	1.39	0.09	2.8	36
Benzene (μg L^{-1})	490	13,462	3,324	1,653	3,493	53
Toluene (μg L^{-1})	458	8,639	2,572	1,917	1,957	53
Ethylbenzene (μg L^{-1})	38	770	242	211	162	53
Xylenes (μg L^{-1})	208	3,904	975	859	656	53
BTEX (μg L^{-1})	1,384	21,624	7,115	4,690	5,749	53
TPH (mg L^{-1})	4.0	251	45	28	51.6	45
Phenols (mg L^{-1})	0.05	83.5	3.48	1.42	12.03	47
PAH (μg L^{-1})	42	1,558	595.9	527.2	348.3	45
Toxicity						
L. variegatus $_{NOEC\ \%}$	<0.1	12.5	3.44	1.3	4.2	45
L. variegatus $_{LOEC\ \%}$	≤0.1	25	7.74	5	8.1	45
M. juniae $_{LC_{50}\%}$	<0.6	9.5	3.87	3.57	2.3	36
Artemia sp $_{LC_{50}\%}$	1.6	>100[a]	53.96	52.55	26.0	44

[a]No toxicity observed

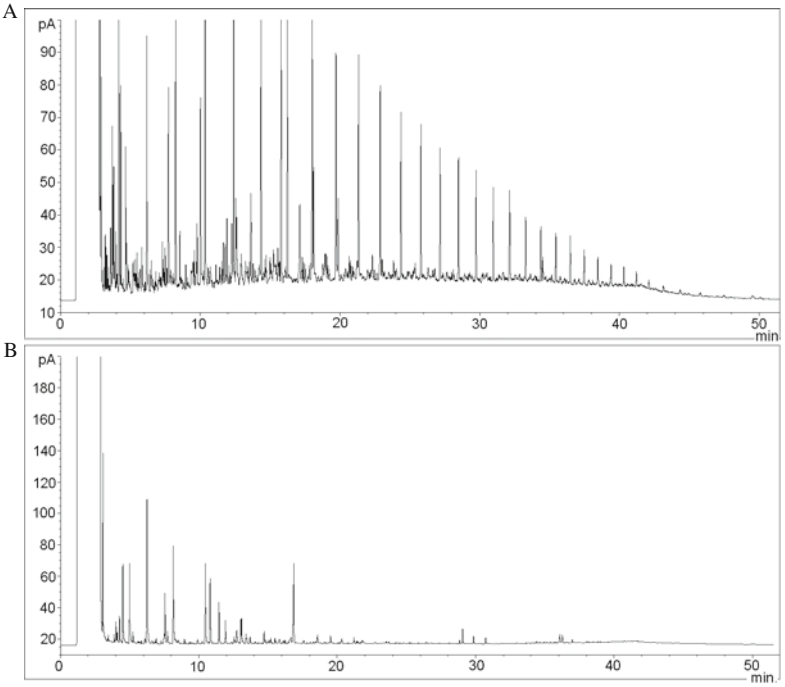

Fig. 3.2 TPH fingerprints obtained by GC-FID for two Brazilian PW with oil signature (*top*) and atypical profile (*bottom*)

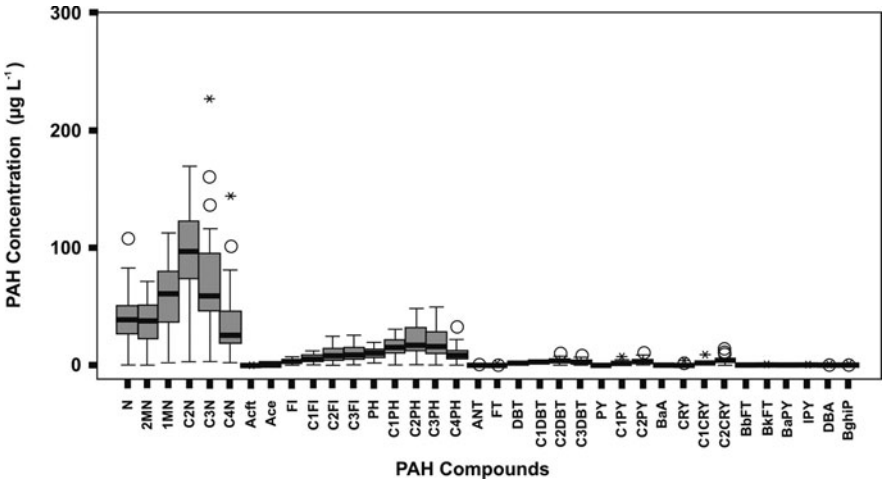

Fig. 3.3 Minimum, maximum and median of the PAH concentrations in Brazilian PW sampled in Study 2: (n = 23 samples) box-and-whisker plot outliers are marked with *open dots*, and extreme values are marked with *asterisks.*
N: Naphthalene; 2MN: 2-MethylNaphthalene; 1MN: 1-MethylNaphthalene; C2N: C_2Naphthalenes; C3N: C_3Naphthalenes; 4N: C_4Naphthalenes; Aceft: Acenaphthylene; Ace: Acenaphtene; FL: Fluorene; C1FL: C_1Fluorenes; C2FL: C_2Fluorenes; C3FL: C_3Fluorenes; PH: Phenanthrene; C1PH: C_1Phenanthrenes; C2PH: C_2Phenanthrenes; C3PH: C_3Phenanthrenes; C4PH: C_4Phenanthrenes; ANT: Anthracene; FT: Fluoranthene; DBT: Dibenzothiophene; C1DBT: C_1Dibenzothiophenes; C2DBT: C_2Dibenzothiophenes; C3DBT: C_3Dibenzothiophenes; PY: Pyrene; C1PY: C_1Pyrenes; C2PY: C_2Pyrenes; BaA: Benz(a)anthracene; CRY: Chrysene; C1CRY: C_1Chrysenes; C2CRY: C_2Chrysenes; BbFT: Benz(b)fluoranthene; BkFT: Benz(k)fluoranthene; BaPY: Benz(a)pyrene; IPY: Indeno(1,2,3-cd)pyrene; DBA: Dibenz(a,h)anthracene; BghiP: Benzo(ghi)perylene

Polycyclic Aromatic Hydrocarbons. Figure 3.3 presents a box-and-whisker plot of the data for Study 2. Outliers are marked with open dots, and the extreme values with asterisks. Based on 38 PAH compounds analyzed the mean was 476.4 µg L^{-1} and the median 438.5 µg L^{-1}, indicating homogeneity of the data. Ninety-one percent of all PAH were composed by two and three-ring aromatic compounds that include naphthalenes, phenanthrenes and dibenzothiophenes (NPD), and the more condensated PAH (4–6 rings) comprise only 2.71%. This was the pattern for all the Brazilian PW analysed and is common worldwide (Terrens and Tait 1996; Utvik et al. 1999; Neff 2002; Durell et al. 2006; OGP 2005, 2002; E&P Forum 1994).

Toxicity. Figure 3.4 shows the maximum, minimum and the median values obtained in each study using different organisms. Acute toxicity ranged from 0.6 to 9.5% PW for *M. juniae*; from 1.5 to 22.4% for *S. costatum*; 9.2 to 25.6% for *V. fischeri* and 5.3 to >100% for *Artemia* sp. The NOEC for *L. variegatus* ranged from <0.1–5%.

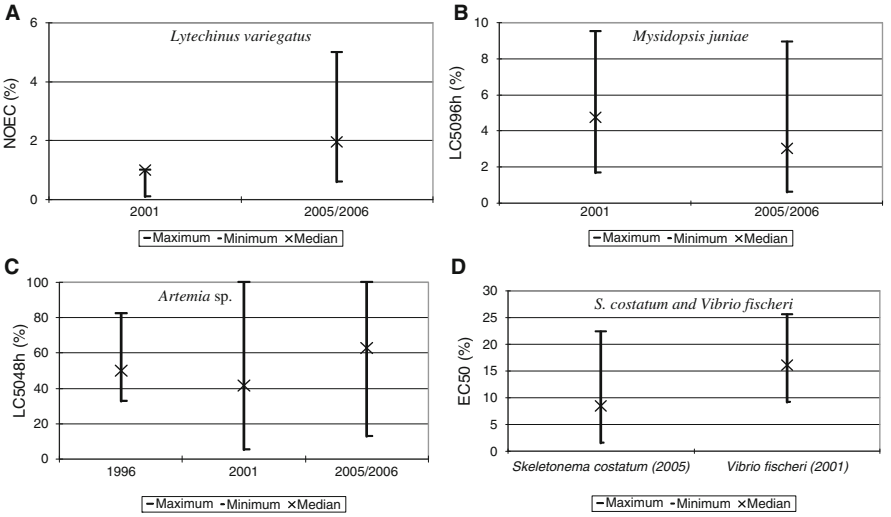

Fig. 3.4 Toxicity tests results: minimum, maximum and the median for the organisms. **a** *Lytechinus variegatus*, **b** *Mysidopsis juniae*, **c** *Artemia* sp. and **d** *S. costatum* and *Vibrio fischeri* for all the surveys

3.3 Results of Study 3

Figure 3.5 presents the results for Study 3 (Variability at the same platform: PCR-1). The only means that were found to be significantly different were the LOEC (23.4% for continuous 24 h sampling vs. 6.3% for individual samples) for *L. variegatus*. ANOVA evaluation was not performed on Ba, B, Fe, TPH, phenols or PAH due to the small sample size and the presence of outliers. Although the trace analyses were performed by different laboratories the results were consistent. When comparing PCR-1 chemistry data with other Brazilian platforms, more elevated BTEX and phenol concentrations were noticed in the PCR-1 produced water, probably, due to its relatively high production of gas. NOEC chronic toxicity values ranged from 0.8 to 12.5%. Fluctuations in toxicity were lower in the continuous 24 h sampling than in the punctual surveys as expected, considering the differences in the PW treatment processes and in the laboratories used (Fig. 3.5).

3.4 Modelling Results

Table 3.4 presents the effluent properties input for the modelling studies and the predicted CORMIX model near-field initial dilution for the platforms studied. For the Campos Basin (southeast region) the dilutions ranged from 96 to 279 times in the summer and 106–348 times in the winter. For PCR-1 in the Ceara Basin (northeast region), the dilutions in near-field were between 713 (winter) and 895 (summer) fold.

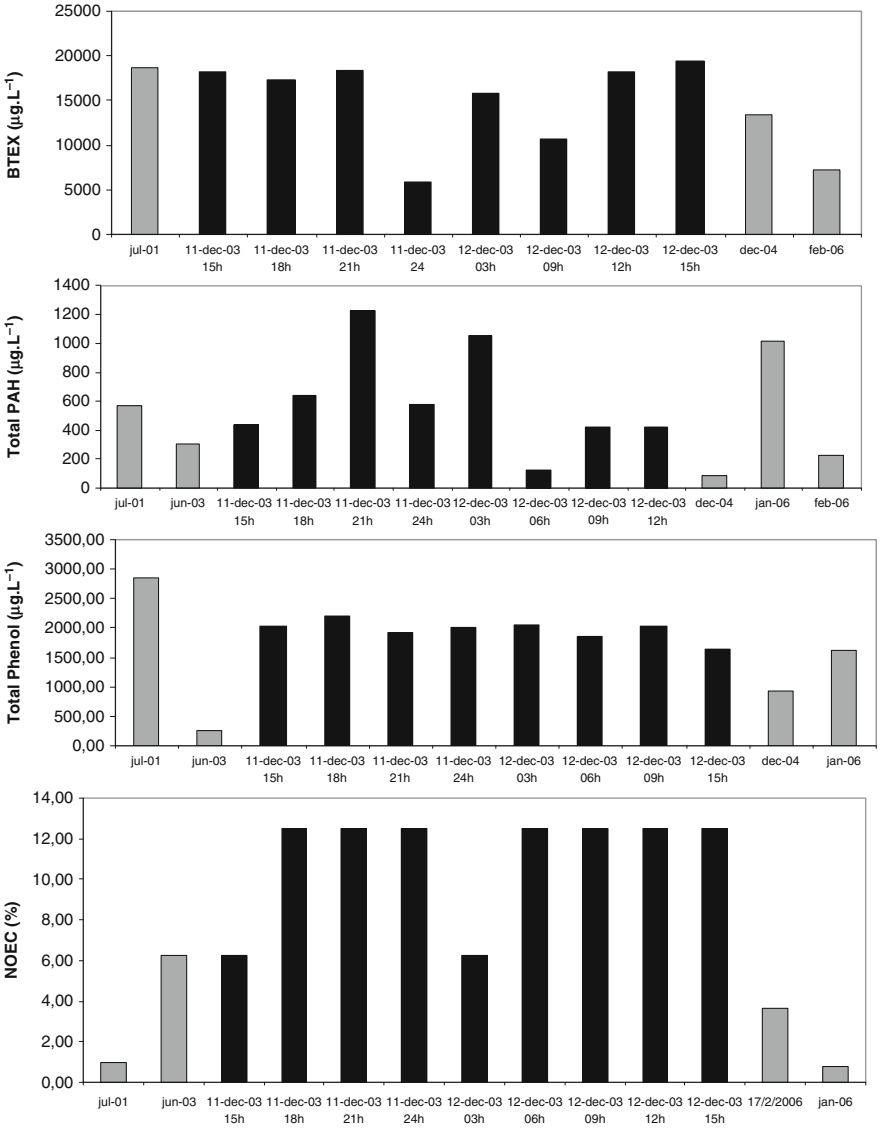

Fig. 3.5 Temporal variability of BTEX, PAH, phenols and chronic toxicity using *Lytechinus variegatus* for the same platform, PCR-1 (*Black bars* = 2 days continuous sampling, *gray bars* = individual samples)

For more than 90% of results, the concentrations of principal analytes, even at near-field dilution, were below the CONAMA Resolution 357/2005 quality criteria for Class I seawater. CONAMA Resolution 393/2007 determines 500 m as the PW mixing zone, and beyond this the seawater quality criteria must be achieved (www.mma.gov.br/port/conama/legiano.cfm?codlegitipo=3), and it was, for the predicted concentrations of all parameters at all the platforms studied (Gabardo 2007).

Table 3.4 Input parameters for plume dispersion studies using CORMIX and CHEMMAP models and the results of dilution and distances from the discharge point in near-field dispersion

	Campos basin – SE				Ceara basin – NE
Parameter	P-32	P-26	PPG-1	SS-06	PCR-1
Pipe diameter	10″	12″	40″	12″	24″
Discharge direction	Vertical	Vertical	Vertical	Vertical	Vertical
Water depth	160 m	990 m	101 m	120 m	45 m
Depth of discharge	Surface	Surface	60 m	8 m	21 m
PW discharge flow m^3/day	4,500	6,400	20,000	12,000	1,000
PW density kg/m^3	1,028	1,028.8	1,054.3	1,060.4	1,056
Benzene (mg L^{-1})	0.917	1.338	1.585		10.18
Toluene (mg L^{-1})	2.265	2.310	0.796	0.349	5.71
Total phenols (mg L^{-1})	1.229	1.577	nr		2.02
Chrysene-PAH (mg L^{-1})	0.0009	0.0012	0.0035		0.0025
Sulphides (mg L^{-1})	6.8	0.05	0.05		1.21
Ammonia (mg L^{-1})	78.0	81.0	90.0		82.0
Barium (mg L^{-1})	1.09	1.21	12.5		1.6
Boron (mg L^{-1})	26.40	21.10	27.2		20.0
Lead (mg L^{-1})				0.71	
Cadmium (mg L^{-1})				0.40	
Nickel (mg L^{-1})				2.60	
Dilution and distance for near-field dispersion (based on Cormix Model)					
Summer dilution (times)	101	156	96	279	895
Summer distances (m)	27	39	111	189	44
Winter dilutions (times)	106	152	110	348	713
Winter distances (m)	29	34	129	221	33

As an example, Fig. 3.6 shows aerial views of the modelled plumes for each parameter analysed at 500 m from the discharge point in the winter for two platforms (PCR-1 and PPG-1), and a comparison with the regulatory parameters for seawater Class I (Conama 357/2005). For each point, the model calculates the average maximum concentration in time and space in the water column; therefore, the predicted results are very conservative from an environmental point of view. For all the platforms studied, all the parameters complied with the Class I seawater legislation criteria within a distance of 500 m from the PW discharge point in summer and winter conditions (Gabardo 2007).

3.5 Environmental Monitoring Data

Environmental monitoring, which included direct measurement of PW constituents as well as seawater chemistry and toxicity, has been required to maintain permits according to Brazilian law (Scofano et al. 2010; Soares and Scofano 2010). Petrobras has been conducting extensive field studies on fate and effects of PW

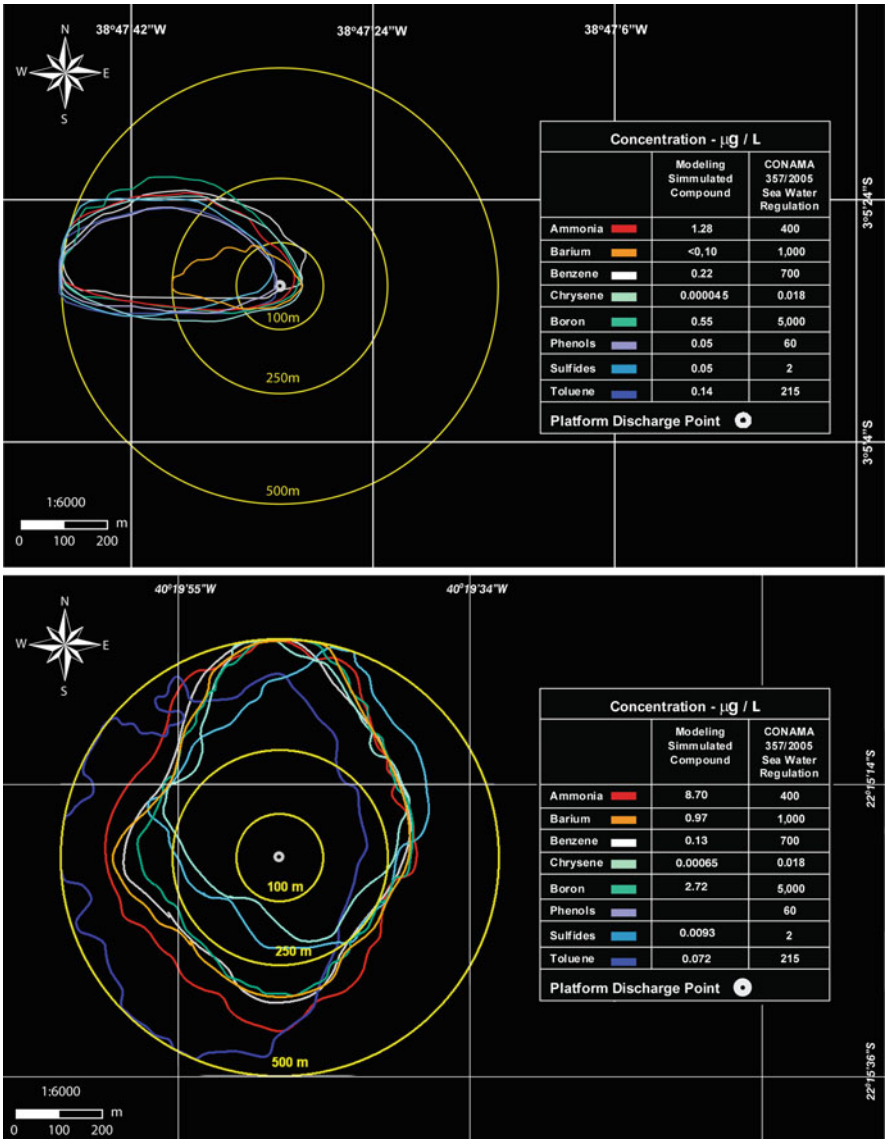

Fig. 3.6 Aerial view of the modelled plumes containing the shape and average of maximum predicted concentration at 500 m distant from the discharge point in winter conditions for PCR-1 (*top*) and PPG-1 (*bottom*) platforms

in the vicinity of its platforms since 1998. Only as an illustrative example, data collected around six platforms are presented in Table 3.5, with about 800 seawater samples collected and more than 12,000 results obtained. Also, there was no observed acute or chronic toxicity for those seawater samples. The data were

Table 3.5 Seawater data in the vicinity of six Brazilian platforms compared to criteria established in CONAMA Resolution 357/2005[a]

Parameter	PPM-1	PPG-1	P-40	FPBR	SS-06	PCR-1	CONAMA 357/2005 seawater class I
Date	Jan–Jul 1998	Jan–Jul 1998	2001–2004	2003–2004	2001–2005	2001–2003	
Number of surveys	2	2	4	2	7	4	
Number of samples/survey	24	24	63	13	41	9	
Total of samples	48	48	252	102	287	36	
Regulatory parameters							
Total phosphorus (mg L^{-1})	A	A	A (99%)	A (95%)	A	–	0.062
Nitrate (mg L^{-1})	A	A	A (92%)	A	A	A	0.4
Nitrite (mg L^{-1})	A	A	A	A	A	A	0.07
Ammonia (mg L^{-1})	A	A	A	A	A	A	0.4
Dissolved oxygen (mL L^{-1})	A	A	A	A	A (98%)	A	> 4.2
pH	A	A	–	A	A	–	6.5–8.5
COT (mg L^{-1})	–	–	–	A	–	–	< 3
Phenols (μg L^{-1})	A	A	–	A	A	A	60
Bz(a)Ant (μg L^{-1})	–	–	A	A	A	A	0.018
Bz(a)Py (μg L^{-1})	–	–	A	A	A	A	0.018
Bz(b)Flu (μg L^{-1})	–	–	A	A	A	A	0.018
Bz(k)Flu (μg L^{-1})	–	–	A	A	A	A	0.018
Chrysene (μg L^{-1})	–	–	A	A	A	A	0.018
Dibz(a,h)Ant (μg L^{-1})	–	–	A	A	A	A	0.018
In(cd) Py (μg L^{-1})	–	–	A	A	A	A	0.018
Non-regulatory parameters							
Chlorophyll a (μg L^{-1})	<0.01–0.79	<0.01– 0.89	<0.02–0.45	<0.02–0.54	0.01–1.87	<0.02–0.25	–
Salinity (g L^{-1})	35.4–37.8	35.0–38.9	34.5–37.9	35.8–37.3	35–37.5		–
Vanadium (μg L^{-1})	2.2–4.9	1.7–2.9	–	–	–		–
Orthophosphate (μg L^{-1})	<0.001–0.0551	0.008– 0.059	0.002–0.210	0.001–0.076	0.01–0.051	<0.1–39	–
TSS (mg L^{-1})	–	–	5.1—12.6	0.27–11.63	3–9.02	3–12.1	–
n-alkanes (μg L^{-1})	–	–	3.6–20.9	0.3–15.1	1.3–6.3	0.03–4.70	–
TPH (μg L^{-1})	–	–	–	0.003–2.89	–	1.45–2.38	–

[a]Conama 357/05: criteria for PAH only for areas with intensive aquaculture for human consumption
A – Result is below the criteria; ( ) – % sample results below the criteria

reported in reports submitted to IBAMA, as part of the documents to obtain environmental permits from those platforms (Petrobras 2001, 2002, 2003, 2004, 2006a, b, c, 2007).

4 Discussion

4.1 Inorganic Constituents

In the present study, total suspended solids (TSS) was in the range of 1.9–106 mg L^{-1} (median = 10.6 mg L^{-1}), while data reported for the North Sea showed concentrations of TSS between 3 and 85 mg L^{-1}, and a study of 10 Louisiana platforms found concentrations ranging from 12 to 840 mg L^{-1} (E&P Forum 1994; OGP 2005).

Metals and radioisotopes are the principal trace inorganic constituents of environmental concern. Brazilian PW metal concentrations ranked closely with the minimum values found for other PW reports (OGP 2005; E&P Forum 1994). For many elements the concentrations were below the detection limit.

Brazilian PW data for Hg was in the range of <0.2–0.63 μg L^{-1}, with a median of <0.2 μg L^{-1} (23 samples). Surprisingly, these values are three orders of magnitude (micrograms/litre) lower than Hg concentrations found in PW from other oil platforms expressed in milligrams per litre (0.02–0.25 mg L^{-1}). The mean concentration for gas platforms was 23 mg L^{-1} (OGP 2005).

Vanadium in PW from the Gulf of Mexico ranged from 6.3 to 22 mg L^{-1} (US-MMS 1992) while for Trinidad and Tobago the literature presents a concentration of 0.011 mg L^{-1} (Maharaj et al. 1996). In this study, the range was <0.002–0.37 mg L^{-1} V, with median of <0.002 mg L^{-1} for 23 samples, which is lower than worldwide documented concentrations.

Other studies have reported maximum Ba concentrations up to 650 mg L^{-1} (Tibbetts et al. 1992) or in the range of 0.2–228 mg L^{-1}, with a median of 87 mg L^{-1}, and those of Fe in the range of 0–15 mg L^{-1} with a median of 4.3 mg L^{-1} (Frost et al. 1998). The concentrations of Ba found in this study (0.2–45 mg L^{-1}; median = 1.3 mg L^{-1}) were less than those mentioned above, while those for Fe in this study were higher (0.04–25 mg L^{-1} with median of 7.4 mg L^{-1}; 55 samples).

Boron occurs frequently in Brazilian PW, ranging from 6–120 mg L^{-1} with a median of 31 mg L^{-1}, but this element has not been found to be toxic (Neff 2002).

For other elements in 23 PW samples, the median results were: As (<0.2 mg L^{-1}), Cd (<0.02 mg L^{-1}) , Pb (<0.1 mg L^{-1}), Cr (<0.005 mg L^{-1}) , Sn (<0.05 mg L^{-1}) Zn (<0.2 mg L^{-1}) , Ni (<0.01 mg L^{-1}), Ag (<0.003 mg L^{-1}) and Ni (<0.01 mg L^{-1}).

Several other elements of little environmental concern were also quantified in Study 2 such as phosphorus (range 0.03–3 mg L^{-1}, mean 0.52 mg L^{-1}, median 0.05 mg L^{-1}), manganese (range 0.04–5.9 mg L^{-1}, mean 0.96 mg L^{-1}, median 0.35 mg L^{-1}), aluminium (range <0.003–0.3 mg L^{-1}, mean 0.09 mg L^{-1}, median 0.1 mg L^{-1}) and selenium (range <0.02–0.4 mg L^{-1}, median <0.02 mg L^{-1}).

Rapid dilution or precipitation of metals with particulate matter when discharged into the ocean has been documented (Hartley 1994; Neff 2002; Neff et al. 1989; Trefry et al. 1995; Trocine and Trefry 1983). Precipitation as metal hydroxides or sulphides is the principal fate of heavy metals in the aquatic environment. The complexation, oxidation and precipitation reactions do not remove the heavy metals from the marine environment, but they do convert them to forms that are not bioavailable (E&P Forum 1994). No acute toxic effects to the sea organisms living around platforms due to metals in PW have been reported as yet (Neff 2002; OGP 2005).

Several naturally occurring radionuclides are present in PW. The most abundant are usually radium-226 and radium-228 (Neff 2002). In this study ^{226}Ra ranged from <0.016 to 10.9 Bq L^{-1} and ^{228}Ra from <0.032 to 10.5 Bq L^{-1} which is similar to a previous study in Campos Basin, where the levels of these radionuclides ranged from 0.012 to 6.0 Bq L^{-1} for ^{226}Ra and from <0.05 to 12.0 Bq L^{-1} for ^{228}Ra (Vegueria et al. 2002). Brazilian PW exhibits the same radioisotope levels as those reported elsewhere (E&P Forum 1994; Utvik 1999; Lysebo and Strand 1998; Guzella et al. 1996).

4.2 Organic Constituents

It is cited in the literature that the most complete non-specific measure of the total amount of organic components is TOC. A North Sea survey conducted in the 1990's showed that TOC concentrations in PW varied from 14 to 552 mg L^{-1}. The range worldwide is 100–700 mg L^{-1}, although one source reported a wider range of 0–1500 mg L^{-1} (OGP 2005). TOC values obtained in this study were in the same order of magnitude.

Total oil content measured as TPH. The range of oil concentrations was 4–66 mg L^{-1}, with a mean of 14.5 mg L^{-1} and median of 10 mg L^{-1}. This is similar to the mean of 17.8 mg L^{-1} in 2006 for PW from the North Sea (OSPAR 2009).

Carboxylic acids. In this study, the carboxylic acids (including acetic and propionic acid) were in the range of 45–928 mg L^{-1}. Reports for produced water in the North Sea showed a range from 81 to 930 mg L^{-1} (E&P Forum 1994), similar to the levels found in Brazilian PW. Carboxylic acid levels are not a cause of environmental concern due to its high biodegradability, but these compounds promote pipeline corrosion.

Aromatic compounds. Volatile aromatic hydrocarbons (BTEX) occur in all PW, but there are significant differences in concentration between oil and gas fields. In PW from PCR-1 there was a high contribution of monoaromatics to the total organic fraction. The same pattern was observed for the other platforms. The main reason for the high BTEX concentrations in PW is due to its solubility. The solubility of the monoaromatics is in range of the hundreds to the thousands of mg L^{-1}, compared with PAH solubility of one to tens of mg L^{-1}, decreasing drastically to very low solubility for the 4–6 ring PAH (Mackey et al. 1992a, b; Neff

2002; Merck Index 2006) like naphthalene (30 mg L^{-1}), phenanthrene (1 mg L^{-1}) and chrysene (0.002 mg L^{-1}). As expected, the levels of monoaromatics (BTEX, 4,690 μg L^{-1}) when compared to the PAH content, represent 92% of the total aromatics, followed by the sum of naphthalenes, phenanthrenes and dibenzothiophenes (NPD 399.2 μg L^{-1}) which was 7.9%. The sum of 14 EPA PAH, excluding naphthalene and phenanthrene which were already counted in the NPD fraction, was 5.9 μg L^{-1} or 0.11% of the total aromatics. Aromatic content of Brazilian PW is in the intermediate to low range of other PW worldwide.

Phenol and alkylated phenols. These compounds occur naturally in oil and will partition into produced water depending on their molecular weight. Data for Brazilian PW are similar to those for the North Sea (Utvik 1999). Phenols with heteroatoms (nitro and chlorophenols) have never been detected in Brazilian PW.

4.3 Toxicity

Acute PW toxicity previously reported in the literature, ranging from 5.2 to 14.5% PW for *Mysidopsis bahia* (Schiff et al. 1992); 4.5–53.5% for *S. costatum* (E&P Forum 1994); 2.4–24.4% for *V. fischeri* (Flynn et al. 1996); and 16–58.8% for *Artemia* sp. (E&P Forum 1994; Holdway 2002), is comparable with the results of this study.

There are few available data for PW chronic toxicity in the literature, but Schiff et al. (1992) published some results for the sea-urchin (*Strongilocentrotus purpuratus*) fertilization test which ranged from 0.74 to 1.73%, similar to the Brazilian NOEC range using *L. variegatus* of <0.1–12.5%. Other studies of PW chronic toxicity reported much lower values, but used different methods and more sensitive endpoints (Krause et al. 1992; Holdway 2002). Chronic toxicity in Study 3 exhibited a narrow range (NOEC 6.25–12.5%) during the 24 h sampling, but a 5-fold range during the annual surveys, indicating that variability is higher in the long-term. Holdway (2002) reported that PW toxicity may fluctuate up to 10-fold, especially due to operational changes in the production process and chemical blends used for oil treatment, but the author did not see significant variation in the intrinsic PW composition.

Considering the differences in sensitivity of the species and methodologies, the overall acute and chronic toxicity results obtained for Brazilian PW can be considered similar to other studies. Gabardo (2007) found no strong correlation between toxicity and chemistry for Brazilian PW as has been also documented in other studies (E&P Forum 1994; Swan et al. 1994).

4.4 Modelling Produced Water Dispersion with Field Data

The impact of marine discharges and its potential environmental effects depend both on the concentrations of the discharged materials and on the capacity of the receiving environment (Smith et al. 2004; Brandsma and Smith 1999). For

the majority of the parameters analysed, the seawater quality criteria (Class I, CONAMA Resolution 357/05) were achieved at near-field dilution, except for ammonia (PPG-1, P-32 and P-26 platforms) and sulphides (P-32) (Gabardo 2007). The concentration limits must be achieved at a distance of 500 m from the discharge point, which is considered the limit of the mixing zone by the CONAMA Resolution 393/2007. Based on the modelling of PW dispersion plumes, all the parameters analysed achieved the quality criteria for seawater before the 500 m limit (Gabardo 2007). Adopting Saline Water Class I (CONAMA 357/2005) criteria for water in the vicinity of offshore PW discharge platforms is very conservative but in agreement with environmental preservation.

4.5 Environmental Monitoring

The vast majority of the environmental monitoring results showed very good quality seawater and 99.7% of the parameter concentrations complied with the Brazilian regulatory limits for high quality seawater. The lack of observed acute and chronic toxicity in seawater reinforced the predicted PW dispersion plume obtained with the CORMIX and CHEMMAP models. Same behaviour was previously reported in the literature for environmental monitoring studies around platforms (US MMS 1992; Veil et al. 2005; OGP 2002, 2005). Concerning the Brazilian environment, two additional factors should be borne in mind: a) the low volume of PW discharged in the northeast (<0.5 m^3 s^{-1}) and southeast (1.39 m^3 s^{-1}) compared to the input rivers of the same regions that are 3–4 orders of magnitude higher; b) the hot weather and warm seawater of Brazil certainly favour an increased rate of hydrocarbon biodegradation and weathering (Gabardo 2007).

Despite the lack of observed toxicity of seawater adjacent to the platforms, further studies are being implemented to investigate the possible biological effects of PW discharges in the ocean. Recent efforts have been made to evaluate the chronic and sub lethal environmental effects due to the PW discharge including studies with oysters to assess bioaccumulation and biomarkers.

5 Summary

This chapter provides a technical summary of 10 years (1996–2006) of monitoring PW discharge from offshore platforms operated by Petrobras in Brazil. The following conclusions were reached with this study:

- In 2005, the average total volume of PW discharged into Atlantic Ocean by 24 platforms offshore in the Brazilian coast was 73 million m^3/year, representing less than 3% worldwide PW discharged to other oceans;
- Results of organic (TPH, BTEX, PAH, phenols, organic acids) and inorganic (metals, anions, cations) parameters, as well as acute and chronic toxicity obtained for Brazilian PW were similar to the literature;

- Brazilian platforms with greater gas production presented relatively high concentrations of BTEX, phenols and low molecular weight PAH in its PW composition, corroborating the worldwide information previously reported;
- Barium is one metal of significant presence in Brazilian PW and both ^{226}Ra and ^{228}Ra concentrations are highly correlated with this element. In contact with sulphate rich seawater, barium precipitates as barium sulphate, reducing concentrations of Ba and radium isotopes in the water column;
- Modelled PW dispersion plumes showed dilution factors of 100–700 within 200 m of platform discharge points;
- Dilution of several PW chemical components was confirmed by sampling seawater within that distance from the platforms;
- Modelling simulations in winter and summer conditions predicted concentrations for all the parameters compliant with the Brazilian regulatory limits for seawater within 500 m from the discharge point;
- Despite the lack of observed alteration in seawater quality around production platforms, the importance of continuing to evaluate the impact of PW discharges from a risk assessment perspective has been recognized, and studies of bioaccumulation and the use of biomarkers among other initiatives are currently being implemented.

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