RESEARCH ARTICLE

The brown mussel *Perna perna* (L., 1758) as a sentinel species for chlorinated pesticide and dioxin-like compounds

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Abstract To contribute to the use of the tropical brown mussel Perna perna as a sentinel species for organochlorine pesticides (OCP) and polychlorinated biphenyls (PCB), the present study reports data on the toxicokinetics of these compounds in P. perna. Specifically, the authors present data on OCP and PCB bioaccumulation for eight sampling months from three bays (SE Brazil) and two transplant experiments (each 1 month long). Although seasonality is observed in the total lipid content of the whole soft tissue, with summer samples showing higher values, no such seasonality is observed in the OCP and PCB concentrations bioaccumulated by the mussel P. perna. Because no seasonal effect is observed in the annual OCP and PCB concentrations bioaccumulated by P. perna, the use of this species as a sentinel organism to monitor organochlorinated compounds is encouraged. One month of transplantation is not enough to allow the transplanted specimens to reach the concentrations observed

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Karl-Werner Schramm schramm@helmholtz-muenchen.de; schramm@wzw.tum.de in animals reared at the destination site. Nevertheless, *P. perna* showed a clear tendency to depurate the DDT metabolites p, p'-DDD and p,p'-DDE after 1 month of transplantation.

Keywords Biomonitoring \cdot Bioaccumulation \cdot POP \cdot Mussel watch \cdot Persistent toxic substance \cdot Seasonality

Introduction

In previous publications, we have explored the potential of the brown mussel *Perna perna* (Linnaeus, 1758) as a sentinel organism for the biomonitoring of organochlorinated compounds in tropical marine ecosystems. It was possible to show that animals sampled in areas with different histories of contamination presented distinct bioaccumulation profiles of chlorinated pesticides and dioxin-like compounds (DLC), suggesting that

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this species is able to reflect environmental exposure (Galvao et al. 2012). We also demonstrate that the chlorinated compound concentration observed in sediment has a clearer statistical relationship to bioaccumulation by P. perna than that measured in suspended solids (Galvao et al. 2014). The lack of data concerning the bioaccumulation of persistent organic pollutants (POPs) by P. perna is a constraining factor to establish its potentials and limitations as sentinel species for POP biomonitoring. It is important to highlight that P. perna has a wide range worldwide, which comprises India, Sri Lanka, the Atlantic coast of South America, North America, and many Caribbean islands (Fernandes et al. 2008), and has commercial value as a seafood. Taking it into account, the establishment of new sentinel specie for POPs in those areas represents a great advantage, especially because the two mussel species that are already well studied (Mytilus edulis and Mytilus galloprovincialis) do not have natural occurrence in most of those areas. To the best of our knowledge, no data are available concerning the temporal variation of the organochlorinated compounds bioaccumulated by P. perna over a long-term sampling period. Such studies are also scarce even in the case of a more frequently studied species from the same genus, i.e., Perna viridis L. 1758. In a 3-year-long study, a minor role of seasonality was observed in the tissue bioaccumulation of polychlorinated biphenyls (PCB) and polyaromatic hydrocarbons (PAH) (Fang et al. 2010). In contrast, there is a large database already available on the most frequently used Mytilidae species (M. galloprovincialis and M. edulis), which have been adopted as sentinel species by the American and European environmental biomonitoring program (O'Connor 2002; UNEP 2004). Results covering a 10-year time window concerning the bioaccumulation of PCB by M. galloprovincialis showed a tendency for the concentrations of these compounds to decrease over time (Carro et al. 2010). Such reports are essential for providing a solid database that facilitates management actions by decision makers at the political level and allows conclusive toxicological findings as well. Accordingly, the present study seeks to assess the seasonal effect on the bioaccumulation of organochlorine pesticides (OCP) and DLC by the brown mussel P. perna to evaluate its temporal response as a sentinel species for such contaminants in tropical bays. With this aim, the toxicokinetics of these target compounds was evaluated by monitoring the bioaccumulation of P. perna over 8 months and performing a field transplantation experiment.

Materials and methods

Experimental design

The study area included three socioeconomically important bays from SE Brazil located in Rio de Janeiro State: Guanabara Bay (GB), Sepetiba Bay (SB), and Ilha Grande Bay (IGB). Descriptions of each bay are available in previous publications (Galvao et al. 2012). GB shows higher OCP and PCB environmental concentrations when compared to the values observed at SB and IGB. The two latest bays show concentrations which are comparable.

The present study covered eight sampling months and was designed to characterize two seasons: summer (from December to March) and winter (from June to September). Eighteen brown mussels were sampled from each studied area every sampling month (a total of 144 animals from each site).

Two transplantation experiments were performed to evaluate the depuration kinetics of PCB and OCP by P. perna: one beginning in December 2008 and the other in June 2009, both lasting 1 month. The transplantation experiments were performed in different seasons to enhance the relevance of any tendency for depuration in the concentrations bioaccumulated by the transplanted mussels because it would reveal no interference from seasonal influence. In both experiments, mussels grown at GB were transplanted to places with lower OCP and PCB environmental contamination; in 2008, they were transplanted from GB to SB and, in 2009, from GB to IGB. Additionally, other P. perna individuals were maintained at the original source location (GB). To represent the initial experimental conditions, time zero (T0), 15 mussels were collected from GB. After 30 days, 15 animals were sampled from each site, i.e., from the original source location (GB) and the destination bays (SB and IGB), totaling 45 individuals. Each set of 15 individuals comprised three composite samples, as described previously. The data concerning the two samples at the original source location (GB), at time zero and 30 days later, were used to assess the variance in the OCP and PCB concentrations bioaccumulated by the mussels grown at GB. If no overlap was observed between the ranges of concentrations of the target compounds in the analyzed organisms, the authors concluded that there was a tendency for accumulation or depuration between the original conditions and the end of the transplant experiment.

In an attempt to reduce the variability of the data, whole soft tissue from six mussels was pooled. Accordingly, three pooled samples per month were obtained from each sampling site (a total of 24 pools from each site). The samples were freeze-dried and homogenized in a mill homogenizer with a stainless blade and aluminum cup (MA345, Marconi[®]). Powdered samples were kept in a glass flask with a screw cap.

Chemical analysis

The analytical method followed in the present study is described in previous publications (Wang et al. 2009; Galvao et al. 2012) and is described briefly here. Accelerated Solvent Extractor (ASE 200 Dionex[®]) was used to extract the analytes from the mussels. A gravimetric method was used to determine the total lipid content in the extracted samples under a nitrogen stream. NaSO₄, alumina, and silica were packed in a glass column for a first step cleanup, followed by the use of a C18-silica column as a second step. For every batch of nine environmental samples, one analytical blank was added. All glassware used was rinsed with solvent (3:1 (ν/ν) toluenedichloromethane and acetone), washed in a laboratory dishwasher, and heated (up to 450 °C).

Prepared solutions were injected into a high-resolution gas chromatograph coupled to a high-resolution mass spectrometer (HRGC-HRMS) system (Thermo Finnigan MAT95 or MAT95S, Bremen, Germany), and the results were reported on a dry weight basis. Three times the standard deviation of the blank was taken to represent the method determination limits (MDL), but a signal-to-noise ratio of 3:1 was used if no signal was detected. Data were reduced to three significant digits. The following target compounds were measured in this study: α -, β -, γ -, δ -, and ε -hexachlorocyclohexane (HCH); pentachlorobenzene; hexachlorobenzene; pentachloroanisole; p,p'- and o,p'-dichloro-diphenyl-trichloroethane (DDT); p,p'and o,p'-dichloro-diphenyl-dichloroethane (DDD); p,p'- and o,p'-dichloro-diphenyl-dichloroethylene (DDE); trans-chlordane, cis-chlordane, and oxychlordane; heptachlor; cis-heptachlor epoxide; aldrin; dieldrin; endrin; endosulfan-I and endosulfan-II; methoxychlor; mirex; and PCB 28, 52, 101, 138, 153, 180, 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189. The average uncertainty, estimated on the basis of control samples and interlaboratory comparisons, in the analysis of OCP and PCB is 21 and 20 %, respectively.

Data analysis

A cluster analysis was used to classify the observations. Ward's method was used as the linkage rule, and the squared Euclidean distance was used as the distance measure. For the statistical assays, the MDL values were assumed for samples in which the compounds were not detected or the concentration was below the MDL.

Results

The present study represents a compilation of extensive data on the toxicokinetics of OCP and PCB in the brown mussel *P. perna*. The results are presented and discussed in the light of the current scarcity of data on the bioaccumulation of such target compounds by the tropical brown mussel *P. perna*. Studies involving sampling periods of 8 months or longer are rare, especially for tropical areas. Note also that the seasonal fluctuations of the environmental parameters are expected to be smaller in tropical areas than in the temperate zone. Such a tropical scenario might result in a more stable physiological response by the bivalves and produce bioaccumulation patterns of OCP and PCB differing from those observed in animals of temperate zones. The study's research advances concerning the evaluation of *P. perna* as a sentinel species for OCP and PCB offer data crucially relevant to the adoption of this species in environmental monitoring programs because *P. perna* occurs worldwide and is economically important.

Lipid content and seasonal variance

As a first approach to evaluate seasonal effects on the bioaccumulation of organochlorinated compounds by *P. perna*, the monthly lipid content (% of soft tissue dry weight) variance of the homogenized soft tissue was analyzed. The lipid content in mussels sampled from the three studied bays is show in Table 1 and was subjected to a cluster analysis. The sampling months were the variables examined in the analysis. Figure 1 shows the graph of the dendrogram of the lipid content in the whole homogenized soft tissue of the analyzed mussels.

This statistical assay identified two highly distinct groups of months: summer months (December to March) and winter months (June to September). Higher median values for the percentage of lipid were observed in the summer months (11.0-12.9 %) than in the winter months (7.9-10.3 %). The lipid content in the tissue plays a special role in the reproductive cycle of the mussels because it is an energy source, as previously reviewed (Narváez et al. 2008). M. galloprovincialis showed seasonal variation in its lipid content in a study performed in the northern Adriatic Sea (Italy) over the reproductive cycle of the species (Bressan and Marin 1985). Despite the observed seasonal variation in the lipid content, previous studies have reported that P. perna spawning is relatively constant throughout the year on the southeastern Brazilian coast (Santos et al. 2006; Marques et al. 2008). The composition of the diet of filter-feeding mussels is also related to the lipid content of the mussels because phytoplankton species vary in lipid content and composition (Orban et al. 2002; Alkanani et al. 2007). A seasonal change in the phytoplankton community of the southeastern Brazilian coast has previously been reported (Brandini and Fernandes 1996). This change might be related to the observed variation of the lipid content of the mussel tissue.

Previous studies have related the lipid content in the soft tissues of mussels to the concentrations of organic pollutants in the soft tissues (Capuzzo et al. 1989; Lee et al. 1996; Solé et al. 2000). Accordingly, the OCP and PCB data were converted to a lipid weight basis to normalize the concentrations in mussel tissue according to the lipid content prior to the cluster analysis.

Monthly monitoring

The analysis of the OCP showed that hexachlorobenzene, octachlorostyrene, *trans*-heptachlor epoxide, and

Table 1 Lipid content (mg) inthe analyzed soft tissue (1 grounded) from the specimens ofPerna perna

Site	December	January	February	March	June	July	August	September
GB		87	108	88	77	66	89	74
GB	103	101	102	95	87	55	88	69
GB	110	92	92	89	64	63	93	89
SB	147	161	117	150	111	102	93	59
SB	112	124	134	115	116	110	100	62
SB	156	133	145	139	101	119	113	88
IGB	65	89	104	104	80	55	57	71
IGB	66	77	104	108	87	55	57	65
IGB	85	90	84	105	91	68	76	67

methoxychlor remained below the MDL (median values of 330, 24, 3, and 21 pg g^{-1}) in all analyzed samples.

In general, the OCP bioaccumulated by *P. perna* sampled in GB were one order of magnitude higher than those observed in the animals from SB and IGB, as shown in Table 2 (reported on a dry weight basis).

The compounds that showed markedly higher concentrations were β -, δ -, and ε -HCH; pentachloroanisole; DDT and its metabolites; chlordane isomers; dieldrin; endrin; endosulfan-I and endosulfan-II; and mirex.

The concentrations of PCB congeners from SB and IGB showed a similar range of values, whereas the samples from GB showed concentrations one order of magnitude higher (for nos. 180, 77, 81, 105, 114, 156, 157, 167, 189) than those from the other two sampling sites, i.e., 5 to 8 times higher, as shown in Table 3 (reported on a dry weight basis).

The ranges of OCP and PCB concentrations observed over the eight sampling months were very comparable to those reported in a previous publication (Galvao et al. 2014) in which only two sampling months were considered. A discussion of the extent of contamination in the studied sites can be



Fig. 1 Dendrogram of the cluster analysis of the lipid content of the whole soft tissue of the mussel, with the sampling month as the grouping variable

found in previous studies, whereas temporal variation is the focus of the present study.

To identify similarities between the concentrations of OCP and PCB bioaccumulated by the mussels, a cluster analysis was performed with the sampling months as the grouping variable and the concentrations of the target compounds as the independent variable. It was not possible to clearly identify two large groups of sampling months (summer and winter) on the dendrograms for the concentrations of the target compounds (Fig. 2), in contrast to the large groups of sampling months that were clearly shown when the independent variable considered was the percentage of lipid content.

The relation between the lipid content and the bioaccumulation of PCB and OCP by filter-feeding marine bivalves has previously been discussed in the literature. A study performed with indigenous mussels from the North Atlantic coast (MA. USA) showed that PCB were better correlated with higher lipid content levels (Bergen et al. 2001), suggesting that normalization by the lipid content should only be performed above some threshold. When chlorinated pesticide concentrations were correlated with lipid content in reared mussels from the Galician coast (Spain), several target compounds showed positive correlations, whereas others showed negative correlations and still others showed no correlations (Carro et al. 2014). As stated above, P. perna reared in the South Atlantic (SE Brazil) spawns relatively constantly during the year, and it is probable that this characteristic reduces the possible seasonal influence on the bioaccumulation of OCP and PCB.

Such a lack of a seasonal tendency in the bioaccumulation of OCP and PCB by *P. perna* reared on the South Atlantic coast is in accordance with previous findings for another *Perna* species, *P. viridis* (Linnaeus, 1758), in a study conducted in the Middle China Sea. That study reported a seasonal change in water quality parameters (temperature, salinity, and dissolved oxygen) between the dry and wet season, whereas no seasonal tendency was found for the sum of PCB and PAH (Fang et al. 2010).

In contrast, mussels *M. galloprovincialis* (Lamarck, 1819) reared on the North Atlantic coast (Galicia, Spain), in the temperate zone, showed strong tendencies toward seasonality

Table 2Concentrations (pg g^{-1} d.w.) of organochlorinated pesticides (OCP) bioaccumulated by the brown mussel *P. perna* (whole soft tissue)

	Mussel—Guanabara Bay			Mussel—Ilha Grande Bay			Mussel—Sepetiba Bay		
Compounds	Summer	Winter	Range	Summer	Winter	Range	Summer	Winter	Range
α-НСН	390	240	<72-880	330	120	<67-440	420	340	<69–750
β-НСН	6300	1000	<180-12,000	1000	500	<170-1800	1200	730	370-2100
γ-ΗCΗ	270	270	<150-1900	210	370	<140-620	230	650	<140-1600
δ-НСН	330	190	<79–500	-	-	<77-<87	110	84	<76-120
ε-HCH	160	88	<33–280	-	_	<33-<37	48	44	<32–50
∑HCH	7600	1900	<33–13,000	1500	830	120-1800	1800	1200	370-4400
Pentachlorobenzene	330	290	<180-400	200	340	<190-420	<190	330	<180-410
Pentachloroanisole	2200	1300	348-13,000	1800	840	430-4300	1400	650	190–15,000
<i>p,p'</i> -DDT	2300	2000	<800-8800	1500	990	<770-3400	910	1700	<760-24,000
o,p'-DDT	1600	730	150-2700	350	220	130-520	280	250	<110-3100
p,p'-DDD	4700	4900	580-7500	730	360	<270-1200	420	340	<260-1900
o,p'-DDD	2600	1200	270-4000	510	130	71–950	150	92	48–250
<i>p,p'</i> -DDE	10,000	16,000	970-26,000	1100	730	520-1800	840	620	390-3300
o,p'-DDE	1400	1000	150-1700	110	75	48-160	75	43	23-130
∑DDT	23,000	28,000	3200-38,000	4600	1800	790–6300	2000	2200	690-33,000
trans-Chlordane	220	150	<23-340	190	57	<23-220	37	29	<22-200
cis-Chlordane	150	100	17-200	27	16	<3–36	28	18	<5-60
Oxychlordane	39	20	<1-56	8	7	<1-12	8	8	<1-14
∑Chlordane	430	270	29-540	220	55	<1–250	75	31	<1–260
Heptachlor	23	29	<1-420	29	23	<1-80	27	17	7–410
cis-Heptachlor epoxide	77	28	12–94	17	9	<6–25	33	16	<7–36
Aldrin	170	110	47-1200	140	140	47–200	100	72	25-1100
Dieldrin	1700	1100	320-2400	310	160	120-410	420	290	150-750
Endrin	230	130	<39–300	40	44	<36-47	48	57	<37–270
∑Drins	1800	1300	490-2800	450	290	240-600	620	370	220-1900
Endosulfan-I	530	94	<55-670	490	100	<55-910	890	120	<54–1400
Endosulfan-II	170	79	<39–540	140	97	<38-220	220	<40	<38–570
Mirex	120	140	71–190	210	190	93-420	150	120	82-270

The median values are presented according to organisms sampled in the summer and winter months and also the data range

in the bioaccumulation of OCP and PCB. The same study reported that the reproductive cycle of the studied mussels was seasonal and that the lipid content in soft tissue followed this seasonality (Suárez et al. 2013). These studies highlight that the local climate in which the sentinel species are sampled should be considered prior to any discussions of the bioaccumulation of OCP and PCB by filter-feeding marine bivalves.

Transplantation experiment

Because the OCP and PCB concentrations observed at GB tended to be higher than those found at SB and IGB, we evaluated the depuration dynamics of the OCP and PCB with transplant experiments using *P. perna* mussels. The observed OCP and PCB concentrations in the mussel samples were displayed as boxplots. We only discuss cases in which a reduction or increasing trend in bioaccumulated PCB and OCP

concentrations in mussels transplanted from GB was observed. In these cases, no overlap was observed between the concentration ranges recorded for the sample sets: T0 and T1 from GB compared to T1 from SB and to T1 from IGB.

Figure 3 shows the OCP concentrations for the experiments conducted in December 2008 and January 2009, when animals were transplanted from GB to SB. Figure 4 shows the OCP data for the transplantation conducted in June and July 2009, when animals were transplanted from GB to IGB.

The DDTs p,p'-DDD and p,p'-DDE showed a clear decrease in the bioaccumulated concentrations in mussels, a pattern that was repeated in the December (GB to SB) and June (GB to IGB) experiments. Other varying trends in OCP concentrations were also observed but were only recorded in one experiment, for *cis*-heptachlor epoxide concentrations, which were lower in the mussels taken to IGB. Unexpectedly, concentrations tended to increase in animals transplanted from

 Table 3
 Concentrations (pg g⁻¹ d.w.) of polychlorinated biphenyl (PCB) congeners bioaccumulated by the brown mussel P. perna (whole soft tissue)

	Mussel—C	Juanabara Ba	ıy	Mussel—I	lha Grande E	Bay	Mussel—Sepetiba Bay		
Compound	Summer	Winter	Winter Range		Winter	Range	Summer	Winter	Range
28	7700	5700	890–14,000	870	650	490-1900	1400	760	490-10,000
52	7900	6200	840-16,000	1100	880	740-1900	1100	810	480-11,000
101	3900	5300	910-9400	1000	890	600–2000	1100	940	580-5000
138	6200	5700	2100-8200	1500	1000	810-2100	1400	1300	470-1900
153	8700	8300	3000-11,000	2000	1500	1200-2900	2100	1900	840-2900
180	2600	2300	960-3200	390	290	210-550	480	500	240-800
77	300	340	47–400	97	48	26-120	61	41	<3–96
81	20	25	<2-36	0	5	<2-5	5	0	<2–5
126	31	26	<1-40	15	15	<1-19	9	6	<1-15
169	7	8	<1-10	6	5	<1-13	0	3	<1–5
105	2100	2100	360-2800	360	240	180-490	260	300	110-390
114	120	120	32-150	20	14	<1-31	20	20	<1-65
118	6800	6000	1500-7900	1000	700	550-1500	1000	920	370-1300
123	830	860	110-1200	200	170	110-300	150	150	62–210
156	230	360	47-460	56	52	38-100	42	49	16-80
157	150	160	36-220	40	33	<1-58	30	29	13–53
167	440	420	160-520	87	68	33-130	80	85	37-140
189	32	34	<1-110	6	10	<1-14	7	4	<1-8
∑PCB	48,000	47,000	11,000–62,000	9100	7000	5000-12,000	9200	7800	4100-32,000

The median values are presented according to organisms sampled in the summer and winter months and also the data range

GB to SB for the pesticides pentachlorobenzene (PeCB), aldrin, and heptachlor.

In contrast to the current findings of the OCP concentrations bioaccumulated by the mussels, a previous publication reported higher concentrations of OCP in sediment and suspended solids from GB than in corresponding samples from SB and IGB (Galvao et al. 2014). Because the mussels from GB were reared in an area with greater environmental exposure to the target compounds, 1 month was apparently not sufficient for the transplanted mussels to clearly reflect the differences in all the quantified OCP. Given that 1 month is a reasonable time window for an assessment of environmental contamination in a field study, the need for a longer time to reach an equilibrium between what is bioaccumulated by the mussels and the environmental levels might limit the potential of mussels as a sentinel organism. Most studies available in the literature involving the use of bivalves in transplantation experiments focus on the kinetics of contaminant accumulation by the organism. In one field experiment, mussels (P. viridis) were taken from a location with low environmental OCP exposure to areas of moderate and high exposure (Siu et al. 2008). The authors of that study followed the bioaccumulation of pesticides of the DDT group, "Drins," and HCH. Among the results of that study, we draw attention to the high OCP concentrations observed on the 16th day, followed by a decrease at day 30. These data, therefore, emphasize the complexity of interpreting data from field experiments.

Similarly, *P. viridis* specimens from less impacted areas on the coast of Hong Kong, after spending 5 days in laboratory acclimation, were taken to more impacted areas, where they remained for 30 days. In this experiment, no increased OCP concentrations in the transplanted animals were observed; the OCP concentrations remained at the same level observed for the organisms from the reference site (Richardson et al. 2001).

A bioaccumulation study with *M. galloprovincialis* and *P. viridis* in Tokyo and Aburatsubo Bays, Japan, indicated that an equilibrium of OCP concentrations was reached in only 2 weeks in animals transplanted from less impacted areas to more contaminated areas (Ueno et al. 1999). In another study, *M. edulis* (Linnaeus, 1758) specimens were taken from an impacted bay to another area with low contaminant concentrations. After 24 days, the sum of p,p'- and o,p'-DDT, DDD, and DDE metabolite concentrations reached values comparable with those observed in the local population in the destination area of the transplantation experiment (Peven et al. 1996). That study did not assess other pesticides but confirmed the indications of the depuration potential of p,p'-DDD and o, p'-DDE found in the present study.

In contrast, in another study, no decrease in p,p'-DDT concentrations in *P. viridis* was observed after 10 days of



Fig. 2 Dendrogram of the cluster analysis of PCB (a) and OCP (b) in the whole soft tissue of the mussel, with the sampling month as the grouping variable. Data was normalized by the lipid content in mussel soft tissue prior to the cluster analysis

controlled laboratory depuration conditions, whereas α -HCH and aldrin concentrations did indeed decrease (Richardson et al. 2005). In the same study, dieldrin also showed a decrease relative to the initial experimental concentrations, as also observed in this study for the transplantation experiment performed in June. Figures 5 and 6 show the results of the transplantation experiments for PCB.

We examined the variation in the concentrations observed in the animals transplanted to IGB. The lowest concentrations showed values up to three orders of magnitude below those observed for mussels at T0 from GB, as in the case of congener PCB 28. However, as we observed some PCB 28 values even higher than those at T0, it was not possible to clearly identify the PCB depuration trend in these transplanted mussels. Likewise, *M. edulis* transplanted from a polluted area to a less polluted site in the Dutch Delta did not show a depuration tendency for the bioaccumulated PCB concentrations in an experiment lasting 150 days (Hummel et al. 1989).

Nevertheless, we observed a depuration trend for congeners 52 and 101 in animals transplanted to IGB. In addition, PCB 81, 189, and 126 were detected in animals from GB but were below the MDL in mussels transplanted to IGB. These observations also represent PCB depuration processes.

Fig. 3 OCP concentrations (pg dry weight basis) in mussels from the transplant experiment conducted in December 2008. Animals collected from Guanabara Bay (initial conditions represented by empty bars) were transplanted to Sepetiba Bay, where they remained for 30 days before collection (gray bars). Black bars represent animals that remained at Guanabara Bay and were collected 30 days after the first sampling. Each bar represents the values of three replicates, and the dash in the middle represents the median. The identities of the compounds are indicated on the abscissa, and the ordinate on which the corresponding values are plotted is indicated as follows: R-right y-axis, L-left y-axis



Based on the results of a detoxification experiment conducted with the bivalve *Tapes philippinarum* at the Venice Lagoon (Raccanelli et al. 2008), the authors of that study proposed a half-life for PCB 114, 167, 157, and 189 of 6.5, 6.2, 5.4 and 6.4 days, respectively (approximately 6 days). These data were obtained by extrapolation of the results obtained by transplanting animals from a contaminated to a clean site and collecting the organisms 60 and 120 days after the beginning of the experiment. In the cited study, the authors used bottom surface sediment to infer the environmental exposure at the studied sites. The PCB concentrations of congeners 114, 167, 157, and 189 found at the transplantation destination were 2.7, 1.5, 3.4, and 3.2 %, respectively, of the PCB concentrations of the place of origin. Accordingly, using bottom sediment as a parameter for assessing PCB environmental exposure in *T. philippinarum*, the transplanted destination represents approximately 3 % of the exposure at the original source site. In the present study, the median concentrations of PCB obtained in sediments collected in December 2008 and February 2009 were considered for the calculation of the percentage concentrations ([transplantation area]*100/ [place of origin]). The results for PCB 114, 167, 157, and 189 at SB were 5, 3, 4, and 5 %, respectively, whereas at IGB, they were, in the same order, 19, 13, 15, and 8 %. Although the percentage fractions obtained at SB were higher than those observed in the study conducted at the Venice Lagoon, the percentage differences are less than one order of magnitude, allowing a comparison between the results from the two areas. An average half-life of 6 days was assumed for the PCB congeners in question. With this half-life, one would

Fig. 4 OCP concentrations (pg dry weight basis) in mussels from the transplant experiment conducted in June 2009. Animals collected from Guanabara Bay (initial conditions represented by empty bars) were transplanted to Ilha Grande Bay, where they remained for 30 days before collection (gray bars). Black bars represent animals that remained at Guanabara Bay and were collected 30 days after the first sampling. Each bar represents the values of three replicates, and the *dash* in the middle represents the median. The identities of the compounds are indicated on the abscissa, and the ordinate on which the corresponding values are plotted is indicated as follows: R-right y-axis, L-left y-axis



expect a decrease of PCB concentrations to 1/5 of the initial concentrations in the mussels that remained 30 days at SB. Paradoxically, the most significant reductions in PCB concentrations in our transplanted bivalves were observed in the transplantation experiment from GB to IGB. However, despite reductions even greater than 1/5 (based on an average half-life of 6 days) compared with the baseline (T0) for animals taken to IGB, we also recorded levels higher than those of T0.

In another study of the depuration kinetics of PCB in bivalves, *M. edulis* individuals sampled from an uncontaminated environment were exposed to suspended sediments collected from a contaminated area. After 40 days of exposure, the animals were placed in another tank with clean water for an additional 40 days of depuration (Pruell et al. 1986), and congener 128 returned to initial exposure concentrations. Based on these results, the authors proposed a half-life for PCB 128 of 36.5 days. A comparison of this result with those for the bivalve *T. philippinarum* from the Venice Lagoon (Raccanelli et al. 2008) yields a difference of 30 days between the proposed half-lives for PCB congeners obtained from laboratory and field tests. This result highlights the complexity of the interactions that occur in the organism-contaminant-environment system.

Several previous authors have cited the role of the quality of organic matter associated with suspended solids and sediment as a determining factor in the process of partitioning involving hydrophobic organic chemicals (Cornelissen et al. 2005) such as PCB and OCP. Accordingly, beyond the differences in the concentrations of contaminants observed at the studied sites, the amount and quality of organic matter at each

Fig. 5 PCB concentrations (pg g dry weight basis) in mussels from the transplant experiment conducted in December 2008. Animals collected from Guanabara Bay (initial conditions represented by empty bars) were transplanted to Sepetiba Bay, where they remained for 30 days before collection (gray bars). Black bars represent animals that remained at Guanabara Bay and were collected 30 days after the first sampling. Each bar represents the values of three replicates, and the *dash* in the middle represents the median. The identities of the compounds are indicated on the abscissa, and the ordinate on which the corresponding values are plotted is indicated as follows: R-right y-axis, L-left y-axis



of the transplantation sites may have determined the bioavailability of those chemicals to *P. perna*. Therefore, the results of the present study indicate that a transplantation experiment

with a duration of 1 month is not sufficient to predict accumulation or depuration trends in the bioaccumulation of these compounds by *P. perna*.

Fig. 6 PCB concentrations (pg g^{-1} dry weight basis) in mussels from the transplant experiment conducted in June 2009. Animals collected from Guanabara Bay (initial conditions represented by empty bars) were transplanted to Ilha Grande Bay, where they remained for 30 days before collection (gray bars). Black bars represent animals that remained at Guanabara Bay and were collected 30 days after the first sampling. Each bar represents the values of three replicates, and the dash in the middle represents the median. The identities of the compounds are indicated on the abscissa, and the ordinate on which the corresponding values are plotted is indicated as follows: R—right y-axis, L—left y-axis



Conclusions

The present data suggest that seasonal variation does not represent a source of noise that must be considered in the interpretation of bioaccumulation of the compounds of interest by the brown mussel *P. perna*. This result verifies the potential of this species as a sentinel species for the monitoring of chlorinated pesticides and dioxin-like compounds. A longer transplantation experiment (up to 3 months longer) and involving transplantation in the reverse direction, from a less polluted to a more polluted site, is required to better elucidate the toxicokinetics of OCP and PCB bioaccumulation by *P. perna*.

References

- Alkanani T, Parrish CC, Thompson RJ, McKenzie CH (2007) Role of fatty acids in cultured mussels, Mytilus edulis, grown in Notre Dame Bay, Newfoundland. J Exp Mar Biol Ecol 348:33–45. doi:10.1016/j. jembe.2007.02.017
- Bergen BJ, Nelson WG, Quinn JG, Jayaraman S (2001) Relationships among total lipid, lipid classes, and polychlorinated biphenyl concentrations in two indigenous populations of ribbed mussels (Geukensia demissa) over an annual cycle. Environ Toxicol Chem 20:575–581. doi:10.1002/etc.5620200317
- Brandini FP, Fernandes LF (1996) Microalgae of the continental shelf off Paraná State, southeastern Brazil: a review of studies. Rev Bras Oceanogr 44:69–80. doi:10.1590/S1413-77391996000100008
- Bressan M, Marin MG (1985) Seasonal variations in biochemical composition and condition index of cultured mussels (Mytilus galloprovincialis Lmk) in the Lagoon of Venice (North Adriatic). Aquaculture 48:13–21
- Capuzzo JM, Farrington JW, Rantamaki P et al (1989) The relationship between lipid composition and seasonal differences in the distribution of PCBs in Mytilus edulis L. Mar Environ Res 28:259–264. doi: 10.1016/0141-1136(89)90240-7
- Carro N, Cobas J, García I et al (2014) Distribution and trend of organochlorine pesticides in Galicia coast using mussels as bioindicator organisms. Possible relationship to biological parameters. Chemosphere 102:37–47. doi:10.1016/j.chemosphere.2013.12.010
- Carro N, Garcia I, Ignacio M, Mouteira A (2010) Spatial and temporal trends of PCBs (polychlorinated biphenyls) in mussel from Galician coast (1998–2008). Environ Int 36:873–879. doi:10.1016/j.envint. 2010.04.002
- Cornelissen G, Gustafsson O, Bucheli TD et al (2005) Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environ Sci Technol 39: 6881–6895. doi:10.1021/es050191b
- Fang JKH, Wu RSS, Zheng GJ et al (2010) Seasonality of bioaccumulation of trace organics and lysosomal integrity in green-lipped mussel Perna viridis. Sci Total Environ 408:1458–65. doi:10.1016/j. scitotenv.2009.12.044
- Fernandes FC, Souza RCCL de, Junqueira A de OR, et al. (2008) Distribuição Mundial e o Impacto de sua Introdução no Brasil. In: Jr CR, Weber LI, Conceição MB da (eds) O Mexilhão Perna perna Biol. Ecol. e Apl., 1st edn. Interciência, Rio de Janeiro, pp 25–29
- Galvao P, Henkelmann B, Longo R et al (2012) Distinct bioaccumulation profile of pesticides and dioxin-like compounds by mollusk bivalves

reared in polluted and unpolluted tropical bays: consumption risk and seasonal effect. Food Chem 134:2040–2048. doi:10.1016/j. foodchem.2012.04.006

- Galvao P, Henkelmann B, Longo R et al (2014) Partition of organochlorine concentrations among suspended solids, sediments and brown mussel Perna perna, in tropical bays. Chemosphere 114:9–15. doi: 10.1016/j.chemosphere.2014.04.008
- Hummel H, UitOudeGroeneveld JP, Nieuwenhuize J et al (1989) Relationship between PCB concentrations and reproduction in mussels Mytilus edulis. Mar Environ Res 28:489–493
- Lee KM, Kruse H, Wassermann O (1996) Seasonal fluctuation of organochlorines in Mytilus edulis L from the south west Baltic Sea. Chemosphere 32:1883–1895
- Marques HLA, Ferreira JF, Grelli VG, et al. (2008) Biologia e Ecologia de Adultos. In: Jr. CR, Weber LI, daConceição MB (eds) O Mexilhão Perna perna. Interciência, Rio de Janeiro, pp 55–68
- Narváez M, Freites L, Guevara M et al (2008) Food availability and reproduction affects lipid and fatty acid composition of the brown mussel, Perna perna, raised in suspension culture. Comp Biochem Physiol B Biochem Mol Biol 149:293–302. doi:10.1016/j.cbpb. 2007.09.018
- O'Connor TP (2002) National distribution of chemical concentrations in mussels and oysters in the USA. Mar Environ Res 53:117–143
- Orban E, Di Lena G, Nevigato T et al (2002) Seasonal changes in meat content, condition index and chemical composition of mussels (Mytilus galloprovincialis) cultured in two different Italian sites. Food Chem 77:57–65
- Peven CS, Uhler AD, Querzoli FJ (1996) Caged mussels and semipermeable membrane devices as indicators of organic contaminant uptake in Dorchester and Duxbury Bays, Massachusetts. Environ Toxicol Chem 15:144–149. doi:10.1897/1551-5028(1996) 015<0144;cmasmd>2.3.co;2
- Pruell RJ, Lake JL, Davis WR, Quinn JG (1986) Uptake and depuration of organic contaminants by blue mussels (Mytilus edulis) exposed to environmentally contaminated sediment. Mar Biol 91:497–507. doi: 10.1007/bf00392601
- Raccanelli S, Favotto M, Vio P (2008) Estimation of PCDD/F and PCB detoxification rates in contaminated Tapes philippinarum in the Lagoon of Venice. Chemosphere 73:S166–S170
- Richardson BJ, Tse ESC, De Luca-Abbott SB et al (2005) Uptake and depuration of PAHs and chlorinated pesticides by semi-permeable membrane devices (SPMDs) and green-lipped mussels (Perna viridis). Mar Pollut Bull 51:975–993. doi:10.1016/j.marpolbul. 2005.04.028
- Richardson BJ, Zheng GJ, Tse ESC, Lam PKS (2001) A comparison of mussels (Perna viridis) and semi-permeable membrane devices (SPMDs) for monitoring chlorinated trace organic contaminants in Hong Kong coastal waters. Chemosphere 45:1201–1208
- Santos M, Galvão N, Henriques MB (2006) Ciclo reprodutivo e infestação parasitária [Reproductive cycle and parasitarian infestation]. Bol Inst Pesca 32:59–71
- Siu SYM, Lam PKS, Martin M et al (2008) The use of selected genotoxicity assays in green-lipped mussels (Perna viridis): a validation study in Hong Kong coastal waters. Mar Pollut Bull 57:479– 92. doi:10.1016/j.marpolbul.2008.03.006
- Solé M, Porte C, Barcelo D, Albaiges J (2000) Bivalves residue analysis for the assessment of coastal pollution in the Ebro Delta (NW Mediterranean). Mar Pollut Bull 40:746–753. doi:10.1016/S0025-326X(00)00011-4
- Suárez P, Ruiz Y, Alonso A, San Juan F (2013) Organochlorine compounds in mussels cultured in the Ría of Vigo: accumulation and origin. Chemosphere 90:7–19. doi:10.1016/j.chemosphere.2012.02. 030

- Ueno D, Takahashi S, Tanabe S et al (1999) Uptake kinetics of persistent organochlorines in mussels through the transplantation experiment. J Environ Chem 9:369–378
- UNEP (2004) Guidance for a global monitoring programme for persistent organic pollutants. 105.
- Wang J, Bi Y, Pfister G et al (2009) Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). Chemosphere 75: 1119–1127