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Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

*Original Citation:*

PBDEs in the supralittoral environment: the sandhopper *Talitrus saltator* (Montagu) as biomonitor? / G. Ungherese; A. Cincinelli; T. Martellini; A. Ugolini. - In: CHEMOSPHERE. - ISSN 0045-6535. - STAMPA. - 86:(2012), pp. 223-227. [10.1016/j.chemosphere.2011.09.029]

*Availability:*

The webpage <https://hdl.handle.net/2158/592778> of the repository was last updated on 2018-04-05T13:02:12Z

*Published version:*

DOI: 10.1016/j.chemosphere.2011.09.029

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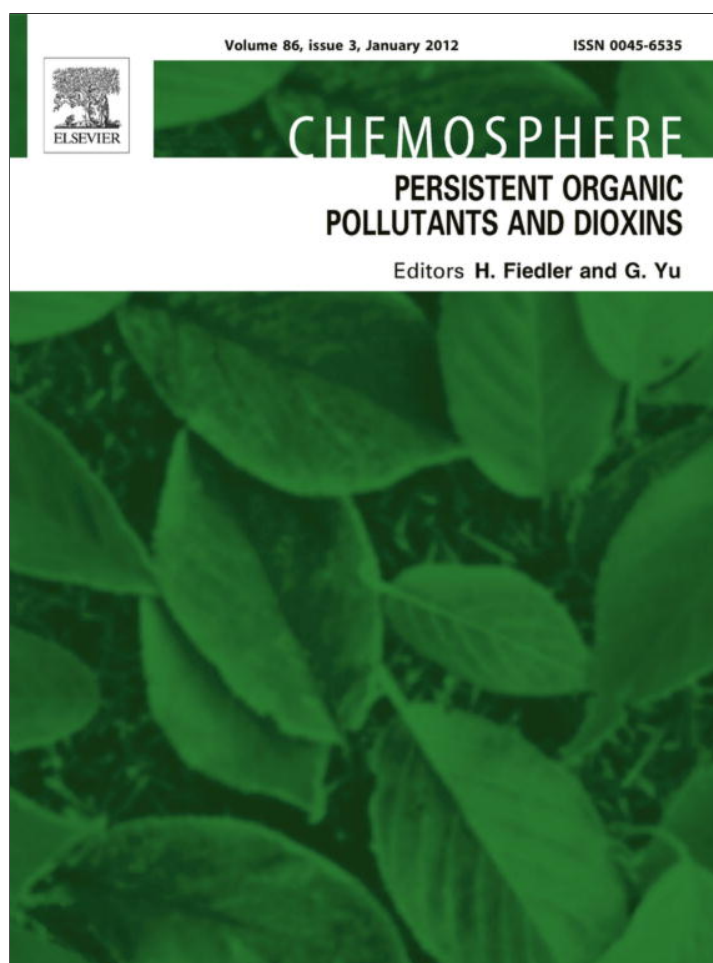
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## PBDEs in the supralittoral environment: The sandhopper *Talitrus saltator* (Montagu) as biomonitor?

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### ARTICLE INFO

#### Article history:

Received 28 February 2011  
Received in revised form 24 August 2011  
Accepted 22 September 2011  
Available online 22 October 2011

#### Keywords:

PBDEs  
Amphipods  
Bioaccumulation  
Invertebrates  
Sandy shores  
Mediterranean

### ABSTRACT

In this study we evaluated the use of *Talitrus saltator* as biomonitor of polybrominated diphenyl ethers (PBDEs) contamination of the supralittoral zone of Mediterranean sandy shores, an area characterized by a strong input of contaminants but not yet investigated about the presence of these pollutants. We detected the presence of twenty PBDE congeners in amphipods and sand samples collected along the Tyrrhenian coast of central Italy. Eight congeners were detected in all samples. Among them, the BDE-209 was the most abundant in both amphipods and sand samples followed by BDE-99, BDE-153 and BDE-47 in animals, and BDE-99, BDE-47 and BDE-100 in sediment. The ΣPBDEs in amphipods was higher (on the average 2.5–5-fold) than in sand for almost the totality of congeners detected and each sampling site, suggesting the good capacity of sandhoppers to accumulate these pollutants. Moreover statistical analysis revealed significant differences in PBDE concentrations recorded in tissues of *T. saltator* among sampling sites. Therefore our results suggested the possible utilization of *T. saltator* as a biomonitor of PBDE contamination of the supralittoral zone of Mediterranean sandy shores.

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### 1. Introduction

A large number of toxic substances, most of them of synthetic origin (e.g. persistent organic contaminants, oils, pathogens, fertilizers), have been introduced into the marine environment since many years by industrial, agricultural and other anthropogenic activities (Dachs and Méjanelle, 2010). In the last decades, the increasing contamination of water bodies with trace elements, especially in coastal areas because of greater anthropogenic input from inland and sea based sources, has required a deeper knowledge of the diffusion of these substances in the environment (Luoma and Rainbow, 2008; Dachs and Méjanelle, 2010). One of the most important biomonitoring method for determining the presence and distribution of environmental contaminants in marine ecosystems (including coastal areas) is based on the measure of their concentrations in organisms both animals and plant species (biomonitors) (e.g. Luoma and Rainbow, 2008).

Despite the great ecological importance of the supralittoral band of sandy shores (representing a functional ecological linkage with adjacent ecosystems), its contamination by persistent organic pollutants (POPs) has received scarce attention (see Ugolini and Ungherese, 2011 for a review). Talitrid amphipods constitute the main animal biomass in sandy beach ecosystems (particularly on

sandy beaches of temperate zones which receive a huge input of algae and seagrass wrack) and play an important role in the energy flow among different trophic levels (Griffiths et al., 1983). As detritivores, grazers and scavengers, sandhoppers feed on plant and animal organic matter of marine and terrestrial origin and constitute an important food source for many species of invertebrates and vertebrates (Griffiths et al., 1983). In recent years one of the most diffuse European–Mediterranean species of sandhopper (*Talitrus saltator*) has been successfully employed as biomonitor of trace metals contamination of the supralittoral band (e.g. Marsden and Rainbow, 2004; Ugolini et al., 2004, 2008; Ungherese et al., 2010; Ugolini and Ungherese, 2011). However, even if sandy shores retain more pollutants than other marine ecosystems (e.g. rocky shores) (McLachlan and Brown, 2006), no investigations have been carried out on the capacity of talitrid amphipods, and/or organisms living in the supralittoral of sandy shores, to accumulate POPs, except for polycyclic aromatic hydrocarbons (PAHs) (Ugolini and Ungherese, 2011). In particular, researches on the polybrominated diphenyl ethers (PBDEs) in supralittoral organisms are absent and those on invertebrates in general are scarce respect to marine sediments, fish and humans (e.g. Ikonomou et al., 2002; Voorspoels et al., 2003; Bragigand et al., 2006; Wang et al., 2009).

Among POPs, PBDEs represent a class of emerging contaminants employed as additive flame retardant in a variety of large consumer products as plastics, textiles and electronics. Because of their persistence, potential to bioaccumulate and possible adverse

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effects to human and wildlife, PBDEs constitute a group of great concern and are among POPs listed in the Stockholm Convention (POPs COP4, 2009). Even though many countries have banned or restricted the use of two (Penta- and Octa-BDE) of the three PBDE technical mixtures, their presence has been recently detected in marine ecosystems and organisms (invertebrates, fish, birds, marine mammals and humans) collected in highly industrialized areas as well as remote areas (see e.g. Hites, 2004; Corsolini et al., 2006). Although the key role of amphipods in many aquatic ecosystems, and consequently in the trophic transfer of pollutants to higher trophic levels, only few investigations on freshwater (Viganò et al., 2009) and polar benthic species (Sørmo et al., 2006; Svendsen et al., 2007) have been carried out regarding the accumulation of PBDEs in these species. Because of the importance of amphipods to the energy flow of sandy shore ecosystems (Griffiths et al., 1983) they constitute a potentially good candidate to monitor contamination of PBDEs in the supralittoral environment. Furthermore, since the PBDEs are subjected to biomagnification (Boon et al., 2002; Sørmo et al., 2006), talitrid amphipods could represent a vector of these contaminants to higher trophic levels.

The aim of this study was to evaluate the possibility to use the talitrid amphipod *T. saltator* as biomonitor of PBDEs in the supralittoral of sandy shores.

## 2. Materials and methods

### 2.1. Sampling

Adults individuals, except for ovigerous females, of the sandhoppers *T. saltator* were collected in June 2009 in 6 localities of the Tyrrhenian coast of central Italy mainly located near river mouth or industrial areas (Table 1). Since size could influence the amount of accumulated PBDEs in other amphipods species (e.g. Viganò et al., 2009) and trace metals in talitrid amphipods (e.g. Marsden and Rainbow, 2004), only individuals of similar weight (0.015–0.02 g) were analyzed. In each locality, together with animals samples (50–60 individuals), sand samples were also collected from the same place in which sandhoppers were captured, i.e. from the damp band of sand in which sandhoppers live during the day, from the surface to about 4 cm of depth. Laboratory, animals were rinsed in double distilled water and killed by freezing.

### 2.2. Chemical analysis

Amphipods samples were extracted following the method described elsewhere (Kannan et al., 2001; Corsolini et al., 2002), with some modifications. Briefly, pool of 1 g of *T. saltator* was homogenized with 100 g of sodium sulfate prebaked at 450 °C for 12 h. The samples were spiked with surrogate standard (BDE-77) and Soxhlet extracted with methylene chloride/hexane (3:1 v/v, 400 mL) for 16 h. The extract volume was rotary evaporated and an aliquot of each extract was used for gravimetric determination of total lipid content. Interferences were removed with a clean-up procedure based on a multilayer silica gel column prepared by packing a glass column (20 mm i.d.) as follows: 2 g of silica, 6 g

**Table 1**  
Sampling sites of amphipods collection.

Population name	Population code	Longitude	Latitude
Morto Vecchio river	FM	43°44'55"N	10°16'31"E
Arno river mouth	A	43°68'18"N	10°28'08"E
Livorno harbor (Calambrone)	C	43°58'15"N	10°29'85"E
Piombino	P	42°57'07"N	10°34'11"E
Rosignano Solvay	R	43°22'24"N	10°26'23"E
Albegna river mouth	FA	42°30'16"N	11°11'41"E

of 40% acidic-silica, 2 g of silica, and a thin layer of sodium sulfate at the top. The column was conditioned with 100 mL of hexane, and then the sample was added and eluted with 200 mL of hexane. The extract was rotary evaporated to 5 mL and concentrated to 100 µL under gentle stream of pure nitrogen. Internal standard BDE-118 was added before analysis. PBDE congeners were identified and quantified using a Hewlett–Packard 6890 GC and a 5973 MSD (mass selective detector) operated in the negative ionization mode (NCI).

Each sand sample was freeze dried, homogenized and a subsample of 10 g, considered representative of that sample, was analysed as described in ISO 22032:2006/E method. Briefly, sand samples were spiked with surrogate standard (BDE-77), Soxhlet extracted with *n*-hexane and acetone (4:1 v/v, 250 mL), rotary evaporated and cleaned up on a multilayer silica gel column prepared by packing a glass column (20 mm i.d.) as follows: 2 g of silica, 5 g of basic-silica, 2 g of silica, 10 g of acidic-silica, 2 g of silica, 5 g of silica treated with AgNO<sub>3</sub> and a thin layer of sodium sulfate at the top. The column was conditioned with 50 mL of methylene chloride followed by 50 mL of cyclohexane, and then the sample was added and eluted with 50 mL of cyclohexane and 50 mL of a mixture of cyclohexane and methylene chloride (4:1 v/v). The extracts were rotary evaporated to 5 mL and then blown down with a gentle stream of pure nitrogen to 100 µL to be analyzed with GC–MS operating in NCI mode. BDE-118 was added as internal standard.

A 30 m HP-5MS column (0.25 mm i.d., 0.25 µm film thickness, J&W Scientific Corp. (CA, USA)) was used. The temperature program was 50 °C for 1 min, ramped at 20 °C min<sup>-1</sup> to 130 °C, and further ramped at 5 °C min<sup>-1</sup> to 300 °C (held for 10 min) and finally ramped at 20 °C min<sup>-1</sup> to 251 °C and held for 6 min. Because of its physico-chemical properties BDE-209 was analysed separately on a 15 m DB-5MS column (0.25 mm i.d., 0.25 µm film thickness) with the following oven program: 90 °C for 1 min, ramped at 30 °C min<sup>-1</sup> to 220 °C, 10 °C min<sup>-1</sup> to 300 °C, held for 8 min.

Quantitative determinations were performed using external calibration curves previously calculated from eight standard solutions prepared using standard mixture solutions purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Twenty PBDE congeners were detected and quantified (BDE-7, -15, -17, -28, -47, -49, -66, -71, -85, -99, -100, -126, -138, -153, -154, -156, -183, -184, -191 and -209). Only PBDEs (BDE-28, BDE-47, BDE-49, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-209) found in both amphipods and sand samples were reported in this study.

Mean recovery values of internal standard were 88.69 ± 13.06% for *T. saltator* samples and 99.15 ± 18.63% for sand samples. Procedural blanks were analysed through the whole analytical procedure to check for interferences and laboratory contamination. The limit of detection (LOD) was defined as the average of all blank concentrations plus three times the standard deviation of the blanks. For compounds not detected in the blanks an instrumental detection limit was applied.

The detection limit was in the range 0.2–6 pg g<sup>-1</sup> depending on congener and sample matrix.

We did not make the granulometric analyses of sand for all the places of sampling; however in a previous paper (Ugolini et al., 2008, Table 2) we reported the granulometric analyses for eight localities from North to South coast of Tuscany. All samples of sand were fairly homogeneous and classified in the medium- to coarse-grained range (from 1.324, SD = 0.507, to 2.166, SD = 0.435).

### 2.3. Statistical analysis

Since lipid and organic carbon content constitute important factors related to the levels of hydrophobic organic pollutants respectively in biota and sediments, in accordance with previous studies,

**Table 2**

Lipid, organic carbon content, mean standardized concentrations of PBDEs in amphipods (in bold) ( $\text{ng g}^{-1}$  lipid weight) and sand samples ( $\text{ng g}^{-1}$  organic carbon weight) recorded in each sampling site. For further details see also Table 1.

Site		Lipid %	Organic carbon %	BDE28	BDE47	BDE49	BDE99	BDE100	BDE153	BDE154	BDE209	$\Sigma$ PBDEs
FM	T.s.	<b>14.2</b>		<b>1.1</b>	<b>3.0</b>	<b>0.9</b>	<b>4.5</b>	<b>1.7</b>	<b>4.8</b>	<b>5.2</b>	<b>16.0</b>	<b>21.3</b>
	Sand		0.04	ND	2.5	ND	6.7	2.4	ND	ND	59.3	11.6
A	T.s.	<b>13.8</b>		<b>1.4</b>	<b>4.8</b>	<b>5.5</b>	<b>6.7</b>	<b>3.3</b>	<b>5.6</b>	<b>6.5</b>	<b>20.3</b>	<b>33.8</b>
	Sand		0.05	ND	2.7	2.0	6.8	2.4	ND	ND	166.7	13.9
P	T.s.	<b>13.9</b>		<b>1.5</b>	<b>3.2</b>	<b>1.5</b>	<b>5.9</b>	<b>2.3</b>	<b>7.1</b>	<b>0.3</b>	<b>36.1</b>	<b>21.9</b>
	Sand		0.05	ND	1.9	ND	5.6	ND	ND	ND	3.0	7.5
R	T.s.	<b>11.2</b>		<b>1.8</b>	<b>2.9</b>	<b>1.9</b>	<b>6.8</b>	<b>2.3</b>	<b>7.7</b>	<b>8.1</b>	<b>35.7</b>	<b>31.6</b>
	Sand		0.74	ND	0.1	0.1	0.3	0.1	ND	ND	0.3	0.6
FA	T.s.	<b>7.0</b>		<b>2.9</b>	<b>7.5</b>	<b>4.5</b>	<b>9.6</b>	<b>4.0</b>	<b>ND</b>	<b>ND</b>	<b>63.9</b>	<b>28.5</b>
	Sand		0.18	0.4	0.4	0.3	1.0	0.4	1.9	2.2	13.3	6.7
C	T.s.	<b>11.7</b>		<b>1.6</b>	<b>7.5</b>	<b>1.4</b>	<b>11.6</b>	<b>3.1</b>	<b>6.1</b>	<b>6.9</b>	<b>18.4</b>	<b>38.2</b>
	Sand		0.08	ND	1.8	ND	4.4	1.6	ND	ND	28.3	7.8

ND = not detected.

$\Sigma$ PBDEs = the sum of all target PBDE congeners except for BDE-209.

PBDE, lipid and organic carbon normalized concentrations were used for statistical analysis of data set. Spearman rank correlation was used both to examine the correlation between PBDE level and lipid content in biota and evaluate the association between total organic carbon and PBDE concentration in sand samples. The comparison between PBDE congener concentration measured in sand and sandhopper samples were performed using the Wilcoxon signed ranks test. Kruskal–Wallis one-way analysis of variance was used to compare the difference between sampling sites for each PBDE congener detected in amphipod samples.

### 3. Results and discussion

Out of the twenty PBDEs congeners analyzed, eight compounds (BDE-28, BDE-47, BDE-49, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-209) were detected in both, amphipods and sand samples (Table 2).

Contrary to the results observed for vertebrates species, mainly fishes (see for instance Eljarrat et al., 2004), invertebrates (Bragigand et al., 2006) and aquatic amphipods (Viganò et al., 2009), our data showed the lack of any significant correlation between concentration (not normalized) of each PBDE congener and lipid content in amphipods samples ( $r_s$  ranged between  $-0.44$  and  $0.29$ ,  $n = 18$ ,  $p = \text{N.S.}$  in each case Spearman Rank-Order Correlation coefficient test). This result could suggest that lipid content, at least in the range recorded in our samples, is not a large determinant of PBDE load. A similar result has also been observed in a biomonitoring study carried out in eels from different points along the Orbetello lagoon (Mariottini et al., 2008). It is worth to underline that the choice of sampling of *T. saltator* within a definite range of size ( $0.015$ – $0.02$  g) could be responsible of the absence of any correlation. However the possible effect of lipid content on PBDE accumulation in *T. saltator* could be better clarified by further analysis (performed on individuals of diverse size and, consequently, characterized by different lipid content).

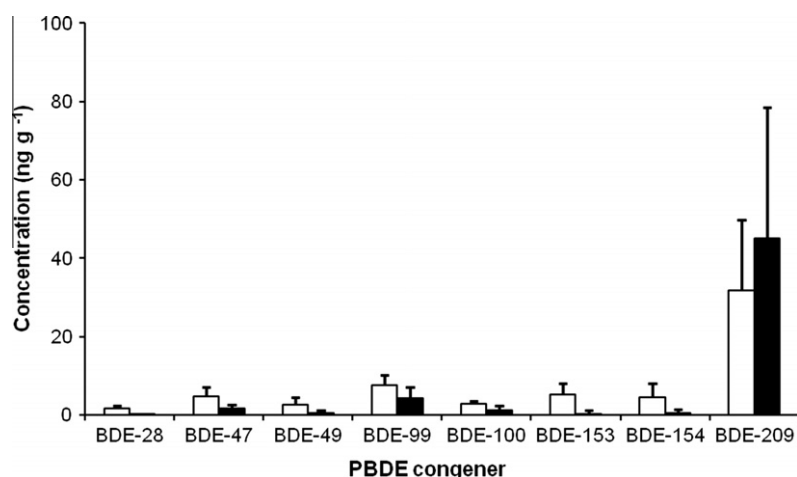
Analogously to the results obtained for amphipods, no significant correlation was found between concentrations (not normalized) of PBDE congeners in sand samples and content of organic carbon ( $r_s$  ranged between  $-0.42$  and  $0.39$ ,  $n = 18$ ,  $p = \text{N.S.}$  in each case Spearman Rank-Order Correlation coefficient test). This result could be explained taking into account not only the small number of samples analyzed but also the similar organic carbon content measured in sand samples collected from different localities (see for instance Morto Vecchio river, Arno river mouth and Piombino) (Table 2).

Total BDE concentrations ( $\Sigma$ PBDEs) (except BDE-209) ranged from  $21.3 \text{ ng g}^{-1}$  lipid weight (Morto Vecchio river) to  $38.2 \text{ ng g}^{-1}$  lipid weight (Calambrone) in amphipods and from  $0.6 \text{ ng g}^{-1}$  lipid

weight (Rosignano Solvay) to  $13.9 \text{ ng g}^{-1}$  lipid weight (Arno river mouth) in sediment (Table 2). The most abundant PBDE congener was BDE-99 in both the investigated matrices, followed by BDE-153 and BDE-47 in animals and by BDE-47 and BDE-100 in sands (Fig. 1) (Table 2). In comparison with the other PBDE congeners, the levels of BDE-209 were much higher, ranging from  $0.3$  to  $166.7 \text{ ng g}^{-1}$  organic carbon weight in sands and from  $16$  to  $63.9 \text{ ng g}^{-1}$  lipid weight in sandhoppers (Fig. 1) (Table 2). In fact, the contribute of this congener to the total  $\Sigma$ BDEs (BDE-209 +  $\Sigma$ PBDEs) was predominant in all *T. saltator* samples, ranging from  $33\%$  to  $69\%$  (Fig. 1) (Table 2). The contribute of BDE-209 in sediments was also greater than in amphipods, ranging from  $66\%$  to  $92\%$  with the exception of two samples (Piombino and Rosignano) that showed a relatively low amount of  $\Sigma$ PBDEs and, in particular, BDE-209 ( $28\%$  and  $33\%$ , respectively) respect to other sampling sites (Table 2). Predominance of BDE-209 for most part of the congener profiles of both amphipods and sand samples could indicate that deca-BDE mixture accounts for most PBDEs consumption around the investigated areas, as reported for other regions of the world (e.g. Mai et al., 2005; Wang et al., 2009). Taking into account that deca-BDE mixture is in the greatest demand all over the world, as indicated in several reports (e.g. BSEF, 2001), and BDE-209, the major component of the deca-BDE commercial product, is the most frequent congener found in marine sediments and soils (e.g. Mai et al., 2005; Xiang et al., 2007), our data seem to be consistent with other records reported in literature.

However this congener has been for long time considered no bioaccumulative in biota due, principally, to its large molecular size and rapid biotransformation (Allchin et al., 1999; Boon et al., 2002; Eljarrat et al., 2004). Our findings confirm recent studies which reported the presence of BDE-209 in many organisms, mainly in invertebrates species living in close-contact with sediment, such as mussels, oysters and estuarine shrimps (Moon et al., 2007; Xiang et al., 2007; Wang et al., 2009). The relevant contribution of BDE-209 has also been detected in freshwater temperate and ice amphipods (Sørmo et al., 2006; Viganò et al., 2009).

Our data showed a good capacity of sandhoppers to accumulate PBDEs at higher concentration than in the sand for all the samples and congeners (except for BDE-209) (Fig. 1) (Table 2). In fact, although it is well-known that marine sediments act as a sink of hydrophobic contaminants (e.g. Dachs and Méjanelle, 2010), our results showed an higher concentration of  $\Sigma$ PBDEs in amphipods than in sand samples ( $Z = 2.16$ ,  $df = 17$ ,  $p < 0.05$ , at least, Wilcoxon Test) (Table 2) (see also Fig. 1).  $\Sigma$ PBDEs was 2.5–5 orders of magnitude higher in most part of localities except for Fiume Morto (1.8-fold higher than in sand) and Rosignano (where this value was extraordinary elevated, 52.6-fold higher than in sand). Instead, BDE-209 concentration was higher in the sediment than in amphipods only in three samples ( $Z = 0.07$ ,  $df = 17$ ,  $p = \text{N.S.}$ , Wilcoxon Test) (Piombino, Rosignano and Calambrone) (Table 2).



**Fig. 1.** Pattern (mean among localities + SD) of each PBDEs congeners detected in sandhoppers (white bars) and in sand samples (black bars). Concentrations reported in the graph are normalized on lipid and organic carbon content.

Despite the small number of sampling sites, our results indicated that tissue concentration of PBDEs varied among the sampling sites (Table 2). In fact, the comparison of concentration of each PBDE congener, detected in amphipods samples collected in the selected locations along the investigated area, revealed significant differences ( $H$  ranged from 14.9 and 16.3,  $df = 17$ ,  $p < 0.02$  at least, Kruskal–Wallis one-way analysis of variance). In particular our data showed that amphipods from Albegna river mouth showed the higher concentration of four out of eight detected PBDE congeners (BDE-28, BDE-47, BDE-100 and BDE-209, see also Table 2) and samples from Rosignano Solvay were characterized by an higher content of BDE-153 and BDE-154 (Table 2). The congeners BDE-49 and BDE-99 resulted more abundant in *T. saltator* samples collected, respectively, at Arno river mouth and Calambrone (Table 2).

Unfortunately there are no data in literature reporting PBDE levels in organisms collected in the investigated area and/or other supralittoral environments that allow us to make a comparison with our results. The only available data regard eels from different points along the Orbetello lagoon (Mariottini et al., 2008). As reported in this study (Mariottini et al., 2008), eels from Albegna river mouth showed the highest levels of PBDEs even though their concentrations were low if compared to levels reported from many other industrialized areas. Our results were consistent with this study, showing that sandhoppers from Albegna river mouth were characterized by an higher concentration of PBDEs respect to the other sampling sites.

#### 4. Conclusions

The presence of PBDEs has been reported in different ecosystems and species all over the world but, to date, no results have been reported about their presence in supralittoral environment although this zone is known to be characterized by a strong input of contaminants and a large use for touristic purposes during the summer. In this study eight PBDEs congeners were identified in the supralittoral amphipod *T. saltator*, a typical inhabitants of European sandy shores, and sand samples from the supralittoral environment of the Tyrrhenian coast of central Italy. The most abundant congener in amphipods and sand samples was the BDE-209 revealing that the deca-BDE mixture was the most important source of PBDE in the selected area. The content of PBDE in amphipods was higher than in the sand indicating the good capacity of this species to accumulate these pollutants. Moreover our

data suggest that the selected species could represent a suitable biomonitor of PBDE contamination of sandy shores since differences among localities were showed despite the small number of sampling sites.

Furthermore, since talitrid amphipods represent a key species in the energy flow of sandy shore ecosystems they could act as a vector of pollutants, transferring PBDE to higher trophic levels. In addition, the use of *T. saltator* in biomonitoring programmes could offer some advantages represented by the simplicity and cheapness of sampling method and the wide geographic distribution of these species that could also offer the possibility to compare different localities.

#### Acknowledgements

The research was financially supported by a grant of the Fondazione Cassa di Risparmio di Livorno (2010 Settore Arte – Educazione – Salute – Ricerca Scientifica) assigned to A. Ugolini. Thanks are due to the Ente Parco Regionale di Migliarino, San Rossore, Massaciuccoli (Pisa) for authorization to samplings.

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