Environ Earth Sci (2015) 74:5813–5826
DOI 10.1007/s12665-015-4599-9

ORIGINAL ARTICLE

Ecological and human risk assessment of long-term produced water discharge to the ocean at the Sonda de Campeche, Gulf of México

Isaac Schifter[1] · C. González-Macías[1] · L. Salazar-Coria[1] · G. Sánchez-Reyna[1] · C. González-Lozano[1]

Received: 25 November 2014 / Accepted: 30 May 2015 / Published online: 12 June 2015

Abstract Management of produced water (PW) is a challenge for mature fields like those of Sonda de Campeche in the southern Gulf of Mexico and for the future development of deep water fields. Past studies suggest that PW effects are local; however, the risk of widespread, long-term impact on the population and ecosystem is considered low, but not verified from the published literature. The study describes monitoring events done in years 2003 and 2013, considering physicochemical characteristics, organic and inorganic environmental measurements as well as comparing the prognostic results of an environmental and health risk assessment. The study examined ambient water samples and sediments for Al, Ba, Ni, Cd, Pb, Zn, V, Cr, Cu, Fe, and As, and also polycyclic aromatics compounds included in tissues of collected fish near the discharge area and a reference coastal site assumed to be unaffected. From a regional perspective, the ecological and human risk data suggest that the effects of the present discharge are not confined locally, but increased with time and space.

Keywords Produced water · Ocean discharges · Southern Gulf of Mexico · Risk assessment

Electronic supplementary material The online version of this article (doi:10.1007/s12665-015-4599-9) contains supplementary material, which is available to authorized users.

✉ Isaac Schifter
ishifter@imp.mx

[1] Instituto Mexicano del Petróleo, Dirección de Investigación, Eje Central Lázaro Cárdenas No. 152, San Bartolo Atepehuacan, Mexico, DF 07730, Mexico

Introduction

The Gulf of Mexico (GOM) is a vital international ecosystem that plays a critical role in the economic health of both the USA and Mexico. Activities such as coastal development, agriculture, fisheries, oil and gas exploration and production, and others that drive the economic health of the region are also placing the Gulf ecosystem under tremendous stress.

Multiple risk and impact assessment regimes have been suggested for monitoring the environmental effects of offshore oil and gas drilling activities. Produced water is an inextricable part of the hydrocarbon recovery processes; yet, it is by far the largest volume waste stream associated with hydrocarbon recovery (Sauer et al. 1997; Balaam et al. 2009; Fakhru'l-Razi et al. 2009).

PW is a complex mixture of water, chemicals and dispersed oil micro-droplets, and formed when hydrocarbons and water are separated during the production of oil and gas (Sundt et al. 2012). Discharge of PW requires that it be injected into a reservoir or be thoroughly treated before disposal into the marine environment (Pillard et al. 1996) Neff et al. 2011; Payne et al. 2011).

PW is high in salinity, usually defined by the total dissolved solids content (TDS) in water (Lee et al. 2005; Vengosh 2003), and typically contains dispersed oil, polycyclic aromatic hydrocarbons (PAHs), alkyl phenols, heavy metals, organic acids, inorganic salts, sulfur and sulfides (Neff et al. 2011; Research Council of Norway 2012). In addition, accompanying injected water can have different chemical additives, for example, to prevent the growth of bacteria, corrosion and the formation of emulsion (Johnsen et al. 2000).

It is widely recognized that total petroleum hydrocarbons may not adequately represent the potential

environmental impact of PW and other oil and gas production discharges (Carroll et al. 2000). The hydrocarbon component of the discharge comprises chemicals with varying potential to cause environmental harm; non-hydrocarbon constituents of produced water also may be important contributors to ecological risk. In addition, the chemical composition of produced water from different sources varies widely (Neff 2002).

Sonda de Campeche (SC) lies in the southern GOM and consists of coastal lagoons and estuaries that are highly productive ecosystems (Rodríguez-Almaraz et al. 2000). On a larger scale, the whole of the SC supports more than 300 demersal fish species, of which 30 are dominants. For example, Atlantic threadfin herring *(Opisthonema oglinum)* and scaled herring (*Harengula jaguana*) dominate in terms of distribution and abundance. Threadfin and scaled herring are typical pelagic-neritic species and are estuarine dependent.

Petroleum extraction in SC produces approximately 80 % of the nation's oil. During the year 2003, about 32,000 m^3 per day of PW was discharged into the ocean, while in 2013 the 262,000 m^3 was discharged. Disposal of produced waters from off-shore drilling has been well studied for marine ecosystems in several parts of the world. Extensive experimental and field studies have been made to assess the ecological effects of the discharges (Bakke et al. 2013).

The northern GOM is a major hub of oil and gas industries in the USA. The offshore areas produce about 1.3 million barrels of crude oil per day, which amounts to ~23 % of the total USA production. In light of recent and ongoing accidents involving human activities in the GOM, there is a growing need for the documentation of the overall condition of this ecosystem.

Efforts to catalog the health of US coastal ecosystems began around the 1960s (Neff et al. 2011; Payne et al. 2011; Balaam et al. 2009; Azetsu-Scott et al. 2007). Moreover, Turner et al. (2003) documented changes in chemical contaminants and biological components of dated sediments collected from the central GOM continental shelf to evaluate the relative sources and concentrations. These include trace metals, selected organic compounds, phytoplankton pigments, diatom remnants and foraminifera (Sharma et al. 2012).

In light of the increase in human activities in the southern part of GOM, there is a growing need for the documentation of the overall condition of this ecosystem. Scarce data exist in the open literature concerning physical and chemical characterization of water and sediments in this area (Macias-Zamora et al. 1999; Vazquez et al. 1999, 2002; Schifter et al. 2004; Botello et al. 2005; Ruiz-Fernandez et al. 2012).

Little is understood regarding the ecological impact of the release of PW in the coastal ecosystems of the Mexican Exclusive Economic Zone, particularly at the Dos Bocas Terminal. Therefore, the present study provides baseline information to determine ecological and human health risk assessment arising from contaminants in water and sediments.

Exposure estimation modeling is a central component of risk assessments. It is used for example for examining the effects of past-practice discharges into the environment, estimating consequences of releases of hazardous materials and determining if and how chemicals may be used in an environmental setting.

In this work, we use the Toolkit for Integrated Impact Assessment (TIIA) developed by Battelle Memorial Institute which is a suite of computer tools modeling system to simulate ecological and human risk impacts (Eslinger and Miley 2012). The toolkit consists of two major modules: ECEM© and HUMAN© (Battelle Memorial Institute 2006).

ECEM is a detailed, pharmacokinetic food web-based, chronic exposure model that calculates impacts to ecological species and concentrations in food products used for human consumption. ECEM has been used to assess the effects of routine and accidental releases associated with oil and gas exploration/production, and chemical facility operations (Brandt et al. 1998, 2002, 2005).

HUMAN is a screening-level, chronic exposure, multimedia model. The contaminants that are evaluated must be measured at the same location in all the media that are to be assessed and cannot be applied for estimating risk from short-term exposures or to contaminants that do not have carcinogenic or toxicity standards.

A weight of evidence approach was used to determine whether adverse environmental effects might be present at nearshore locations. The overall approach was similar to that described by Salazar-Coria et al. (2010). For this study, three levels for assessing potential adverse environmental impacts were defined: small potentials, when the toxicological effects were not detectable; moderate potential, when toxicological effects were detectable and adverse environmental impacts were possible; large potential, when toxicological effects were clearly noticeable and adverse environmental impacts were likely.

Risk evaluations were based on concentrations of contaminants of concern that were measured in the year 2003 and again in 2013 in the SC environment. This provides an assessment tool separate from those based on bioassays, bioaccumulation studies, and community structure analysis. Both direct measurements and modeling approaches proved to be valuable for assessing the overall impacts of the oil company operations on nearshore environments.

Materials and methods

The study site

The Dos Bocas Marine Terminal, located near Paraiso, Tabasco, is the single-point discharge source for all PW generated within the SC area. PW from offshore activities is collected at the terminal, treated along with collected rainwater, and later discharged to the coastal zone through a 75 m-long submarine diffuser at a depth of 13 m (Fig. 1).

The region is characterized by a shallow platform, representing the submarine extension of the Yucatan Peninsula, and which consists of carbonaceous material and lacks terrigenous material inputs to the sea (Macias-Zamora et al. 1999). Communication between the Mecoacan lagoon and the Gulf occurs through a wide inlet limited by two littoral bars formed of ridges and dunes.

The field and laboratory investigations were generated from two field surveys, both performed during the windy season. The first survey was conducted in 2003, and the second one in 2013 at the same sites as part of the national oil company to identify impacts associated with current or past practices.

Water depth of the coastal region varied from 12 to 20 m. The Barra de Tupilco, at about 16 km west of the Marine Terminal outside of the Gulf surface water circulation area, was employed as a coastal reference site. Fish were collected for contaminant analysis at the discharge site close to the diffuser, and at a reference site 21 km west of the diffuser.

Sampling

A global positioning system (Micro logic ML-150) was used to record details of the sites. At the Dos Bocas facility, nine samples representative of the water discharged to the ocean were collected in both years.

A total of 18 ambient water samples were collected around the diffuser area in Van Dorn; sampling bottled water was unfiltered and dispensed into acid-washed 1 L plastic bottles for metal analysis. After adding 1 mL of ultrapure nitric acid, samples were refrigerated until analysis. Additionally, each sample was monitored for pH, conductivity, salinity, dissolved oxygen, and temperature as outlined in the Public Health Association methods (APHA 1992). At the terminal facility, nine individual samples of PW were collected from the holding tank pipes on two alternate days.

A total of 27 bottom sediment samples were collected in both years: 18 from the diffuser area and 9 from the Tupilco reference site, using a Van Veen grab sampler, and taking special care to retain fine-grained materials. Sediment grain size was estimated by a combination of wet sieving (2 mm–63 μm) and pipette analysis (<63 μm) (Folk 1974).

In both years, 2003 fishing trawls for analysis of contaminants of concern were used at the discharge site close to the diffuser and at a reference site 21 km west of the diffuser, looking specifically for species that live over deep reef banks (near artificial reefs, oil rigs, and other underwater structures).

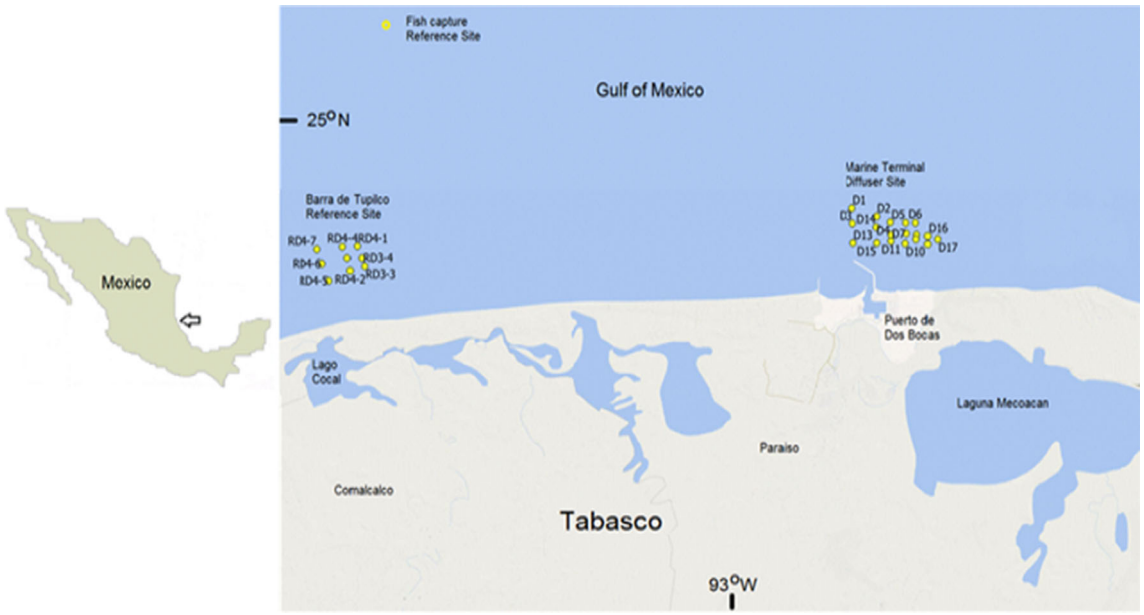

Fig. 1 The study area

Hydrographic model

Contaminants discharged by the Dos Bocas facility through the submarine diffuser were modeled with CORMIX and WQMAP. The CORMIX is a software system for the analysis, prediction, and design of aqueous toxic or conventional pollutant discharges into diverse water bodies (Doneker and Jirka 2001).

Hydrographic data were modeled with the WQMAP to establish the dispersion field of potential contaminants during the sampling period. (Bahadur et al. 2013). The discharges were modeled as 262,000 m^3 day^{-1} of PW from pipes located 13 m below the sea surface. The transport modeling used a generic source term of 100 units concentration and 1 L s^{-1} flow. These were converted to actual values using maximum discharge flows and maximum discharge chemical concentrations reported during the study periods.

Ecological and human risk modeling

The ecological risk modeling uses concentration values for surface water, sediment, and pore water as inputs to the risk modeling. Pore-water chemical concentrations used surface water values for metals and partition coefficient for organics as described by Baker et al. (1997). Species chemical parameters were obtained from the FishBase (Froese and Pauley 2005), and the USEPA biota-sediment accumulation factor (BSAF) database (Burkhard 2009).

The output from ECEM was used in the consumption pathway in the HUMAN model which estimates exposure and determines the risk of cancer. The effects of contaminated sediment and water on absorption through the skin were considered.

Analysis

Discharge water samples from the terminal were analyzed for metals, PAHs, volatile aromatics (BTEX), and total petroleum hydrocarbons (TPH). Samples were analyzed using inductively coupled plasma-atomic emission spectrometry using a Thermo Jarrell Ash, model Atom Scan 16. Analysis of PAHs and phenols was performed by GC/MS with the MS operating in the SIM mode.

Detailed information on the methods employed in the analysis is provided in the Electronic Supplementary Material.

Statistical analysis

Statistical analyses of data were performed using Statistica software package (1998). The statistical techniques included the Pearson multiple correlation analysis and the Student's t test for independent samples with unequal variances, with a significance level of $p < 0.01$ (Townend 2002). Databases were analyzed by calculating the mean, standard deviation, median, minimum and maximum values, and the first and third quartiles (Q 25 % and Q75 %, respectively). The coefficient of variation (CV = standard deviation/mean) was also calculated.

Results

Hydrodynamic modeling

The evolution of the Dos Bocas diffuser plume of a generic contaminant between November 3 and December 14, 2013 showed that the initial plume was confined within 10 km of the mouth of the diffuser with concentrations on the order of 0.3 units. About 2 weeks later, concentrations between 0.2 and 0.3 units reached the coastline in the vicinity of the diffuser; the limits of the plume stretched about 45 km westward.

By week 5, concentrations of 0.2 units were found within 10 km from the mouth of the diffuser and the limits of the plume stretch westward outside of the domain. By the end of the simulation period, a well-developed contaminant gradient between 0.1 and 0.3 units was found along the coastline to the west of the diffuser in the direction of the Barra de Tupilco reference site.

Produced water analysis

Table 1 provides information concerning the physical/chemical parameters of PW, along with those of the diffuser and reference sites recorded in the year 2013. As expected, high values for temperature, salinity, nitrates, and turbidity were recorded at the PW at the Marine Terminal. The salinity value at the diffuser discharge is typical of the surface waters in the GOM, but is lower at the reference site as a result of the close proximity of rivers inflow.

In Table 2, the concentration ranges of several classes of metals and organic chemicals in PW discharges all over the world (Neff 2002; Battelle Memorial Institute 2006) are compared with the mean (±standard deviation) values of the PW analyzed in 2003 and 2013. Differences in values among years were found to be significant ($p < 0.01$). There was a twofold increase in TPH and similar increased values for the BTEX and PAHs that could be a consequence of a decrease in the efficiency of the treatment process in separating the oil from water.

Most of the phenols in the PW on both years were of low molecular weights, moderately water soluble, highly biodegradable, and had a low potential to bio-accumulate

Table 1 Physical/chemical parameters recorded in the year 2013

Parameter, mean (±SD)	Produced water terminal	Diffuser sites	Reference sites
Temperature (°C)	44.77 ± 16.30	24.05 ± 0.77	27.63 ± 1.47
pH	6.48 ± 0.05	8.03 ± 0.02	8.04 ± 0.04
Dissolved oxygen (mg L^{-1})	4.03 ± 0.34	4.41 ± 0.42	5.25 ± 0.29
Salinity (UPS)	80.38 ± 0.61	35.51 ± 0.19	28.85 ± 7.90
Conductivity (ms cm^{-1})	52.06 ± 0.82	53.74 ± 0.24	44.41 ± 13.81
Turbidity (NTU)	145.15 ± 2.63	1.18 ± 1.01	4.77 ± 3.99
Nitrates (mg L^{-1})	4.74 ± 5.02	0.45 ± 0.11	0.19 ± 0.09

Table 2 Comparison of mean (±SD) concentrations (μg L^{-1}) of selected chemicals in produced water in the years 2003 and 2013

Chemical class [Mean (± SD)]	*2003	*2013	Ratio between years	**World range
Total petroleum hydrocarbons (TPH)	8270 ± 3810	17126 ± 4245	2.1	3680–30000
Benzene, toluene, ethylbenzene, xylenes (BTEX)	5100 ± 1400	8900 ± 1345	1.7	680–578000
Total polycyclic aromatics hydrocarbons (TPAHs)	91 ± 50.85	132 ± 12.3	1.5	40–3000
Total phenols	793 ± 240	1145 ± 323	1.4	600–23000
Arsenic (As)	0.13 ± 0.21	50 ± 0.1	385	0.004–320
Copper (Cu)	10.75 ± 1.6	122 ± 23	11	0.001–55000
Chromium (Cr)	2.55 ± 3.0	150 ± 47	59	0.001–390
Zinc (Zn)	7.85 ± 4.8	285 ± 94	36	0.005–200000
Cadmium (Cd)	3.11 ± 3.1	321 ± 100	103	0.0005–490
Lead (Pb)	1.91 ± 1.0	951 ± 154	498	0.001–18000
Aluminum (Al)	28.32 ± 4.7	949 ± 122	34	<0.5–83
Nickel (Ni)	3.01 ± 8.9	1170 ± 361	389	0.001–1670
Iron (Fe)	23.02 ± 3.8	1264 ± 324	55	0.1–465000
Vanadium (V)	24.31 ± 2.7	3627 ± 123	149	<1.2
Mercury (Hg)	ND	ND	ND	<0.001–0.075
Barium (Ba)	23.89 ± 6.4	7309 ± 1123	306	<100–2000000

* Student's *t* test; significant differences between years

* Neff (2002); Battelle Memorial Institute (2006)

because of being rapidly metabolized and excreted by marine animals (OOCC 1997).

The concentrations of metals in PW were in the range reported from elsewhere in the world (Neff 2002), but very high increases in the concentrations of As, Cd, Pb, Ni, V and Ba are highlighted in the Table when the ratio of variation in concentrations are calculated between years.

Metals in ambient water and sediments

Figure 2 shows the concentration (95 % CI) of metals in water (μg L^{-1}) at the diffuser sites (A) and reference sites (B) in the years 2003 and 2013. If comparisons are made between the years 2003 and 2013 at the diffuser and reference sites, the highest increases are observed for Ba, Ni, Cu, V, and Fe with values for all of them greater than the acute criteria described by Buchman (2008).

Our results indicated that only lead (average concentration 0.57 μg $L^{-1)}$ exceeded the Mexican limit for coastal/recreational and fishery waters (0.40 μg L^{-1}). However, a comparison with international marine water data revealed a non-attainment condition because only chromium and aluminum met the criteria described by USEPA (USEPA 2014) and McPherson et al. (1999). Figure 3 depicts the concentration of metals in sediments for the years 2003 and 2013. A wide variability was observed in the distribution of metals, although a trend to higher pollution levels was detected for the reference sites.

A comparison of the average values of metals with international limits for surface marine sediments showed that the threshold effects level (TEL) and/or probable effects level (PEL) values were not attained in both programs for Cr, Ni, Pb, Fe, Al, Ba, V, and at least in one of the two areas. At reference sites, Ni and Cd were above TEL limits in the year 2003, while in the year 2013 Ni and As exceeded the TEL limits.

The grain size analysis demonstrated that sand, silt, and clay content depended on the area, showing the highest

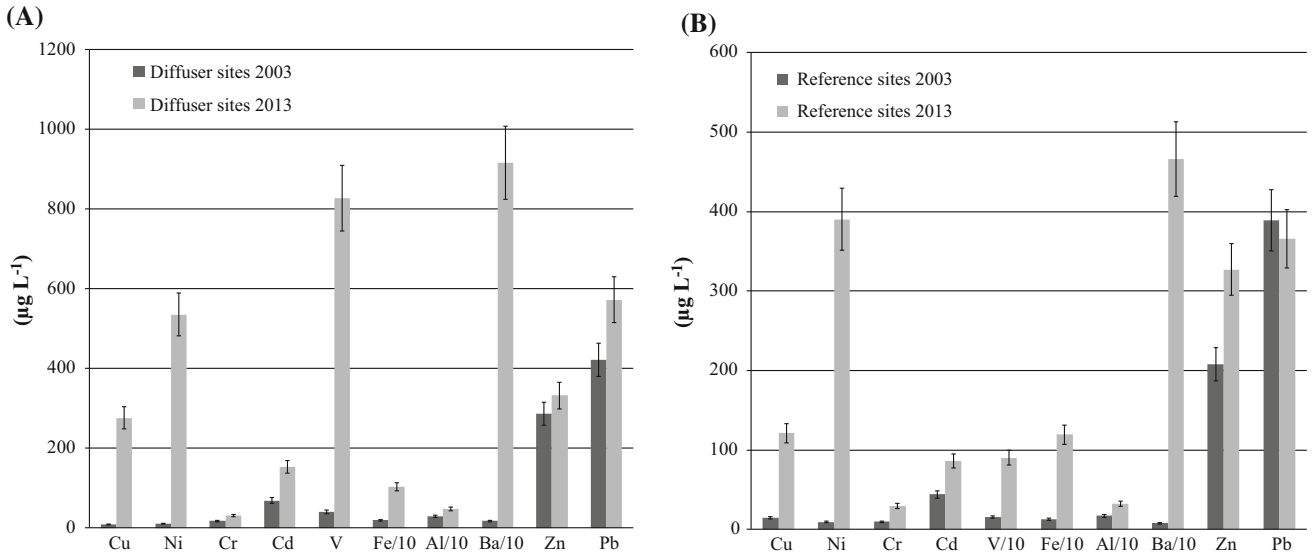

Fig. 2 Concentration (95 % CI) of metals in ambient water (µg L^{-1}) at the diffuser sites (**a**) and reference sites (**b**) in the years 2003 and 2013

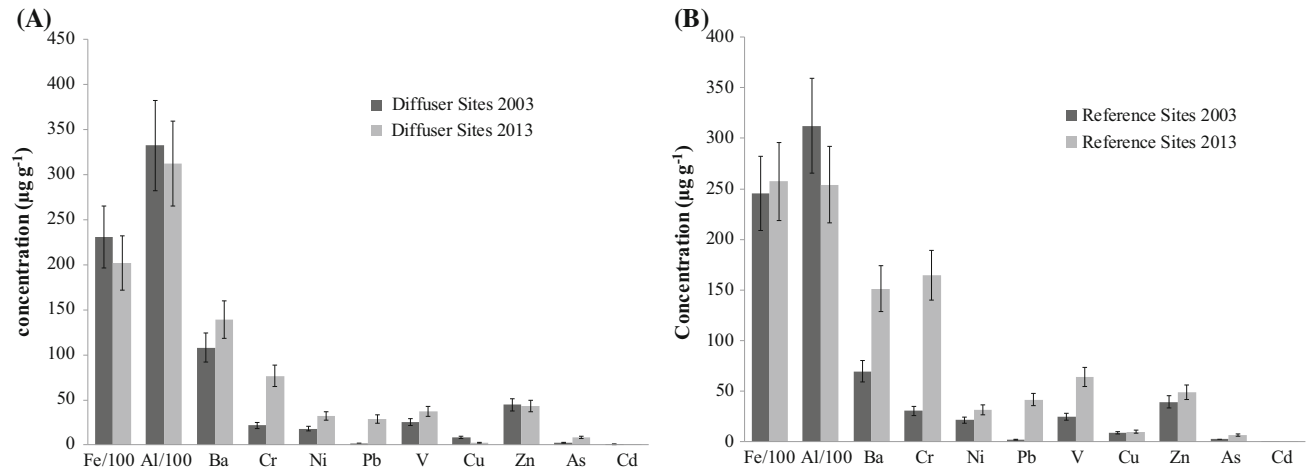

Fig. 3 Concentration (95 % CI) of metals in the sediments (µg g^{-1}) at the diffuser sites (**a**) and reference sites (**b**) in the years 2003 and 2013

percentage of fine particles in the reference sites (17 %), followed by the Dos Bocas area (7.3 %). Nevertheless, only aluminum, barium, nickel, zinc, and lead indicated a positive association with fine grain size sediments.

Organics in water and sediments

The chemical group in wastewater and PW that is of greatest environmental concern is PAHs, due to their mutagenic and carcinogenic effects. The PAHs that are present in the marine environment in relevant concentrations are divided into two groups depending on their origin, namely pyrogenic and petrogenic (Neff et al. 2005).

Pyrogenic PAHs are formed by incomplete combustion of organic material, while the petrogenic PAHs are present in oil and some oil products. Alkylated PAHs are more abundant than the parent PAHs in petrogenic PAHs assemblages (Neff et al. 2005).

PAHs in water were not detected at the diffuser or the reference sites in both years. Table 3 compares the mean PAH concentrations in sediments at the diffuser and reference sites in the years 2003 and 2013. In the year 2003, sediment samples were essentially devoid of PAHs except in one station (D7) close to the diffuser discharge.

The data indicate that the 2/3-ring PAH concentrations are about 80 % the total PAHs near the discharges and decrease to about 45 % at the reference site area. Concentrations of 4- and 5-ring PAHs did not exceed 1 % of the TPAH concentrations, indicating relatively low proportions of PAHs in the water column that were from

Table 3 Comparison of mean PAH concentrations in sediments at the diffuser and reference sites in the years 2003 and 2013

Year	Site	Low molecular weight polycyclic aromatic hydrocarbons (ng g^{-1})	High molecular weight polycyclic aromatic hydrocarbons (ng g^{-1})	Mean total polycyclic aromatic hydrocarbons (ng g^{-1})
2003	Diffuser site D7	23.8	6.3	30.3
	Tupilco reference site	2.8	3.4	6.3
2013	Diffuser site D7	2586	326	2911
	Diffuser site D11	2050	274	2324
	Diffuser site D12	270	97	367
	Tupilco reference site	nd	nd	nd

pyrogenic sources. In the year 2013, three stations located in the diffuser area showed much higher concentrations of total PAHs compared to the 2003 values.

D-7 and D-11 are close to the major produced water discharge, and D-12 is further away from the discharge area. The concentrations of pyrogenic PAHs increases with distance from the diffuser site (from about 1 % to about 26 % of the total PAHs). At the reference site, PAH concentrations were below the method detected limits.

According to Neff et al. (2006), the naphthalenes persist over a greater distance in the water column than the less soluble 2/3-ring compounds, and their contribution to the total PAHs assemblage increases with distance from the discharge area, while 2/3-ring compounds likely adsorb organic matter and other suspended solids in the water column and may settle with it to deeper water layers and to the sediment.

Metals and organics in fish

Metal concentrations (mg kg^{-1} wet) and impact assessment of fish from nearshore sites are shown in Table 4. In the table, differences in values among years were found to be significant ($p < 0.01$). For the year 2003, the concentrations of metals were compared to benchmarks derived from the ECEM model to determine the potential for adverse impacts.

Comparisons for the year 2003 predicted large adverse impacts of arsenic at the Dos Bocas diffuser and reference sites, a moderate potential for adverse impacts of copper at Dos Bocas, a large potential for impact of copper associated with the Dos Bocas reference, and a moderate potential for impact of nickel at Dos Bocas.

In the year 2013, metal concentrations were higher at the diffuser and reference sites. At the diffuser sites, Cd, Cr,

Table 4 Metal concentrations (mg kg^{-1} wet weight) and impact assessment for fish from nearshore sites

Metal	Site	Year 2003 mean (±SD)*	Year 2013 mean (±SD)*	Chronic criteria**	Acute criteria**
As	Diffuser sites	1.16 ± 0.23	1.55 ± 0.20	0.42	0.82
	Tupilco reference sites	1.40 ± 0.26	1.81 ± 0.23		
Cd	Diffuser sites	0.19 ± 0.12	0.47 ± 0.11	0.99	4.5
	Tupilco reference sites	0.19 ± 0.10	0.37 ± 0.10		
Cr	Diffuser sites	0.81 ± 0.63	1.79 ± 0.43	8.02	176
	Tupilco reference sites	1.43 ± 0.37	1.74 ± 0.22		
Cu	Diffuser sites	1.28 ± 0.53	2.35 ± 0.43	1.62	2.52
	Tupilco reference sites	1.41 ± 0.58	2.54 ± 0.38		
Ni	Diffuser sites	0.36 ± 0.35	0.91 ± 0.46	0.67	6.03
	Tupilco reference sites	0.24 ± 0.10	0.36 ± 0.10		
Hg	Diffuser sites	0.012 ± 0.01	0.047 ± 0.01	0.78	1.49
	Tupilco reference sites	0.010 ± 0.02	0.060 ± 0.02		
Pb	Diffuser sites	0.49 ± 0.21	076 ± 0.20	0.92	20.4
	Tupilco reference sites	0.28 ± 0.16	0.61 ± 0.16		
V	Diffuser sites	<MDL	<MDL	0.92	20.4
	Tupilco reference sites				

* Student's *t* test; significant differences between sites

** Benchmarks based on Barred Grunt (*Conodon nobilis*)

Table 5 Total PAHs (ng g^{-1} wet weight) and percent contributions of 2/5 rings compound classes in fish

Year	Site	*N*	Mean total PAHs	Min total PAHs	Max total PAHs	2-ring PAHs (%)	3-ring PAHs (%)	4/5-ring PAHs (%)
2003*	Diffuser sites	8	69 ± 2.20	49.2 ± 2.33	104 ± 23.25	84	16	nd
	Tupilco reference sites	7	62 ± 3.01	41.9 ± 3.18	81.2 ± 19.89	79	20	1
2013*	Diffuser sites	8	56.8 ± 2.14	21.57 ± 2.22	92.15 ± 21.33	83	17	nd
	Tupilco reference sites	7	1.38 ± 0.10	1.35 ± 0.10	1.41 ± 0.23	56	44	nd

* Student's *t* test; significant differences between years

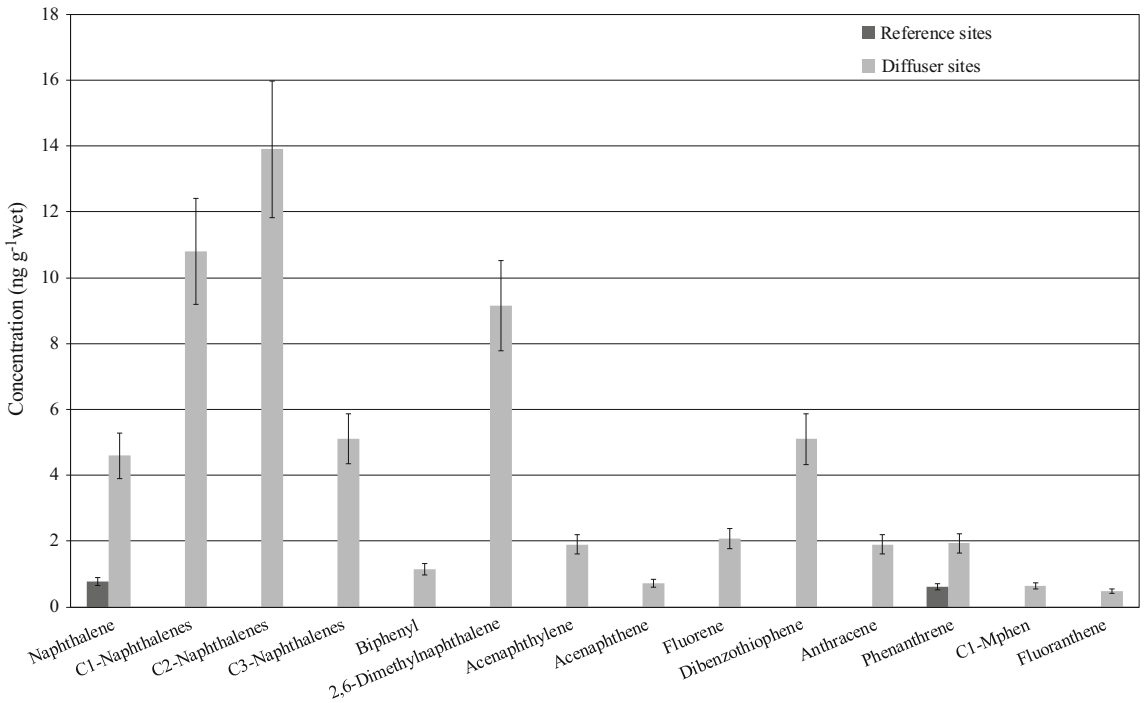

Fig. 4 Mean concentration of polycyclic aromatic hydrocarbons in tissues of collected fish, year 2013

Ni, and Hg increased by more than 50 % with respect to the year 2003, while at the reference sites the major increments were observed for Cd, Cu, Hg, and V.

Table 5 shows the mean total concentrations of PAHs in fish at the diffuser and reference sites for both sampling programs, as well as the percent contributions of 2-ring, 3-ring, and 4-ring PAHs compound classes. In Table 5, the differences in values among years were found to be significant ($p < 0.01$).

Overall in the year 2003, the total PAH concentrations in fish were consistently low throughout the study area. The mean total PAH concentrations were 69 and 62 ng g^{-1} at the diffuser and reference sites, respectively. Equal amounts of naphthalene and phenanthrene were found in fishes at the reference site in 2013. Figure 4 shows the mean concentration of individual PAHs in the tissues of collected fish in the year 2013.

At the reference sites, only naphthalene and phenanthrene were detected, but at the diffuser PAHs included naphthalene and their alkyl compounds as the major contributors, followed by 2, 6 dimethylnaphthalene, fluorene (an USEPA target analyte), and phenanthrene, but also small amounts of fluoranthene. Naphthalene, fluorene, phenanthrene, dibenzothiophene, and their alkyl homologs, in that order, are the most abundant PAHs in produced water (OOCC 1997).

Therefore, the produced water PAHs signature was evident in the fish samples in both years. The low concentration of metals and PAHs observed at the reference site in the year 2013 could be explained by the fact that the

Table 6 Organic and metal contaminants of concern that were evaluated individually and combined as carcinogenic or toxic chemicals

Carcinogenic, mutagenic, or tumorigenic chemicals*		Toxic chemicals*	
Organics	Metals	Organics	Metals
Benzo[a]anthracene	Arsenic	Acenaphthene	Arsenic
Benzo[a]pyrene		Acenaphthylene	Barium
Benzo[b]fluoranthene		Anthracene	Cadmium
Benzo[e]pyrene		Biphenyl	Chromium
Benzo[g,h,i]perylene		ibenzofuran	Copper
Benzo[k]fluoranthene		Fluoranthene	Lead
Chrysene		Fluorene	Mercury
Dibenzo[a,h]anthracene		Naphthalene	Nickel
Indeno[1,2,3-c,d]pyrene		Phenanthrene	Vanadium
Perylene		Pyrene	

* USEPA (1996); Suter and Tsao (1966); ATSDR (2000)

species recovered were mostly coastal pelagic fish which typically inhabit waters below the continental shelf.

Ecological and risk assessment

For the general conceptual exposure model of the receptors to contaminants in both the abiotic and biotic media of the study area, the food web and trophic transfer of the Terminos Lagoon (Manickchand-Heileman et al. 1998) are to a large extent representative of the general Sonda environment and thus may be used to describe the food chain exposure of the receptors to contaminants: detritus → detritivores → primary carnivores → secondary carnivores (Battelle Memorial Institute 2006).

Consequently, it is anticipated that the greatest food chain exposure to the more persistent and hazardous hydrocarbons, as well as the heavy metals, would likely occur in the benthic invertebrate communities via consumption of detritus and incidental ingestion of associated surface sediments.

Dermal exposure to sediments and pore water would also be expected to play a role in the exposure of invertebrates. In the human health impacts evaluation, only the chemicals that were found at concentrations greater than background levels were evaluated. This approach allowed evaluation of the various exposure scenarios and identification of the carcinogenic or toxic chemicals that represented the greatest potential for adverse risk. The organic and metal contaminants of concern that were evaluated are identified in Table 6.

Measurement end points selected include concentrations that are known to be lethal to 50 % of an exposed population (median lethal concentration [LC_{50}] or dose [LD_{50}]), and the lowest concentrations that are known to produce clinically toxic responses in any member of a population (lowest observed adverse effect concentration or level). These benchmarks were obtained from toxicological databases (USEPA 1996; Suter and Tsao 1966; ATSDR 2000).

Arsenic has micronutrient value, but is toxic above trace levels (Newman and McIntosh 1991). Arsenic is present in tissues of marine animals at high and highly variable concentrations. In mammals, barium may cause adverse effects that range from muscular paralysis to cardiovascular effects (Reeves 1986). In aquatic organisms, toxicity is variable, even to closely related species (Wlodarczyk et al. 2000). Most cadmium compounds are relatively easily soluble in water, and therefore have great mobility and tend to accumulate in living organisms.

Cd is toxic to a wide range of microorganism; however, the toxicity is reduced when it is incorporated in sediments, in the presence of high saline concentrations (Vasile and Vlădescu 2010). Chromium is carcinogenic, may cause mutations, and is a teratogen in mammals (Domingo 1994). Ingestion of copper in excess can lead to accumulation in the liver, anorexia, edema, disorientation, and scale protrusion (Rand and Petrocelli 1985). Lead can be carcinogenic, cause reproductive effects, and inhibit growth and development in mammals, birds, and aquatic organisms (Dayan and Paine 2001). Mercury is one of the most hazardous contaminants present in the marine environment and may be transferred to biota from contaminated abiotic matrixes (Palma et al. 2009). Nickel is carcinogenic and mutagenic in birds and mammals (Cempel and Nikel 2006). There is little information about the toxicity of vanadium in terrestrial and aquatic organisms, although it is thought that the effects are related to enzyme inhibition (Barceloux 1999).

Ecological impact evaluation

The contaminants released may have either of two general classes of effect on human receptors, depending upon the level of exposure. Some contaminants are carcinogenic;

others have various non-carcinogenic, but hazardous consequences when ingested or inhaled. Carcinogenic chemical risks were provided as the risk of fatal cancer while risks from hazardous chemicals were provided as Hazard Quotients which is the ratio of the estimated intake to a standard reference dose. Exposures are calculated assuming a lifetime of continuous exposure at a constant level. The result is lifetime cancer risk and hazard quotient at any time during life.

Toxicological reference values for ecological species considered in the impact assessment consisted of tissue concentrations that corresponded to critical environmental concentrations, which is sometimes termed the critical body residue (Driscoll and Landrum 1997). Receptors were restricted to organisms known to occur in the study area that represent significant human resource species or species of ecological importance, including those that are commercially exploited and hence serve as potential contaminant migration pathways to humans.

The assessment of the food-ingestion pathway used measured or modeled contaminant concentrations in water, sediment, and pore water, and the results from the ecological risk modeling for tissue concentrations of aquatic organisms. The aquatic species that were chosen as representative of human consumption included fish (*Lutjanus campechanus*), crustaceans (*Farfantepenaeus aztecus*), and mollusks (*Octopus maya*).

Tissue benchmark concentrations for each of the taxonomic groups were based on values analyzed for each individual species addressed in the assessment. These reference values were used as the denominator in the ecological hazard quotient (EHQ) for species i from contaminant j at location k:

$$\mathrm{EHQ}_{ijk} = \text{Field} - \text{based tissue concentration}_{ijk} / \text{Tissue benchmark concentration}_{ij},$$

where tissue benchmark concentration$_{ij}$ is derived from the critical body residue calculations that used TEL/continuous chronic concentrations and PEL/continuous maximum concentration, and the field-based tissue concentration$_{ijk}$ is obtained using concentrations from water and sediment samples from the region of study modeled through ECEM.

Human health impacts evaluation

Risk resulting from the exposure to carcinogenic compounds is a measure of the potential for the occurrence of cancer. In addition, mutagenic or tumorigenic chemicals may also result in cancer, but scientific evidence confirming this is incomplete. Generally, regulatory agencies consider an excess cancer risk of less than one in 1 million (<1E−06 risk) acceptable and below a level of concern. This was considered a small potential for adverse impact. Regulatory agencies consider a risk between 1 in 1 million and 1 in 1000 (>1E−06, <1E−04 risk) sufficient to warrant further investigation (considered a moderate potential for adverse impact).

This means that there is a need to investigate the uncertainties associated with the impact assessment further or to continue monitoring the environmental conditions associated with the scenario that produced the impact. A risk that is greater than 1 in 1000 (>1E−04) is of concern to regulatory agencies and can lead to immediate actions to prevent adverse human health impacts (e.g., closures of selected fisheries, advisory notices). This level of risk was considered as a large potential for adverse impacts. In many instances, regulatory agencies have changed those values, for example, modifying the level of acceptable risk (ITRC 2005).

A hazard quotient approach was also used to determine the human health risk associated with non-carcinogenic, but toxic chemicals. A hazard quotient is the ratio between the measured contaminant dose and a reference dose determined to be safe. Generally, if the ratio is less than 0.1 there is no concern for toxic health effects (small potential for impact). If the ratio is between 0.1 and 1, then regulatory agencies consider the risk to warrant further investigation (moderate potential for impact). If the ratio is greater than 1, regulatory agencies may be concerned about the environmental conditions and immediate action may be required to prevent impacts to human health (large potential for impact).

Scenarios were developed that represented the most likely types of exposures to people living close to the Marine Terminal and fishermen who catch and eat fish from nearshore areas. People living close to the Marine Terminal and fishermen were assumed to consume local seafood about once per week, and coastal fisherman may also experience dermal exposure to any contaminated seawater while harvesting seafood.

The onshore facilities at Dos Bocas are located adjacent to the coast, in an area of the northern Tabasco state where lagoons, estuaries, and riverine systems meet. These areas are highly productive for certain marine fish and shellfish. The risks to coastal fisherman were considered for nearshore impacts, because most likely the fishermen's catch is from the nearshore region.

Table 7 shows the results of nearshore human health impacts on carcinogenic risk and hazard index calculated for the year 2003. Cancer risks at the diffuser sites warranted further investigation based on data derived from maximum, minimum, and average chemical concentrations.

Carcinogenic risk was reduced at the reference sites, but still suggested the need for further investigation or continued monitoring. This assessment was based on estimated contaminant concentrations in fish, mollusks, and crustaceans derived by the ecological risk assessment, and

Table 7 Results of nearshore human health impacts on carcinogenic risk and hazard index

Impact	Diffuser sites	Tupilco reference sites
Carcinogenic risk		
Maximum	1.00 ± 0.2 E−04	2.00 ± 0.3 E−05
Minimum	1.00 ± 0.2 E−05	1.00 ± 0.2 E−05
Average	4.00 ± 0.6 E−05	1.00 ± 0.2 E−05
Hazard index		
Maximum	0.5	0.15
Minimum	0.13	0.11
Average	0.25	0.13

assumed the exposed groups were eating fish that contained similar levels of contaminants.

The 2003 results suggested that the greatest potential for adverse human health impacts were from the exposure of fishermen near the Dos Bocas facility to increased carcinogenic, mutagenic, or tumorigenic chemicals. These results were based on water concentrations estimated from the conservative transport models.

Table 8 shows the ecological and human analytes impact summary for the year 2003. Based on the results, the environmental assessment identified Cu, Cd, and Ni in diffuser discharges present at concentrations, indicating a moderate to large potential for adverse risk. Cd, Ni, and TPAHs were also present in the sediment near the diffuser at concentrations representing a moderate for adverse environmental risk.

Human health risk assessment identified at the diffuser sites one carcinogen (benzo(a)pyrene (BAP), one suspected carcinogen dibenz(a, h)anthracene, and two toxic metals (Cd, Pb) at concentrations that warrant additional investigation. At the Dos Bocas reference sites, Cu in ambient water represented a moderate potential for ecological risk based on ECEM assessment.

The HUMAN model identified two carcinogens (As and BAP), one suspected carcinogen (dibenz[a,h]anthracene), and one toxic metal (Hg) present at levels that warrant additional investigation. BAP is generally associated with pyrogenic (combustion) sources and may be present in trace levels in petroleum. However, BAP is of particular concern because it is an identified carcinogen, which concentrates in tissues, and is an analyte of concern in fish advisories.

Table 9 shows the results of nearshore human health impacts for carcinogenic risk and hazard index calculated for the year 2013. According to the HUMAN results, 1533 values for analytes were greater than $1.00E^{-04}$ (considered a moderate potential for adverse impact), most of them corresponding to metals, particularly Cr, Pb, and As which were also detected in the year 2003 and in 2013 at much higher risk values. Among the PAHs, the highest values correspond to maximum values found for 3/5-ring compounds: phenanthrene, fluoranthene, pyrene, and perylene found mostly in sediments at the diffuser area.

Table 10 presents a summary of the ecological and human impacts found at the diffuser and reference areas during the 2013 study. It is clear that more impacts to sediments by metals and organics are seen at the diffuser site, concomitant with an increase of toxicity levels for metals at the reference site, particularly two of them (Ni and V) associated with crude oil.

Consequently, it is anticipated that the greatest food chain exposure to the more persistent and hazardous hydrocarbons, as well as heavy metals, would likely occur in the benthic invertebrate communities via consumption of detritus and incidental ingestion of associated surface sediments.

Conclusions

From a regional perspective, the ecological and human impacts on the inhabitants of the area have increased with time, particularly those related to sediment arising from the aqueous discharges from the diffuser. Concentrations of

Table 8 Ecological and human impact summary, year 2003

Site	Ecological risk (ECEM) 2003		Carcinogenic risk (HUMAN) 2003	
	Impact to water column	Impact to sediments	Impact to water column	Impact to sediments
Diffuser sites	Cu*** Cd**, Ni**	Cd**, Ni**, TPAH**	Cd**, Pb**	Carcinogenic = Benzo[a]pyrene***, toxics(Cd**, Pb**) Suspected carcinogen = Dibenz(a,h)anthracene)***
Tupilco reference sites	Cu***	Low risk	Carcinogenic = Benzo[a]pyrene**, As Suspected carcinogen (Dibenz(a,h)anthracene)** Toxic **Hg	

* Low impact (<1.00E−04); ** moderate impact (≥1.00 E−04 and < 1.00); *** high impact (≥ 1.00)

Table 9 Ecological and human impact results, year 2013

Analyte	Carcinogenic risk				Hazard index
	Mean (±SD)	Max.	Quartile 75 %	*n*	
Acenaphthene	1.22 ± 0.3 E−11	2.90 ± 0.4 E−09	0.00 E+00	540	0.04
Acenaphthylene	6.35 ± 1.2 E−12	2.12 ± 0.4 E−09	0.00 E+00	540	0.04
Anthracene	2.30 ± 0.4 E−10	3.03 ± 0.6 E−08	0.00 E+00	540	0.05
Benzo[e]pyrene	9.52 ± 0.6 E−11	3.62 ± 0.6 E−08	0.00 E+00	864	0.04
Benzo[b]fluoranthene	2.50 ± 0.3 E−11	3.32 ± 0.5 E−09	0.00 E+00	864	0.04
Benzo[a]pyrene	3.30 ± 0.3 E−10	6.14 ± 0.6 E−08	0.00 E+00	864	0.05
Benzo[g,h,i]perylene	4.57 ± 0.6 E−11	1.84 ± 0.6 E−08	0.00 E+00	864	0.04
Chrysene	1.43 ± 0.3 E−10	2.58 ± 0.3 E−08	0.00 E+00	864	0.05
Dibenzofuran	2.04 ± 0.3 E−10	6.02 ± 0.5 E−08	0.00 E+00	540	0.05
Fluoranthene	6.71 ± 0.4 E−10	1.89 ± 0.3 E−07	0.00 E+00	540	0.05
Fluorenes	1.96 ± 0.3 E−10	7.75 ± 0.9 E−08	0.00 E+00	540	0.05
Naphthalene	6.56 ± 0.6 E−11	2.32 ± 0.4 E−08	0.00 E+00	540	0.05
Perylene	2.03 ± 0.3 E−09	3.77 ± 0.3 E−07	0.00 E+00	864	0.04
Phenanthrene	9.58 ± 0.6 E−09	3.31 ± 0.6 E−06	0.00 E+00	540	0.06
Pyrene	3.77 ± 0.4 E−09	9.18 ± 1.4 E−07	0.00 E+00	540	0.06
Arsenic	5.20 ± 0.4 E−03	1.93 ± 0.4 E−01	2.10 ± 0.4 E−05	1728	0.25
Barium	2.46 ± 0.3 E−03	9.34 ± 1.3 E−02	1.13 ± 0.4 E−03	540	0.25
Cadmium	8.57 ± 0.6 E−04	2.49 ± 0.4 E−02	5.41 ± 0.6 E−06	1296	0.45
Chromium	3.71 ± 0.3 E−02	3.04 ± 0.3 E−00	1.98 ± 0.6 E−06	1296	0.50
Copper	1.52 ± 0.3 E−03	9.32 ± 1.8 E−02	1.20 ± 0.4 E−04	540	0.40
Lead	2.31 ± 0.3 E−0.1	4.77 ± 0.9 E−00	4.14 ± 0.6 E−03	540	0.60
Nickel	2.05 ± 0.3 E03	9.83 ± 1.3 E−02	2.06 ± 0.6 E−05	1296	0.40
Vanadium	4.39 ± 0.3 E−03	1.23 ± 0.3 E−01	3.61 ± 0.3 E−04	540	0.40
Combined	5.68 ± 0.4 E−-01	8.24 ± 0.7 E−00	4.18 ± 0.5 E−02	324	0.60

Table 10 Impacts summary

Site	Ecological risk (ECEM) 2013		Human risk (HUMAN) 2013	
	Impact to water column	Impact to sediments	Impact to water column	Impact to sediments
Diffuser sites	Toxics (As, Cd, Cr)**	Toxics (Ba, Pb, Cr, Ni, Cu, V, As)***. Carcinogenics (total PAHs, phenanthrene, anthracene, dibenzothiophene)***	Toxics (Pb, Cr)***	Toxics (As, V, Ni, Ba, Cu, Cr)**
	Carcinogenic (naphthalene, anthracene, dibenzotiophene)**	Carcinogenics (Fluorene, chrysene, benzo(a)pyrene, pyrene, benzo(b)fluoranthene)**	Carcinogenics, no risk	Carcinogenics (phenanthrene, perylene, pyrene, fluorene, dibenzophenanthrene, benzo(e)pyrene, anthracene, naphthalene, crysene, benzo(a)pyrene, benzo(b)fluoranthene)*
Tupilco reference sites	**Toxics (Cd, Cu)	Toxics (Cr, Pb, Ba, V, Ni, Cu, As, Cd)***	Toxics (Pb, Cr)***	Toxics (As, V, Ni, Ba)***
	Carcinogenics, no risk	Carcinogenics, no risk	Carcinogenic, no risk	Carcinogenic, no risk

* Low impact (<1.00 E−04); ** moderate impact (≥1.00 E−04 and <1.00); *** high impact (≥1.00)

toxic metals and hydrocarbons in 2013 at nearshore locations likely reflect high regional background concentrations, and the discharge of pollutants from the Dos Bocas diffuser resulted in a potential impact simply because it elevated the already high background environmental concentrations.

Environmental risk assessment modeling showed significant potential threshold-level effects on biota in the sampled region around the Dos Bocas diffuser.

The primary pathways by which contaminants present in the Sonda de Campeche influence human health is through ingestion of contaminated fish and shellfish, and incidental dermal exposure to contaminants that are associated with sediments or released from the sea surface.

Management of PW is a challenge for mature fields like those of Sonda de Campeche and for the future development of deep water fields. Effective measures to handle unwanted or excess PW depend on the asset maturity, the type of reservoir, production rates, location, legislation, and history; therefore, the life cycle of water should always be assessed as part of reservoir management.

References

APHA (American Public Health Association) (1992) Standard methods for the examination of water and wastewater, 18th edn. APHA, Washington, DC

ATSDR (2000) United States Agency for Toxic Substances and Disease Registry Division of Toxicology and Human Health Sciences, Atlanta. http://www.atsdr.cdc.gov/toxprofiles/

Azetsu-Scott K, Yeats P, Wohlgeschaffen G, Dalziel J, Niven S, Lee K (2007) Precipitation of heavy metals in produced water: influence on contaminant transport and toxicity. Mar Environ Res 63:146–167

Bahadur R, Amstutz DE, Samuels WB (2013) Water contamination modeling—a review of the state of the science. J Water Resour Protect 5:142–155

Baker JR, Mihelcic JR, Lluehrs DC, Hickey JP (1997) Evaluation of estimation methods for organic-carbon normalized sorption coefficients. Water Environ Res 69:136–144

Bakke T, Klungsøyr J, Sanni S (2013) Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry. Mar Environ Res 92:154–169

Balaam JL, Chan-Man Y, Roberts PH, Thomas KV (2009) Identification of nonregulated pollutants in North Sea-produced water discharges. Environ Toxicol Chem 28:1159–1167

Barceloux DG (1999) Vanadium. J Toxicol Clin Toxicol 37:265–278

Battelle Memorial Institute (2006) Evaluation of the environmental impacts of offshore oil activities and associated coastal facilities on the marine environment of the Campeche Sound. Programmatic integrated report PNWD-3632. October 2004. Pacific Northwest Laboratories, Richland

Botello AV, Rendón-von Osten J, Gold-Bouchot G, Agraz-Hernández C (2005) Golfo de México, Contaminación e Impacto Ambiental: Diagnóstico y Tendencias, vol 2. Universidad Autónoma de Campeche, Universidad Nacional Autónoma de México, Instituto Nacional de Ecología, Mexico, p 696

Brandt CA, Huesemann MH, Becker JM, Hanrahan TP, Dauble DD, O'Neill TK, Mueller RP (1998) Ecological Assessment, Trecate No. 24 Blowout, 1997 Progress Report. Pacific Northwest Laboratories, Richland

Brandt CA, Bunn AL, Eslinger PW, Napier BA, Miley TB, Nieves LA, Prendergast EL, Scott ML (2002) Risk/impact module. In: Bryce, RW, Kincaid, CT, Eslinger, PW, Morasch, LF (eds) An initial assessment of hanford impact performed with the system assessment capability. PNNL-14027. Pacific Northwest National Laboratory, Richland, pp 119–136

Brandt CA, Aimo NJ, Becker JM, Napier BA, Bunn AL, Miley TB, Stegen JA, González-Macias MC, Salazar L (2005) Evaluation of the environmental impacts of offshore oil activities and associated coastal facilities on the marine environment of the sonda de campeche. WBS 4.5.1 integrated diagnosis and reporting impact metrics. Battelle Memorial Institute, Pacific Northwest Division, Richland, p 324

Buchman MF (2008) NOAA screening quick reference tables. NOAA OR&R Report 08-1, Seattle WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, pp 34

Burkhard L (2009) Estimation of biota sediment accumulation factor (bsaf) from paired observations of chemical concentrations in biota and sediment EPA/600/R-06/047. US Environmental Protection Agency, Ecological Risk Assessment Support Center, Cincinnati

Carroll M, Pearson T, Dragsund E, Gabrielsen KL (2000) Environmental status of the Norwegian offshore sector based on the Petroleum Regional Monitoring Programme, 1996–1998. Report prepared by Akvaplan-NIVA, DNV, and Unilab Analyse for the Norwegian Oil Industry Association (OLF). ISBN 82-449-0053-9

Cempel M, Nikel G (2006) Nickel: a review of its sources and environmental toxicology. Polish J Environ Stud 15:375–382

Dayan AD, Paine AJ (2001) Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. Hum Exp Toxicol 20:439–451

Domingo JL (1994) Metal-induced developmental toxicity in mammals. A review. J Toxicol Environ Health 42:123–144

Doneker RL, Jirka GH (2001) CORMIX-GI systems for mixing zone analysis of brine wastewater disposal. Desalination 139:263–274

Driscoll SK, Landrum PF (1997) A comparison of equilibrium partitioning and critical body residue approaches for predicting toxicity of sediment-associated fluoranthene to freshwater amphipods. Environ Toxicol Chem 16:2179–2186

Eslinger PW, Miley TB (2012) User instructions for the computer codes of the toolkit for integrated impact assessments (TIIA), version 1. PNWD-4357. Battelle Memorial Institute, Pacific Northwest Division, Richland

Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ (2009) Review of technologies for oil and gas produced water treatment. J Hazard Mater 170:530–551

Folk RL (1974) The petrology of sedimentary rocks. Hemphill Publishing, Austin **184 pp**

Froese R, Pauley D (eds) (2005) FishBase. Retrieved August 5, 2005, from www.fishbase.org/search.php

ITRC (Interstate Technology and Regulatory Council) (2005) Examination of risk-based screening values and approaches of selected states. RISK-1. Interstate Technology and Regulatory Council, Risk Assessment Resources Team, Washington. http://www.itrcweb.org

Johnsen S, Frost TK, Hjelsvold M, Utvik TR (2000) The environmental impact factor—a proposed tool for produced water impact reduction, management and regulation. SPE 61178, Presented at the SPE HSE Conference, Stavanger, Norway. Society of Petroleum Engineers, Richardson

Lee K, Azetsu-Scott K, Cobanli SE, Dalziel J, Niven S, Wohlgeschaffen G, Yeats P (2005) Overview of potential impacts of produced water discharges in Atlantic Canada. In: Armworthy SL, Cranford PJ, Lee K (eds) Offshore oil and gas environmental effects monitoring: approaches and technologies. Battelle Press, Columbus, pp 319–342

Macias-Zamora JV, Villaescusa-Celaya JA, Muñoz-Barbosa A, Gold-Bouchot G (1999) Trace metals in sediments cores from the Campeche shelf, Gulf of Mexico. Environ Pollut 104:69–77

Manickchand-Heileman S, Arreguin-Sanchez F, Lara-Dominguez A, Soto LA (1998) Energy flow and network analysis of Terminos Lagoon, SW Gulf of Mexico. J Fish Biol 53 (Suppl A):179–197

McPherson CA, Chapman PM, Vigers GA, Ong KS (1999) ASEAN Marine Water Quality Criteria: Contextual Framework, Principles, Methodology and Criteria for 18 Parameters. ASEAN Marine Environmental Quality Criteria—Working Group (AMEQCWG), ASEAN-Canada Cooperative Programme on Marine Science—Pase II (CPMS-II). EVS Environment Consultants, North Vancouver and Department of Fisheries, Malaysia. p 568

Neff JM (2002) Bioaccumulation in marine organisms. Effects of contaminants from oil well produced water. Elsevier, Amsterdam, p 454

Neff JM, Stout SA, Gunster DG (2005) Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: identifying sources and ecological hazard. Integr Environ Assess Manage 1:22–33

Neff JM, Johnsen S, Frost TK, Utvik TIR, Durell GS (2006) Oil well produced water discharges to the North Sea. Part II: comparison of deployed mussels (*Mytilus edulis*) and the DREAM model to predict ecological risk. Mar Environ Res 62:224–246

Neff JM, Lee K, DeBlois EM (2011) Produced water: overview of composition, fates, and effects. In: Lee K, Neff JM (eds) Produced water: environmental risks and advances in mitigation technologies. Springer, USA, pp 3–54

Newman MC, McIntosh AW (eds) (1991) Metal ecotoxicology: concepts and applications. Lewis Publishers, Chelsea

OOCC. Offshore Operators Committee Continental Shelf Associates, Inc. (1997) Gulf of Mexico produced water bioaccumulation study. Executive Summaries. Jupiter, Florida

Palma C, Lillebo AI, Valenca M, Pereira E, Abreu MP, Duarte AC (2009) Mercury in sediments of the Azores Deep sea platform and on sea mounts of the archipelago-Assessment of background concentrations. Mar Pollut Bull 58:1566–1587

Payne JF, Andrews C, Fancey L, French B, Lee K (2011) Risks to fish associated with barium in drilling fluids and produced water: A chronic toxicity study with Cunner (*Tautogolabrus adspersus*) In: Lee K, Neff J (eds) Produced water, Springer, New York, pp 401–417

Pillard DA, Tietge JE, Evans JM (1996) Estimating the acute toxicity of produced waters to marine organisms using predictive toxicity models. In: Reed M, Johnsen S (eds) Produced water 2. Environmental issues and mitigation technologies. Plenum Press, New York, pp 49–60

Rand GM, Petrocelli SR (1985) Fundamentals of aquatic toxicology: methods and applications. Hemisphere Publishing Corporation, Washington, DC

Reeves AL (1986) Barium. In: Handbook on the Toxicology of Metals, vol. II: Specific Metals. In: Friberg L, Nordberg GF, Velimir B (eds) Elsevier Science Publishers, Amsterdam, Oxford, New York, pp 84–93

Research Council of Norway (2012) Long-term effects of discharges to sea from petroleum-related activities. The results of ten years' research. Oslo

Rodríguez-Almaraz GA, Leija-Tristán A, Mendoza R (2000) Records of caridean shrimps (*Crustacea: Decapoda*) from the coasts of the Mexican Pacific Ocean, Gulf of Mexico and Mexican Caribbean. Bull Mar Sci 67:857–867

Ruiz-Fernandez AC, Sprovieri M, Piazza R, Frignani M, Sanchez-Cabeza JA, Feo ML, Bellucci LG, Vecchiato M, Perez-Bernal LH, Paez-Osuna F (2012) Pb-210-derived history of PAH and PCB accumulation in sediments of a tropical inner lagoon (Las Matas, Gulf of Mexico) near a major oil refinery. Geochim Cosmochim Ac 82:136–153

Salazar-Coria L, Schifter I, González-Macías C (2010) Weighing the evidence of ecological risk from PAHs contamination in the estuarine environment of Salina Cruz Bay, México. Environ Monit Assess 162:387–406

Sauer TC, Costa HJ, Brown JS, Ward TJ (1997) Toxicity identification. Evaluations of produced water. Environ Toxicol Chem 16:2020–2028

Schifter I, Gonzalez-Macías C, Miranda A, López-Salinas E (2004) Air emissions assessment from offshore oil activities in Sonda de Campeche, Mexico. Environ Monit Assess 109:135–145

Sharma J, Baguley JG, Montagna PA, Rowe GT (2012) Assessment of longitudinal gradients in nematode communities in the deep northern Gulf of Mexico and concordance with benthic taxa. Int J Oceanogr. doi:10.1155/2012/903018

Statistica (1998) Statistica for windows (volume I). General Conventions General Conventions and Statistics I, 2nd edn. Stat Soft, Inc., Tulsa OK, USA

Sundt RC, Ruus A, Jonsson H, Skarphéðinsdóttir H, Meier S, Grung M, Beyer J, Pampanin DM (2012) Biomarker responses in Atlantic cod (*Gadus morhua*) exposed to produced water from a North Sea oil field: laboratory and field assessments. Mar Pollut Bull 64:144–152

Suter GW-II, Tsao SL (1966) Toxicological benchmarks for screening of potential contaminants of concern for effects on aquatic biota on oak ridge reservation: 1996 revision. Oak Ridge National Laboratory, Oak Ridge, p 1996

Townend J (2002) Practical statistics for environmental and biological scientists. Wiley, England, p 276

Turner RE, Overton EB, Rabalais NN, Sen Gupta BK (eds) (2003) Historical reconstruction of the contaminant loading and biological responses in the Central Gulf of Mexico shelf sediments. US Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, pp 140. OCS Study MMS 2003-063

USEPA (United States Environmental Protection Agency) (1996) AQUIRE (aquatic toxicity information retrieval) database. National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division, Duluth

USEPA (United States Environmental Protection Agency) (2014) National Recommended Water Quality Criteria. Office of Water, Office of Environmental Protection Agency, Science and Technology 4304T, US Washington DC. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

Vasile GD, Vlădescu L (2010) Cadmium partition in river sediments from an area affected by mining activities. Environ Monit Assess 167:349–357

Vazquez FG, Sharma VK, Magallanes VR, Marmolejo AJ (1999) Heavy metals in a coastal lagoon of the Gulf of Mexico. Mar Pollut Bull 38:479–485

Vazquez FG, Sharma VK, Perez-Cruz L (2002) Concentrations of elements and metals in sediments of the southeastern Gulf of Mexico. Environ Geol 42:41–46

Vengosh A (2003) Salinization and saline environments. In: Heinrich D, Holland KK Turekian (eds) Treatise on Geochemistry, Pergamon, Oxford, pp 1–35

Wlodarczyk B, Minta M, Biernacki B, Szkoda J, Zmudzki J (2000) Selenium protection against cadmium toxicity in hamster embryos. Pol J Environ Stud 9:323–327