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Occurrence of pharmaceutical and personal care products (PPCPs) in marine sediments in the Todos os Santos Bay and the north coast of Salvador, Bahia, Brazil

Magda Beretta · Vicky Britto · Tania Mascarenhas Tavares · Sonilda Maria Teixeira da Silva · Adelmo Lowe Pletsch

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Abstract
Purpose The Todos os Santos Bay is the largest bay in Brazil and receives drainage from various watersheds. For more than 450 years, it was the main destination for the domestic and hospital sewage from the city of Salvador, Bahia. With the growing concern regarding the presence of pharmaceutical and personal care products (PPCPs) in the environment, an investigation was undertaken to determine the presence and levels of some commonly used drugs (i.e., atenolol, caffeine, carbamazepine, diazepam, diclofenac, erythromycin, ibuprofen) and personal care products (i.e., galaxolide, tonalide), using sediments as an indicator of their presence in the water column.
Material and methods Surficial sediment samples from 17 stations located in the intertidal zone of the Todos os Santos Bay and infralittoral zone along the north coast of Salvador were tested for the presence of some PPCPs using LC-MS/MS (for drugs) and GC-MS/MS (for fragrances).
Results and discussion The PPCPs examined were present in all sediment samples at levels of parts per billion of dry sediment. The highest concentrations were found for the fragrances galaxolide (52.5 ng g^{-1}) and tonalide (27.9 ng g^{-1}), followed by caffeine (23.4 ng g^{-1}) and pharmaceuticals ibuprofen (14.3 ng g^{-1}), atenolol (9.84 ng g^{-1}), carbamazepine (4.81 ng g^{-1}), erythromycin (2.29 ng g^{-1}), diclofenac (1.06 ng g^{-1}), and diazepam (0.71 ng g^{-1}).
Conclusions Pharmaceuticals were found to be ubiquitous in the sediments of the study areas. The texture of the sediment was an important factor in PPCPs fixation and deposition. The concentrations of all PPCPs had statistically significant positive correlations with the percentage of clay in the sediments.

Keywords Emerging contaminants · Endocrine disrupting chemicals · Marine pollution · Sewage

1 Introduction

Up until the end of the 1990s, the focus of research on organic pollution was almost exclusively on conventional priority pollutants; that is, pollutants that have been proven to be harmful to living beings and for which associated risks are known, and legislation and international recommendations exist. Such pollutants include pesticides, petroleum derivatives (petroleum hydrocarbons, especially polycyclic aromatic hydrocarbons, PAHs), and by-products of industrial processes such as polychlorinated biphenyls (PCBs), dioxins, and furans. As new analytical techniques were developed and improved upon, the presence of additional organic compounds, often called "emerging contaminants", was discovered. The study of these compounds has become a priority among the main bodies responsible for protecting public health and the environment, such as the World Health Organization (WHO/UNEP/ILO 2004), the US Environmental Protection Agency (EPA 2011) and the European Commission (EEA 2010).

Among these new classes of pollutants, pharmaceuticals have received a lot of attention, for they are designed for specific uses and are persistent and maintain their properties

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M. Beretta · V. Britto
Escola Politécnica, Universidade Federal da Bahia, UFBA,
Rua Aristides Novis, 2, Federação, 40210-630 Salvador,
Bahia, Brazil

T. M. Tavares (✉) · S. M. T. da Silva
Instituto de Química, Universidade Federal da Bahia (UFBA),
Rua Barão de Geremoabo, 147, Campus de Ondina,
40170-115 Salvador, Bahia, Brazil
e-mail: ttavares@ufba.br

A. L. Pletsch
Universidade Tecnológica Federal do Paraná (UTFPR),
Avenida Brasil, 4232, Câmpus Medianeira, 85884-000 Medianeira,
Paraná, Brazil

for their original therapeutic purposes. These drugs can be administered in various ways: enteral (internal use) as in the cases of oral, rectal, and sublingual routes, or parenteral (route other than the digestive tract), for example, intravenous, subcutaneous, intra-arterial, respiratory, and conjunctival. Oral administration is one of the most widely used methods, and is normally prescribed in higher doses to compensate the loss of the drug through the gastrointestinal tract and subsequent metabolism in the liver before reaching the bloodstream (Souza 1978).

In order to ensure that chemical substances reach the blood stream at a minimum concentration required to achieve their therapeutic objectives, even after being subjected to the influences of the human or animal body, the drugs are produced at a concentration higher than necessary for absorption and with the goal of being persistent (Mulroy 2001). Thus, a large part of these drugs are eliminated in their original form and released into waterbodies, either in sewage, or in rainwater drainage from regions with animal production (Hirsch et al. 1999; Kulshrestha et al. 2004).

The first evidence of the presence of pharmaceuticals in the environment emerged in the 1970s in the USA, with the identification of clofibric acid in wastewater, which is an active metabolite of several lipid regulators in the blood (e.g., clofibrate, etofylline clofibrate, and etofibrate) (Kümmerer 2004). However, only since ca. 2000 pharmaceuticals have received increased attention.

The risk of adverse effects in humans—2 l day^{-1} for 70 years—and animals by ingestion of potable water containing pharmaceuticals is negligible. In the case of humans, the maximum possible dose that could be ingested during a lifetime is much lower than the therapeutic doses used (Kümmerer 2004). However, at the moment, there is not sufficient understanding to gauge precisely the risk to human health from decades of continuous exposure to random combinations of low levels of pharmaceutical products and more importantly, in regard to toxicity, the possible effects on organisms in the environment (Kümmerer 2004).

Knowledge about the environmental impact of direct or indirect exposure to these compounds in the environment is very restricted. Generally, environmental risk assessments for new substances that need to be approved for launching in the market are conducted using mathematical modeling based on physicochemical properties and in vitro tests. Studies are lacking on the real environment, that describe the levels, distribution, and behavior of these compounds in environmental compartments, as well as the stable chemical substances and metabolites generated, in order to generate information regarding the toxicity and potential effects. Given the lack of information and legislation to regulate the presence of these pollutants in environmental matrices, these substances continue to be emitted indiscriminately and at increasing rates into the environment, without regard to their persistence and the irreversible damage they could be causing (Stumpf et al. 1999; Di Guardo et al. 2004).

The presence of residuals from drugs in rivers and estuaries has been associated with impacts in various parts of the world, for example, the feminization of fish (high vitellogenin synthesis) and intersex conditions (imbalance between the female part and male part) (Nash et al. 2004; Pawlowski et al. 2004; Peters et al. 2007). In many cases, the consequences of the presence of these compounds in the environment are not yet clear; however, in other cases the risk seems evident and alarming (Huggett et al. 2002). There is evidence that diclofenac affects the kidneys of mammals, and in one case study in India and Pakistan, it was associated with the disappearance of birds and found to have caused an ecological disaster comparable to what happened in the past with DDT (Barceló et al. 2008). The harmful effects of propranolol on zooplankton and benthic organisms have also been identified (Huggett et al. 2002).

The presence of these compounds in the environment can facilitate the development of resistant bacterial strains—in the case of the presence of antibiotics—and can cause other specific effects, for example, the endocrine disruptors, which cause disturbances in the hormonal system causing adverse effects on both the organism and its progeny, in populations and subpopulations of the organism (EPA 1997). Several compounds have this type of effect on organisms, with some emerging contaminants already having been identified with some of these characteristics. The hormones that belong to this group are considered endocrine disruptors, and can interfere—once present in the environment—with the natural functioning of the hormonal system of animal species, including humans. In addition to their anthropic origins, in this case called xenoestrogens, these substances can be from a natural origin; for example, the phytoestrogens (EPA 1997; Huggett et al. 2002; Nash et al. 2004; Pawlowski et al. 2004; Ghiselli 2006; Peters et al. 2007).

Several authors reported the release of pharmaceuticals into the environment through complex mixtures via several different routes, especially sewage and wastewater treatment plant (WWTP) discharges, industries, hospitals, storm waters, landfills, and animal production waste, both from land and water (Daughton and Ternes 1999). Growth promoters used in fish aquaculture and field application of excrement from animals treated with drugs are examples that occur in coastal and rural areas, respectively (Ternes et al. 2002a, b; Sanderson et al. 2004; Ellis 2006; Fent et al. 2006).

Pharmaceuticals and personal care products (PPCPs) are used extensively, and most of these substances can enter waterways. This is due not only to the excretion of pharmaceuticals or their metabolites after use but also from manufacturing and through the disposal of unused or expired products. The global production of pharmaceuticals is high. Ibuprofen production, for example, reaches several kilotons

per year. A high rate of ingested pharmaceuticals is excreted from the body without being altered. These unaltered drugs are often substances with a lower potential for biodegradation.

In Brazil, there is indiscriminate use of medications, and the disposal of expired products happens randomly. Since they are considered waste with chemical risks, they should always be properly treated and disposed of so that they do not present risks to health or the environment. The Brazilian federal government does not require any safety tests and does not set concentration limits for drugs for any type of environmental matrix.

Sediments are natural repositories of many chemical substances present in the water column. Substances discharged into waterbodies generally come into contact with particulate matter in suspension, which eventually is deposited and is incorporated into the sedimentary deposits. Sedimentation generally occurs in areas of low flow velocity. In coastal marine environments, sedimentation increases in areas where freshwater meets seawater, since an increase in salinity causes the precipitation of dissolved substances in low salinity water. The incorporation of substances generally increases with decreasing particle size and, in the case of organic substances, with increasing quantity of organic material present (Salomons and Stigliani 1995). The fixation of substances to the sediment can inhibit their chemical degradation (Pan and Xing 2011). Degradation of some PPCPs has been proven to be enhanced under aerobic conditions as compared to anaerobic ones (Conkle et al. 2012). Although contaminants bound to sediments are often considered unavailable, it is possible that they could bioaccumulate, becoming incorporated into the food chain and affecting people via food, or being toxic to one or more links in the food chain, thus affecting ecosystems more broadly. The chemical composition of the sediment reflects the quality of the habitat. In the particular case of PPCPs, it is believed that their environmental behavior is controlled for the most part by their interaction with soil and sediment particles. Despite this fact, few extensive studies have been done on the distribution of PPCPs in the solid-phase portion of the environment (Pan and Xing 2011).

The Todos os Santos Bay, the largest in Brazil (~1,000 km^2), receives drainage from various watersheds with the three main outlets discharging 200 $m^3\ s^{-1}$ into the bay, which has areas with extensive mangroves. For more than four and a half centuries, the Todos os Santos Bay was the main destination for the domestic and hospital sewage from the city of Salvador. In the early 1970s, the first sewage collection basins were built for the boroughs, which were located on the coast but not on the Todos os Santos Bay. The sewage from these basins drained out to sea via an outfall located directly on the Atlantic Ocean coastline, and this situation remains until today.

Only in this century was the sewage of the entire city of Salvador and other cities around the Todos os Santos Bay collected for discharge with preconditioning—but without treatment—through the existing outfall. Although most of the collection system has been installed, <80 % of the residential connections have been completed (Borja and Moraes 2012). Due to high sedimentation rates (~2.4 mm yr^{-1}) and the presence of areas of low energy, especially in the northern half of the bay, >50 % of the sediment at the bottom of the bay is muddy, composed predominantly of clay and silt. It is, therefore, an area that is prone to become a sink of chemical contaminants, especially organic compounds including PPCPs.

The objective of this study was to investigate the presence and levels of the main PPCPs in the Todos os Santos Bay, where untreated sewage and runoff from farms (free-range livestock, confined poultry, and aquaculture) that use modern animal husbandry techniques were discharged for several decades in the last century. The choice of drugs to be analyzed was based on the information obtained from the Health Department of the State of Bahia on the drugs distributed to the population. The compounds were then selected as representative of different classes of compounds: antibiotics, erythromycin; analgesics/anti-inflammatory, diclofenac and ibuprofen; psychiatric drugs, diazepam, and carbamazepine; beta-blockers, atenolol; and fragrances, tonalide, and galaxolide. Caffeine was also included as it is currently being used as an indicator of sewage contamination because it is continuously present in the human diet; it is stable and not completely metabolized and is easily determined. Since a large part of the bay has a high content of silt and clay, which generally favors assimilation of organic compounds, sediment was selected as the environmental indicator in this study. There are practically no studies of these compounds in marine sediments worldwide, and no studies of PPCPs in sediments in Brazil. To the best of our knowledge, this is the first study of this type carried out in Latin America.

2 Materials and methods

2.1 Sample collection

The selection of sampling stations took into consideration the location of Salvador's ocean sewage outfall in the borough of Rio Vermelho and the location of terrestrial and aquatic animal production, as well as the level of urbanization surrounding the bay. The samples were collected from 17 sites (Fig. 1) within the Todos os Santos Bay. Eight samples were collected from the eulittoral zone and five from the infralittoral zone, near the intertidal zone, as well as four samples from the bottom of the bay on the Atlantic coast of Salvador, at distances of 500 m to 5 km from the coast. Table 1 presents the geographic coordinates and code of all samples. In the eulittoral zone, the sediment samples from beaches and mangroves were composed of 20 surface subsamples (0–2 cm depth) from a 25 m^2 area, collected during low tide. The

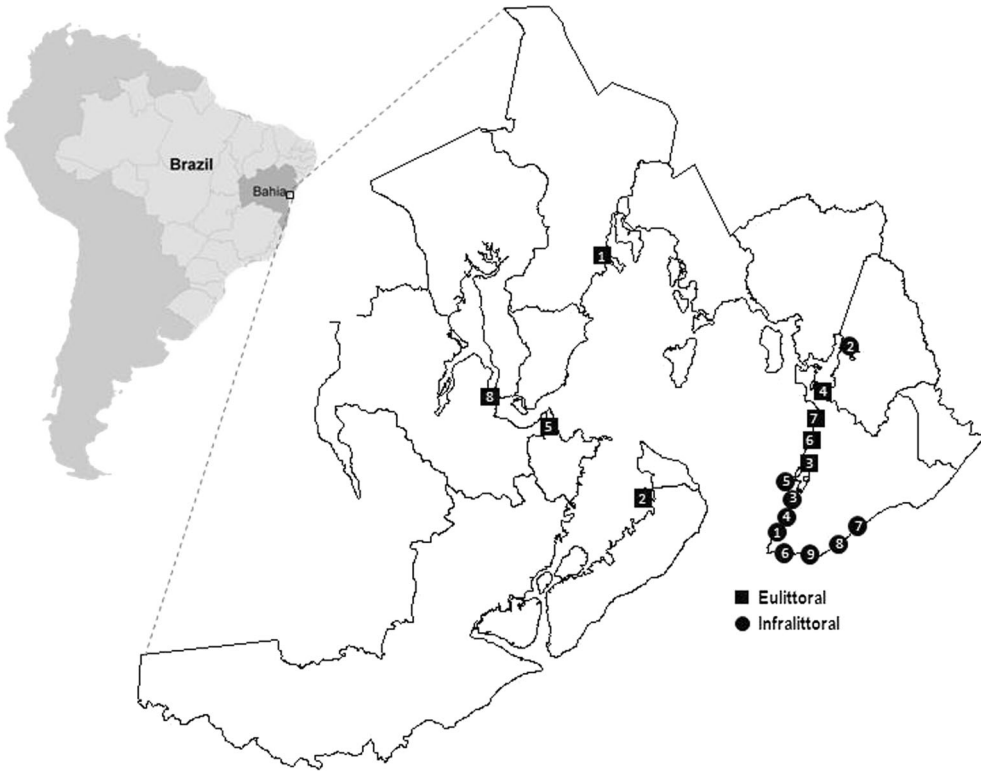

Fig. 1 The location of Todos os Santos Bay within the State of Bahia and Brazil and the geographic distribution of the sediment sampling sites

surface sediment samples were taken using a Shipek dredge, launched from a boat, and several subsamples of the surface layer were taken. All of the samples were homogenized, lyophilized, and stored at temperatures between 18 and 23 °C until analysis, which was performed in the laboratory of Analytical Center of University of La Coruña, Spain.

Table 1 Geographic coordinates and sample identification for the sediment samples collected from the Todos os Santos Bay and the north coast of Salvador, Bahia, Brazil

Sample identification	Location	Geographic coordinates	
Infralittoral			
I1	Baia Marina	12° 58′	38° 31′
I2	B. Naval Aratu	12° 47′	38° 29′
I3	Porto/Salvador	12° 57′	38° 30′
I4	T. São Joaquim	12° 57′	38° 30′
I5	Porto da Ribeira	12° 71′	38° 30′
I6	Rio Vermelho	13° 01′	38° 28′
I7	Rio Jaguaribe	12° 58′	38° 22′
I8	Jardin de Allah	13° 00′	38° 25′
I9	Pituba	13° 00′	38° 27′
Eulittoral			
E1	Acupe	12° 39′	38° 44′
E2	Baiacu	12° 59′	38° 42′
E3	Cabrito	12° 54′	38° 28′
E4	Mapele II	12° 47′	38° 26′
E5	Salinas da Margarida	12° 52′	38° 45′
E6	São Tomé	12° 49′	38°28′
E7	Lobato	12° 54′	38° 27′
E8	Maragojipe	12° 42′	38° 56′

2.1.1 Sample preparation

The following methodology was used for the extraction of all compounds in the sediment samples. To 2.0 g of previously homogenized sample, surrogate standards were added (ibuprofen-D3), which traces the recovery of all investigated substances. Extraction was then proceeded by adding 15 ml of methanol (Merck, HPLC grade) and agitating for 20 min with the aid of ultrasound. The extract was filtered into a flask with a 0.45-μm filter. The procedure was repeated twice and the extracts combined. The final volume was evaporated in a rotary evaporator to approximately 1 ml, transferred to a 5-ml flask, and dried with an ultrapure nitrogen flow. To the dry extract, 1 ml of methanol was added and a deuterated internal standard, diclofenac-D4, for quality control of the determination of all compounds of interest, followed by injection of the solution into the chromatograph.

2.2 Analytical methods

Liquid chromatography coupled to triple quadrupole mass spectrometry (Applied Biosystems API 3200 LC-MS, Foster City, CA, USA) was used for analysis of the pharmaceuticals. The conditions used for the separation were as follows: Thermo Aquasil column 3 μm, 150 mm×4.6 mm (purchased from

ThermoFisher Scientific, Waltham, MA, USA); gradient elution, A=water + 5 mM ammonium acetate and B = methanol + 5 mM ammonium acetate; temperature = 50 °C; injection volume of 20 μl; and eluent flow rate of 1 m min^{-1}. The detection conditions were triple quadrupole mass spectrometry, with ESI ionization and MRM (multiple reaction monitoring) mode, with selection of a precursor ion and two ion products to quantify and qualify each compound.

In the case of fragrances, analysis was conducted using GC-MS (Thermo Finnigan Polaris Q, Austin, TX, USA). The analytical conditions used were as follows: column, J&W DB-XLB 60 m×0.25 mm×0.25 μm (Agilient Technologies, Folsom, USA); injection, PTV mode; initial temperature 50 °C; split flow, 50 ml min^{-1}; splitless time, 5 min; injection time, 0.5 min; transfer velocity 4 °C min^{-1} of the final temperature 290 °C; injection volume, 9 μl; elution, 50 °C (2 min), 150 °C variation of 10 °C min^{-1} up to 300 °C (5 min); constant flow of 1 ml min^{-1}; linear transfer, 290 °C; and detection, SIR (selected ion recording) mode.

2.3 Quality control

The linearity and the precision of the method were evaluated using sediment sample blanks (not contaminated, previously extracted) spiked with four concentration levels (0.5, 5.0, 50, and 100 ng g^{-1}) with ten replicates each. The recoveries obtained were in the range 87–94 %, with a reproducibility of >90 % (RSD, n=10). The detection limits were 0.1 ng g^{-1} (dry weight) for all of the drugs and fragrances analyzed. For each of the sample batches, one intermediate control sample was analyzed (x=5 ng g^{-1}) to ensure that the recovery was always maintained >87 %.

2.4 Granulometric analysis

The sediment samples were subjected to granulometric analysis to determine the fractions of sand (coarse and fine), silt, and clay. The analyses were conducted by total dispersion using the pipet technique (EMBRAPA 1997) in the soil laboratories of the National Department of Projects Against Drought Brazil (DNOCS).

3 Results and discussion

The concentrations of the compounds studied in the sediments at each site are presented in Table 2. The drugs and fragrances present in the sediment samples were as follows: the drugs atenolol and ibuprofen and the personal care products galaxolide (100 %) and tonalide, as well as caffeine, were

Table 2 Concentrations (in ng g^{-1} dry weight) of pharmaceuticals and personal care products (PPCPs) found in sediments collected in the Todos os Santos Bay and north coast of Salvador

Sample	PPCP								
	Caffeine	Carbamazepine	Ibuprofen	Diclofenac	Galaxolide	Tonalide	Atenolol	Diazepam	Erythromycin
I1	0.64	<0.10	15.6	0.85	7.90	7.57	8.07	0.56	<0.10
I2	0.65	<0.10	14.4	0.86	3.02	6.33	8.36	0.59	<0.10
I3	1.62	<0.10	13.7	1.06	5.53	6.28	9.84	0.71	0.17
I4	0.80	0.15	18.8	0.77	6.52	4.18	9.74	0.53	<0.10
I5	0.88	<0.10	7.44	0.31	52.5	27.9	4.12	<0.10	<0.10
I6	0.62	<0.10	0.77	0.58	4.42	3.14	6.60	0.38	<0.10
I7	0.95	<0.10	7.99	<0.10	6.25	4.35	4.32	<0.10	0.10
I8	0.76	<0.10	13.8	0.70	6.45	9.53	7.12	0.48	<0.10
I9	0.31	0.12	15.1	0.98	4.92	3.43	7.83	0.64	<0.10
E1	0.45	<0.10	8.45	0.61	5.58	5.73	3.98	0.40	<0.10
E2	0.71	<0.10	11.4	0.76	4.14	6.59	5.52	0.51	<0.10
E3	0.76	4.81	11.4	0.67	13.1	16.5	5.76	0.49	<0.10
E4	0.48	0.17	12.4	0.69	5.02	3.38	0.48	0.48	<0.10
E5	0.81	0.15	12.5	0.63	9.54	7.17	6.47	<0.10	<0.10
E6	23.4	0.40	14.3	0.54	4.14	8.00	6.12	<0.10	2.29
E7	7.66	0.62	9.52	0.45	14.54	9.77	4.92	<0.10	0.75
E8	0.28	<0.10	9.54	0.80	2.39	2.81	4.41	0.54	0.12
Average	2.46	0.41	11.6	0.67	9.17	7.80	6.10	0.39	0.24
Standard deviation	5.66	1.15	4.12	0.24	11.6	6.16	2.35	0.24	0.56
Frequencies	100 %	41.2 %	100 %	94.1 %	100 %	100 %	100 %	70.6 %	29.4 %

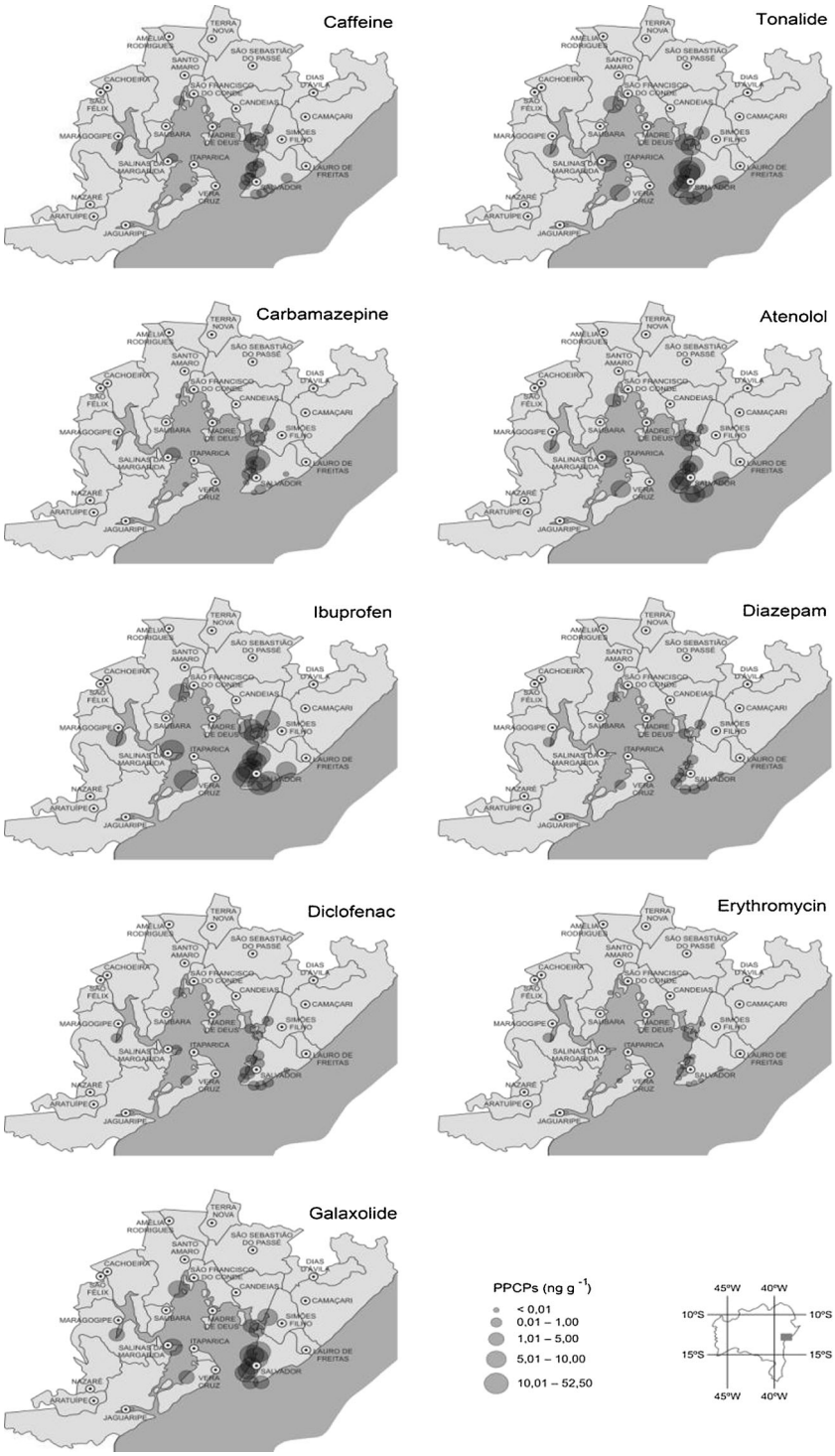

Fig. 2 Distribution and concentration of pharmaceuticals and personal care products (PPCPs) in the Todos os Santos Bay and north coast of Salvador, State of Bahia, Brazil

present in 100 % of the sites, while diclofenac was present in 94.1 %, diazepam in 70.6 %, carbamazepine in 41.2 %, and erythromycin in 29.4 % of the sampled sites. The concentrations for individual PPCBs are in the range <0.10 to 52.5 ng g^{-1} (dry weight). Ibuprofen and galaxide had the highest mean concentrations for all samples, 11.6 and 9.17 ng g^{-1} (dry weight), respectively, followed by atenol and tonalide, with equivalent concentrations of 7.8 and 6.1 ng g^{-1}. The largest variability between the concentrations of the sampled sites were found for caffeine, with 230 % of the mean value, followed by galaxide and tinolide, with 126 % and 79 %, respectively.

The geographical distribution of each drug and fragrance is presented in Fig. 2. The shaded circle area denotes the concentration; sites with a clear circle indicate that the concentration of the compound is equal to or below the limit of detection of the method. The geographical distribution and the sum

of all compounds investigated indicate that the stations most impacted by the presence of these compounds are I5, E3, E6, and E7, coinciding with the high population density, the presence of muddy coastal sediment, and the area where sewage was discharged from the city of Salvador before the introduction of sewage sanitation. Low average values of PPCPs were observed in the area where the sewage outfall is located in Rio Vermelho (site I6) compared to other stations. This fact is probably due to the nature of the sediment, which is sandy, and the region is of high energy with constant turnover of the surface sediment at the bottom of the water column (Pletsch et al. 2010).

According to data provided by the Department of Health regarding the average monthly consumption of medicine in 417 municipalities in Bahia, the anti-convulsant drug carbamazepine is the most consumed among the drugs analyzed in the sediment samples, followed by the psychiatric drug diazepam, the anti-inflammatory ibuprofen and the antibiotic erythromycin. The anti-inflammatory diclofenac and the blood pressure regulator atenonol did not appear among the data provided (SESAB 2009). Since the average monthly consumption data are not available by municipality, it is difficult to explain the levels found in the bay and north coast of Salvador based on consumption data from the state as a whole.

The substances found have different physicochemical properties, and these properties determine the preferred paths in the environment and the distribution in environmental compartments. The presence of these compounds in the sediments studied is regulated by the emission of these compounds from various sources—the main sources being domestic and animal production effluents and runoff—and once in waterbodies, they undergo processes of degradation and persistence. The data show that the fragrances are found at higher levels in the sediments, probably due to their use in greater quantities compared to pharmaceuticals, although their physicochemical properties and degradation should also have an influence.

The textures of the sediment samples at the various sites are presented in Table 3. The locations sampled within the bay are concentrated mainly on the east coast, where most of the urban and industrial activities are located. The west coast, which is the more pristine area, has subsistence agricultural activities, coconut and palm oil plantations, and some aquaculture activity. The mudflats, from the Tainheiros inlet (I5, Porto da Ribeira) to the entrance of the Aratu Bay (I2, Naval Base), are locations with a higher content of finer grained sediment. On Salvador's north coast (i.e. sites I6, I9, I8, and I7), there is predominance of sand.

The linear correlations of the concentrations of each PPCP and the percentage of clay in the sediments were established at a 95 % confidence level using the program Origin (Solfonic, Barcelona, Spain, availble free on http://origin.solfonic.com) and shown in Table 4. Statistically significant positive correlations at a 95 % confidence level were found for six of the nine PPCPs determined in the sediment of the Todos os Santos Bay and north coast of Salvador. Tonalide had the highest correlation (R=0.82) and also the most significant P value (5.59×10^{-4} at a 95 % confidence level), indicating that the clay content of the sediment is most important for the retention and chemical integrity of this fragrance in the marine environment. Caffeine, carbamazepine, and erythromycin showed moderate correlations (R equal to ~0.5) and with statistical significance only at the 90 % confidence level (P= 0.6–0.7 at the 95 % confidence level). Although these values indicate that the percentage of clay in the sediment is not the determining factor in the retention and integrity of these

Table 3 Granulometric composition of the sediment from the sampling sites in the Todos os Santos Bay and north coast of Salvador

Sample	Fine sand (%)	Coarse sand (%)	Silt (%)	Clay (%)	Bioclastic material
I1	9	43	16	32	0
I2	6	1	8	85	0
I3	2	51	13	34	0
I4	7	35	19	39	0
I5	4	1	12	83	0
I6	8	87	2	3	0
I7	12	76	7	5	0
I8	3	93	2	2	0
I9	3	94	1	2	0
E1	96	0	2	2	0
E2	70	0	7	23	0
E3	1.9	0	7.7	13.8	76.6
E4	85	0	13.3	0.7	1.7
E5	77.2	0	8.1	0.9	13.8
E6	55.1	0	15.3	29.6	0
E7	45	0	6	49	0
E8	60	0	2	388	0

Table 4 Linear correlations between pharmaceutical and personal care products (PPCPs) concentrations and the clay content (%) of the sediment in the infralittoral and eulittoral zones of the Todos os Santos Bay and north coast of Salvador

PPCP	R (95 %)	P
Caffeine	0.5330	0.0607
Carbamazepine	0.5207	0.0681
Ibuprofen	0.7394	0.0039
Diclofenac	0.7043	0.0072
Galoxide	0.7372	0.0040
Tonalide	0.8224	5.588×10^{-4}
Atenolol	0.7255	0.005
Diazepam	0.6238	0.0227
Erythromycin	0.5134	0.0727

substances in this environment, it is important to remember that the number of samples is low for statistical purposes, and that a higher number of samples could shed light on the situation. The other PPCPs showed correlations ranging between 0.6 and 0.7, all of them highly significant at the 95 % confidence level ($P \leq 0.02$) indicating that the clay content is an important factor in the fixation and thus inhibiting biodegradation of the other PPCPs in the bay and north coast of Salvador; however, other factors should also play a role.

There are many studies reporting levels of PPCPs in water and wastewater (e.g., Ternes 1998; Hartig et al. 1999; Heberer 2002; Gros et al. 2008), but very few in sediment and only for some compounds, such as estrogens (e.g. Ternes et al. 2002a, b) and phthalates and bisphenol A and F (e.g., Fromme et al. 2002). The awareness of the presence of PPCPs in the environment and its adverse effects on wildlife and humans is recent, dating from one and a half decades ago. Pharmaceuticals and personal care products include a wide range of chemicals. Due to the hydrophilic characteristics of PPCPs, sorption on soil and sediment particles is complex, involving more mechanisms than those of hydrophobic organic contaminants. For these reasons, studies on PPCPs—soil and sediment interactions are very limited. Most existing studies focus on occurrence and toxicology aspects (Pan et al. 2009). Knowledge of the fate of PPCPs in soils and sediments is critical for determining environmental exposure and risk assessment, and the US EPA is presently conducting a series of studies of several PPCPs for this purpose (EPA 2011). The present study reports the occurrence of some PPCPs for the first time in marine sediments in Latin America.

4 Conclusions

Pharmaceuticals are ubiquitous in the sediment of Todos os Santos Bay and on the north coast of Salvador. The levels found correspond to the previous contribution of sewage that was discharged without any treatment up until the beginning of this century; it also reflects contribution from farming. The presence of fine-grained sediment over a large part of the coast and at the bottom of Todos os Santos Bay is responsible for the fixation of these compounds. The fragrances had the highest levels of the analyzed PPCPs. The presence of the Rio Vermelho marine outfall on the Atlantic coast of Salvador—which for 30 years has been draining some boroughs of Salvador and, more recently, parts of the main municipalities surrounding the Todos os Santos Bay—did not result in a significant accumulation of PPCPs in the sediment. This was because it is essentially composed of coarse sand. Thus, sediment texture is an important factor in PPCP fixation and deposition, as well inhibiting its biodegradation. As the present study is the first in the literature reporting concentration levels for PPCPs in marine sediment for this area, no data exists from other similar regions to allow for comparisons between the levels found in Bahia with those for other locations, as well as the factors affecting their sorption. This fact attests to the necessity of additional studies on coastal sediment in Brazil and in other parts of the world.

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