Marine Pollution Bulletin 125 (2017) 501–512

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Phthalates, heavy metals and PAHs in an overpopulated coastal region: Inferences from Abruzzo, central Italy

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ARTICLE INFO

Keywords:
Phthalates
Baseline study
Marine sediments
Social concern
Risk
Abruzzo
Italy

ABSTRACT

Phthalates are an emerging class of environmental pollutants whose distribution and effects in aquatic environments are not well characterized. We analyzed intertidal and emerged beach sediments from the Abruzzo coastline, along the Adriatic Sea, finding significant phthalate concentrations in marine sediments. Phthalate baseline levels in the intertidal environment, marked by substantial interplay of sediment, water and air, were determined. We used statistical rank methods to select representative phthalate compositions, for which we derived risk levels for ingestion, dermal absorption and inhalation. Our study shows that phthalates are a major cause of pollution along the Abruzzo coast, with river transport of sediments a continuous source of replenishment. Phthalate concentrations in two specific sites were determined to be of the same order of magnitude as the safety, remediation-warranting, threshold set by Italian law. Phthalates, heavy metals, PAHs appear to be correlated. We discuss possible intervention and mitigation strategies.

Phthalates are esters of phthalic acids that are commonly used as additives by the plastic industry to enhance elasticity and durability of consumer products. Since they are not chemically bound to plastic polymers, phthalates are often released to the environment and may be found in wastewater, soil, freshwater and sediments across the sea floor. In 2003, the US Center for Disease Control and Prevention reported widespread exposure to phthalates within the general US population and recommended further studies of the effects of phthalates on human health (CDC, 2003). Within the European Union (Agenzia per la Protezione dell'Ambiente e del Territorio (APAT), 2006), low molecular weight phthalates are not allowed unless authorization for a specific use has been granted. Concerns include possible disruption to the endocrine signaling system, neuron-developmental abnormalities, and carcinogenesis (Becker et al., 2004; Latini, 2005; Fossi et al., 2007; Sathyanarayana, 2008; Matsumoto et al., 2008; Chen et al., 2008; Singh and Li, 2011; Singh and Li, 2012). The Italian National Institute of Health (ISS) and the Italian Occupational Safety and Prevention Institute (INAIL) classify phthalates as chronic, acute toxins and carcinogens (Musumeci et al., 2015). Although earlier studies were conducted on the presence of phthalates in the rivers and lakes of the Rieti District (Vitali et al., 1997), little is known on the abundance of phthalates in Italian marine environments and associated sediments.

Following a preliminary report, in 2011, the local press issued a series of warnings regarding phthalate contamination along the coast of Pescara, a major coastal city and port along the Adriatic Sea in the region of Abruzzo, central Italy (Prima da Noi, 2011; Il Centro d'Abruzzo, 2011). Levels of di-n-butyl phthalate (DBP, $C_6H_4[COO(CH_2)3CH_3]_2$) and diisobutyl phthalate (DIBP, $C_6H_4[COOCH_2CH(CH_3)_2]_2$) were determined to be well beyond the limits of analytical sensitivity (0.01 mg/kg). Possible phthalate exposure pathways include contact with polluted soil and water, ingestion and inhalation of vapors containing organic (PON) and inorganic (PM) chemical compounds associated with particulates (Cini et al., 1994; Robinson and Gronow, 1993; Bauer et al., 1998; Berge et al., 2014). Epidemiological studies conducted within the greater Pescara-Chieti area indicate that endocrine disruptors may be responsible for the observed increase of cardiovascular diseases in the region (Belcaro et al., 2007; Muscogiuri and Colao, 2016). Mapping the spatial and chemical distribution of phthalates, and determining associated risk estimates are crucial in identifying vulnerable areas and in determining possible mitigation and remediation strategies. Despite the well documented effects of phthalate contamination of soil and water and its influence on living organisms, phthalates are not bio-monitored in Abruzzo on a regular basis and there is no regional or national agency that conducts periodic assessments of phthalate contamination along the 130 km Abruzzo coastline. To the best of our knowledge our work is one of the first to

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http://dx.doi.org/10.1016/j.marpolbul.2017.08.008
Received 21 September 2016; Received in revised form 31 July 2017; Accepted 4 August 2017
Available online 12 August 2017
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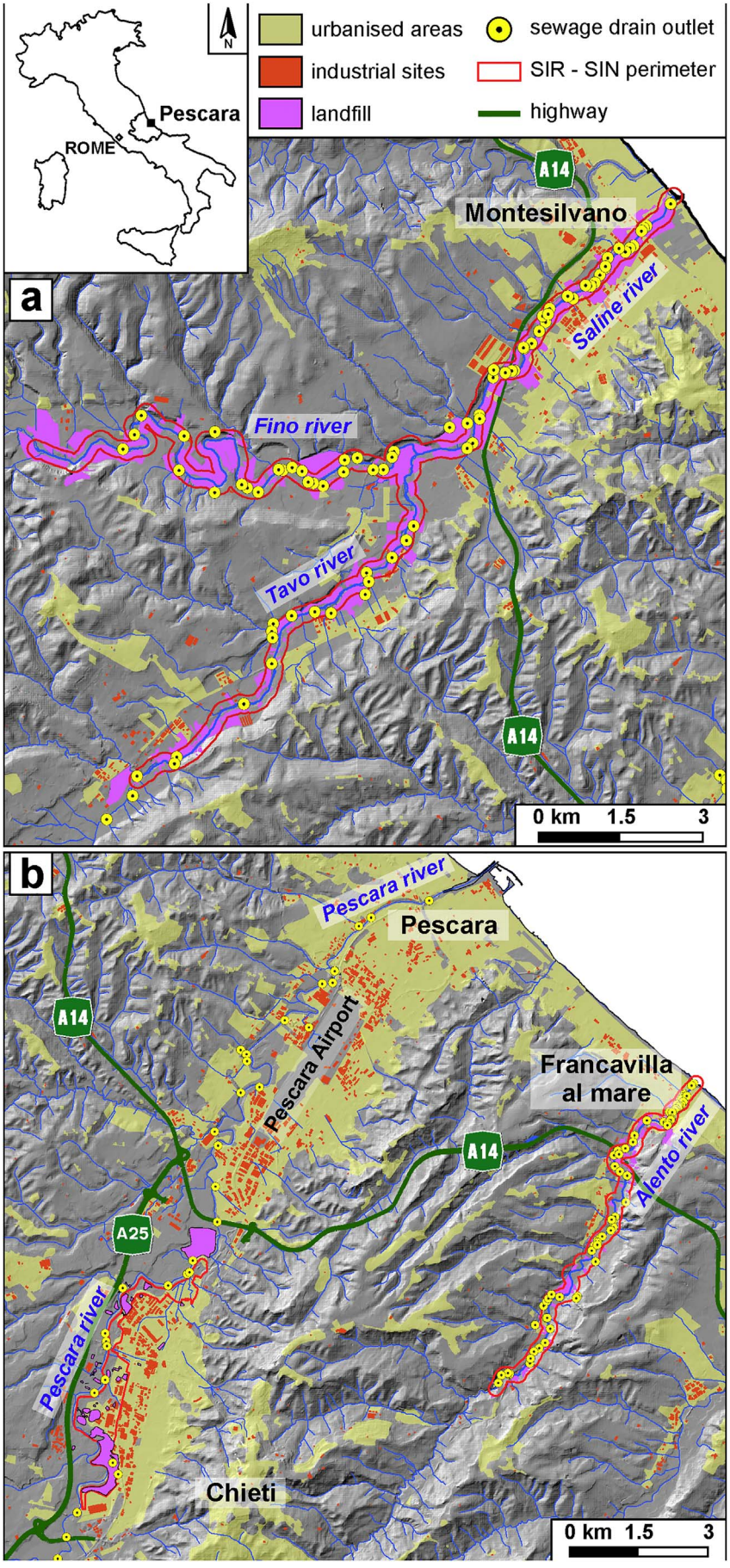

Fig. 1. Location map. (a) Saline River basin and (b) Pescara and Alento River basins. The shaded topography shows land use and contaminated critical points. Symbols are shown in the legend. Note the metric scale of (b) is slightly different from that of (c). Waste disposal sites and sewage discharge points are indicated for the three main rivers, namely the Saline, the Pescara, and the Alento. The Foro River is to the south of the Alento River and is not shown here. The distance between the Saline and the Foro rivers, the two endpoints of our analysis, is roughly 16 km. Maps are courtesy of ARTA Abruzzo and were developed by RES.GEA, a spin-off from the G. D'Annunzio University in Pescara.

systematically study the distribution and origin of phthalates in the greater Pescara-Chieti coastal area, one of the most densely populated in Abruzzo. We also analyze the distribution of heavy metals and polycyclic aromatic hydrocarbon (PAH) compounds in the area to study possible three-way synergistic action. Our study reveals alarming concentrations of phthalates, especially in close proximity to river estuaries, underlying a possible anthropogenic origin of phthalate content. We hope these results may spur further investigations and initiate a dialogue with residents and decision makers to mitigate phthalate contamination in the region.

We collected twenty-seven sediment samples in the intertidal and sub-aerial beach across a 16 km distance, from the mouth of the Saline River (Montesilvano, province of Pescara) to the mouth of the Foro River (Francavilla al Mare, province of Chieti) as shown in Fig. 1. The city of Pescara and its homonymous river are roughly halfway between the two-endpoint locations. Samples were collected in March and April 2013, when waste discharge from rivers to sea is moderate as a result of large volumes of snow melt, relatively stable weather, and limited influx of tourists. Collection during the spring months also ensures that degradation of phthalates by solar radiation and biotic activity is balanced against supply, since night and day are of similar duration (Liang et al., 2008).

The greater Pescara-Chieti area makes for an interesting case study as its mixed residential, industrial, and leisure activities are undergoing rapid expansion, accompanied by increasing soil, water and air contamination. The coastline has major environmental problems due to erosion, marine ingression, over-building and over-fishing (Stoppa, 2010; Stoppa and Brozzetti, 2013). The population of the Pescara-Chieti metropolitan area, currently numbering about 173,000 (3.522/km^2) is growing at annual average rate of 0.72%, ten times the national average. Several containment cells in the form of wharves and breakwaters have been erected along the eroding coast, some examples are shown in Figs. 2a,b. These impede the mobility of fine-grained coastal sediments, concentrating pollutants in local clay and silt. Furthermore, as most of the smaller rivers between the Saline and the Foro rivers empty into the sea, the containment cells block the water flow, causing further trapping of contaminated sediments. Frequent seabed dredging from the Pescara harbor basin and other local ports has resulted in the accumulation of polluted sediments in landfill cells as shown in Fig. 2c. Dredge material is occasionally used for beach restoration and shore protection (Redazione Indipendent, 2015).

The twenty-seven sand and silt/clay samples we collected contain up to 50% limestone by volume; the remainder is bioclasts, quartz, feldspars, kaolin, chlorite, montmorillonite and biotite in variable proportions. Due to the small diameters involved, the complete absence of micro-plastics cannot be confirmed, as typical sizes are in the clay granularity range. The measured average dry density of our samples is 1.46 g/cm^3. Granulometric studies are a crucial factor in determining phthalates distribution (Wu et al., 2016). Larger rock grains are not expected to retain large amounts of pollutants; phthalates however can chemically bind to smaller, more mobile sediment components such as inorganic particulate matter and particulate organic nitrogen. As a result, smaller sediments typically retain high levels of surface phthalates. Brine precipitates by marine aerosols have been shown to increase the phthalate content transferred from water to fine particles in beach sediments (Cini et al., 1994).

Following the granulometric study of Folk and Ward (Folk and Ward, 1957) we determine particle mean sizes and skewness. The mean is a measure of the statistical central size of a typical sediment unit. Values of skewness vary between 1 and + 1 and represent the sediment transport energy level. Negative skewness corresponds to high-energy conditions and likely beach erosion, whereas positive values represent low energy and likely beach accretion. In Figs. 3a,b we plot total phthalate content versus average particle size. The observed skewness indicates that fine-grained sediments (including possible micro-plastic particle residues) typically contain more phthalates while high-energy environments tend to disperse them. Quite unexpectedly we find that larger rock grains show considerable phthalate content; we attribute this to phthalates being absorbed through grain porosity.

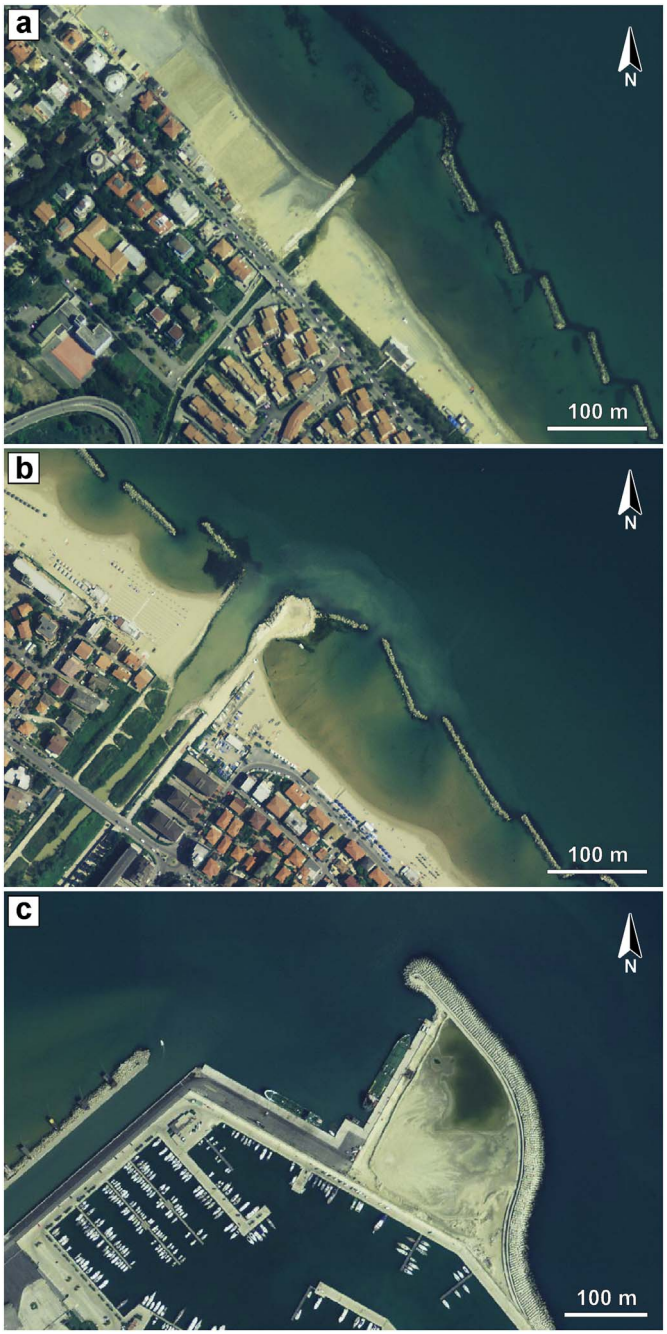

Fig. 2. Polluted water entrapped by containment cells, wharves, breakwaters, and landfill sites. Images from Google Earth 2006. Rows of containment cells extend along almost the entire 130 km length of the Abruzzo coast; (a) Containment cells formed by breakwater barriers perpendicular and parallel to the beach at the Fosso Vallelunga mouth (see Fig. 6). (b) Polluted sediments, marked by murky water from the Alento River, are dragged from rip currents within containment cells; (c) Landfill cells used to accumulate polluted sediments from the Pescara port. Pictured in 2006, the cell looks partially filled, but as of this 2017 writing it is completely filled and vegetated.

We analyzed all samples for phthalate content using United States Environmental Protection Agency (EPA) protocols EPA 3550C 2007 + EPA 8270 D 2007 (United States Environmental Protection Agency, 2007; United States Environmental Protection Agency, 1998). The method detection limit (MDL) was set at 0.01 mg/kg for all phthalates. We used EPA 6010C 2007 (United States Environmental

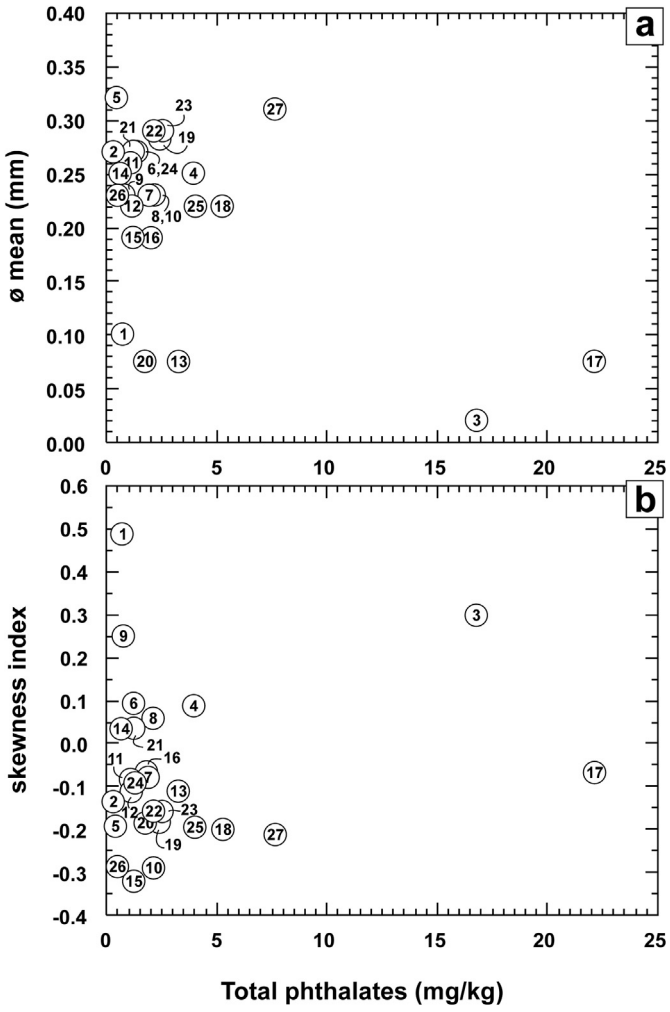

Fig. 3. Granulometry of the sampled sediments showing average diameters and skewness versus total phthalate content.

Protection Agency, 2000) to determine heavy metal content with the corresponding MDL ranges varying between 0.1 and 0.5 ppm. Finally, PAH concentrations were determined via EPA protocols 3550C 2007, EPA 8270 D 2007 (United States Environmental Protection Agency, 2007; United States Environmental Protection Agency, 1998) with the corresponding MDL set at 0.02 mg/kg for all PAHs. Analytical procedures and basic instrumentation information are outlined in Section 1 of the Supplementary Files. Phthalate concentrations are summarized in Table 1 and in Fig. 4 as pie charts showing the percentages of various chemical species in each sample. Concentrations of at least one chemical type (dimethyl, diethyl, dibutyl, butylbenzyl, ethylhexyl, dipropyl) exceeded 1 mg/kg in twenty out of twenty-seven samples.

Total phthalate content was typically larger that 1 mg/kg in all samples, and was larger than 10 mg/kg at the 3 and 17 sites, as can be seen from Table 1. The spatial distribution across the 16 km coastline study is shown using a color scale in the chemometric map of Fig. 5 and displays a high level of geographic heterogeneity. High phthalate concentrations are predominantly associated with the Saline and Foro rivers, with a third hotspot to the south of the Pescara River. The only phthalates present in two reference samples taken from the beach in Francavilla al Mare and in Pescara, away from the Saline and Foro river mouths and upstream the main coastal current (Fig. 1), were di-n-butyl phthalate, with a concentration of 0.0161 mg/kg, and diisobutyl phthalate, whose concentration was in the range of 0.0636–0.0656 mg/kg. The corresponding heavy metals and PAH concentrations are below the respective safety threshold levels as can be verified from Table 2, making these samples the least polluted of the ones we analyzed.

In contrast, port sediments around the city of Pescara yielded much higher concentrations of pollutants. The Environmental Protection Agency for the region of Abruzzo (ARTA), reported on port sediment distribution in the Pescara basin in 2009–2013 (*Agenzia Regionale per la Tutela dell'Ambiente*, 2009). Among the heavy metals that were probed, mercury was found to exceed the natural background level (GBL) in 50% of samples. An extra 10% of samples exceeded the safety threshold (ST) as shown in Figs.6a–h. Upon comparing measurements over the three-year span of the ARTA data, the overall picture in 2011 seems much worse than in 2009, with large levels of mercury above 1 mg/kg as can be seen from Table 2. Mercury levels found in fish harvested from the Pescara River were similar to those measured in local sediments, ranging from 0.06 to 0.08 mg/kg (Piccoli et al., 2010). Sediments originate at the source of the Pescara River and surrounding limestone rocks (calcarenites), which are located 50 km inland, towards the Apennine mountain range. At the source, sediments from the river carry negligible traces of Cr, Ni Zn, Pb, and Cd as shown in Table 2 and in Fig. 6, leaving little doubt that pollutants are of an anthropogenic nature and accumulate as water flows downstream through populated areas. In most cases, as can be seen from Fig. 6, the prediction curve intersects with the safety threshold at about 5% Al_2O_3 or about 15% clay. Pollutant levels from the samples with higher Al_2O_3 content were more likely to exceed the safety threshold. The observed linear correlation between Al and Cr, Zn, Cu, Pb, Cd, Ni concentration suggests that metals are mainly bound to the Al phase, either through clay minerals or as hydroxide. Arsenic and PAHs are not related to Al_2O_3 content and are generally below the safety threshold. However, PAHs are not present in the geological background and thus, although within safety levels, their presence in the observed sediment samples is entirely due to anthropogenic factors.

The concentration of metals such as Pb, Cr, Zn and to a lesser extent Cu, appear to be monotonically decreasing towards the estuary of the Pescara River. Likewise, the total organic carbon (TOC) distribution shows sediment organic matter content decreasing in the same direction. Thus, TOC positively correlates with heavy metals. We also observe increasing TOC content towards the breakwater barrier of the Pescara port, suggesting that reduced river flow velocities lead to higher deposition of organic matter as can be seen from Fig. 6i. Changes in salinity may also be a leading factor in the observed metal and TOC content reduction in sediments as the harbor is reached. The phthalate chemical distribution profile shows considerable variation among various sampling sites as can be seen from Figs. 4 and 5. We used rank analyses methods to assign entropic and anentropic factors in modeling phthalate distribution (Petrov, 1971; Petrov, 2001; Petrov and Moshkin, 2015; Petrov et al., 2016). Details are outlined in Section II of the Supplementary Files. Data were organized into five main sets and several subsets defined by distinct phthalate mixtures in terms of relative abundance as depicted in Fig. 7a. However, data clustering in terms of entropy-anentropy produced only three sets plus an outlier with very high anentropy, as shown in Fig. 7b.

We observed that fairly high anentropy levels, which can be associated with high phthalate content and indicate a potential phthalate risk, characterized sediments near the mouth of most of the main rivers in the area. Sediments harvested from non-fluvial sites, where phthalates have already been subjected to various environmental, biological and degrading processes, had higher entropy but lower total phthalate content. Risk is here lower and non-specifically related to a specific dominant phthalate as shown in Figs. 7b,c. The apparent paradox seen in the 'green' group of Fig. 7b is almost entirely due to sample 17, which had an extremely high total phthalate content (almost 22 mg/kg) but relatively low anentropy. This indicates potential higher risk. In all other samples, especially those comprising the 'red' group, a strong correlation was observed between the anentropy-entropy ratio and total phthalate content (Fig. 7b). These conservative figures indicate an average phthalate content, determined over all twenty-seven samples,

Table 1
Total phthalate concentration and distribution across the twenty-seven samples collected at twenty three-sites. Concentrations vary across the study area. Notably, total phthalate concentration in samples 3 and 17 is of the same order of magnitude of the risk threshold concentration (38.12 mg/kg for adults and 23.28 mg/kg for children for residential and recreational use, and exposure through dermal contact) for cancerogenic risk, as later outlined in the text. Phthalates are transported to the coast mainly through river-ways, while their accumulation seems to be influenced by marine longshore currents (NW-SE). Standard analyses of phthalates were conducted following the EPA Method 3550C 2007 and 8270 D 2007.

Sample	Lat.	Long.	Dimethyl phthalate (DMP)	Diethyl phthalate (DEP)	Dibutyl phthalate (DBP)	Butyl benzyl phthalate (BBP)	Di(2-ethylhexyl) phthalate (DEHP)	Diisobutyl phthalate (DIBP)	Total phthalates on site
			mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.
1	42.530444°	14.145194°	< 0.01	0.05	0.09	< 0.01	0.24	0.39	*0.77*
2	42.528389°	14.148472°	0.03	< 0.01	0.10	0.04	0.02	0.16	*0.35*
3	42.525278°	14.150639°	0.09	0.10	1.32	0.05	10.1	5.17	*16.83*
4	42.525972°	14.153639°	< 0.01	0.13	0.96	0.02	1.72	1.19	*4.02*
5	42.518917°	14.160917°	0.05	0.05	< 0.01	0.01	0.12	0.24	*0.47*
6	42.512917°	14.167000°	< 0.01	0.41	0.15	0.08	0.35	0.32	*1.31*
7	42.505203°	14.174567°	0.07	0.55	0.39	0.05	0.43	0.48	*1.97*
8	42.497569°	14.182064°	< 0.01	0.09	1.36	0.16	0.33	0.26	*2.20*
9	42.490961°	14.189664°	0.10	0.01	0.22	0.05	0.12	0.31	*0.82*
10	42.484194°	14.198833°	0.20	0.07	1.03	0.11	0.20	0.58	*2.18*
11	42.477889°	14.206806°	0.03	0.02	0.17	0.14	0.09	0.71	*1.16*
12	42.474500°	14.212556°	0.11	0.03	0.13	0.13	0.09	0.68	*1.18*
13	42.474528°	14.212833°	< 0.01	0.12	0.25	0.01	1.26	1.68	*3.32*
14	42.469083°	14.222361°	0.09	0.05	0.15	0.05	0.02	0.33	*0.70*
15	42.460556°	14.233750°	0.03	0.15	0.16	0.06	0.12	0.76	*1.28*
16	42.452750°	14.244111°	< 0.01	< 0.01	0.53	0.12	0.73	0.51	*1.90*
17	42.452733°	14.244237°	< 0.01	0.55	1.56	4.30	12.0	3.78	*22.16*
18	42.446889°	14.251417°	0.05	2.18	0.47	0.35	0.37	1.91	*5.32*
19	42.440028°	14.261306°	0.19	0.07	0.62	0.29	0.50	0.75	*2.43*
20	42.440119°	14.261606°	< 0.01	0.66	0.44	< 0.01	0.14	0.59	*1.82*
21	42.433833°	14.271389°	0.08	0.07	0.12	0.39	0.44	0.17	*1.27*
22	42.427840°	14.282090°	< 0.01	0.04	0.25	1.53	2.36	0.33	*4.52*
23	42.427714°	14.282724°	< 0.01	0.25	0.29	< 0.01	0.97	1.04	*2.56*
24	42.420472°	14.292306°	< 0.01	0.21	0.27	0.18	0.36	0.36	*1.38*
25	42.417111°	14.298953°	< 0.01	0.06	0.63	2.17	0.20	1.00	*4.05*
26	42.409278°	14.312972°	< 0.01	0.09	0.05	< 0.01	0.12	0.31	*0.57*
27	42.402611°	14.325111°	< 0.01	0.32	0.97	4.86	0.22	1.33	*7.69*

of about 2 mg/kg and a profile dominate by DIBP (0.4743 mg/kg), DEHP (0.3767 mg/kg), DBP (0.3747 mg/kg), and DEP (0.2709 mg/kg), with smaller proportions of BBP (0.1113 mg/kg) and DMP (0.0518 mg/kg).

Damage caused to humans by phthalates through multiple exposure routes should be assessed by including interference and amplification effects due to co-pollutants such as PAHs and heavy metals (Belcaro et al., 2007; Cini et al., 1994). This would require extensive data acquisition and elaborate calculations that are outside the scope of this paper. However, we can calculate phthalate risk levels and use these estimates as a preliminary indicator of the local status of environmental hygiene. Workers and people who use beaches for recreational purposes are in direct contact with both sediments and water. Furthermore, residents are continuously exposed to aerosol and atmospheric particulates, and to the toxic effects of phthalates via inhalation. Marine water aerosols are able to efficiently transfer phthalates compounds from water to the air, due to their phthalate surfactant properties (Cincinelli et al., 2001). Phthalate content in aerosols may be as high as 0.18 mg/kg due to the high affinity of phthalates for air/water interfaces (Cincinelli et al., 2001; Cini et al., 1994). Another route of human exposure to phthalates and heavy metals is through bioaccumulation and biomagnification in the food chain (Li et al., 2016), suggesting that exposure may be largest during the summer months when local seafood is mostly consumed. Data on human hair collected from daily consumers of fish in Pescara, reveal mercury concentrations of 11.18 mg/kg, about fourteen times higher than typical adult levels and 10.5 times higher than levels found in children (Giaccio et al., 2004). Mercury concentrations in Italy are reported to be 0.81 mg/kg for adults and 1.065 mg/kg for children (Pastorelli et al., 2012). Fish collected from the Pescara harbor were found to have values of mercury equal to 4.30 mg/kg, about 5 times higher than typical levels in adults and about 4 times higher than the levels found in children (Caracciolo et al., 1972).

Phthalate exposure routes through sea sediments have seldom been analyzed in the literature, and related health risk assessment studies are lacking. A thorough risk evaluation requires the use of different exposure scenarios that may depend on each individual's personal history. The Italian Agency for Environ-mental Protection and Technical Services (Agenzia per la Protezione dell'Ambiente e del Territorio (APAT), 2006) uses a 'first level' risk analysis to screen the environment at large by factoring in pollutant concentration (expressed in mg/kg), land use type (residential or recreational), adsorption routes (ingestion, dermal contact and inhalation) and contamination targets (adults or children). The Risk Threshold Concentration (CSR) is defined as the maximum allowable concentration for a single contaminant or a group of pollutants based on nominal limits set for carcinogenic and toxic effects. The CSR for a given substance may vary from location to location owing to non-uniform in situ characteristics. According to Italian law, sites where pollutant contamination exceeds CSR levels must be subject to remediation.

Our measured values determine what is referred to as the Source Contaminant Concentration (CRS). Derived quantities are based on given estimates for chronic daily intake of carcinogenic and/or toxic contaminants, and the maximum tolerable dosage under the assumption of an average human lifespan. In particular, we used parameters and formulas listed in the ISS-INAIL database (Musumeci et al., 2015). More details can be found in Section II of the Supplementary Files. From the measured levels of CRS we derived the carcinogenic and toxicity risks for different exposure pathways to contamination. The toxicological hazard index HI and carcinogenic risk R levels may be evaluated both for individual pollutants as well as for a combination of several pollutants. They express how much exposure to a pollutant exceeds the tolerable or reference dose. We define both HI and R for ingestion, dermal adsorption, and particulate inhalation as follows

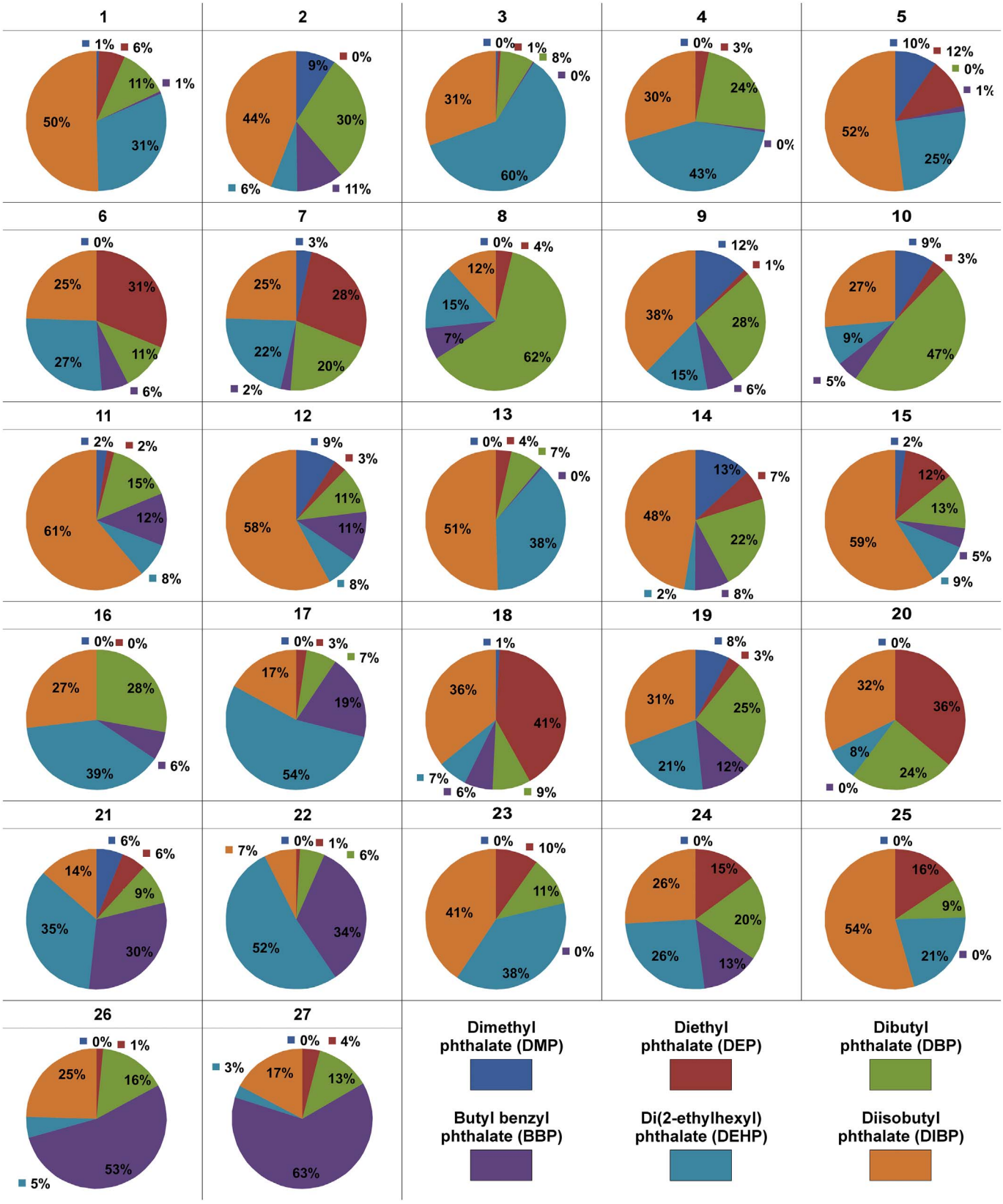

Fig. 4. Pie charts depicting single phthalate content as a percentage of total phthalate concentration for each sample. Color key in legend.

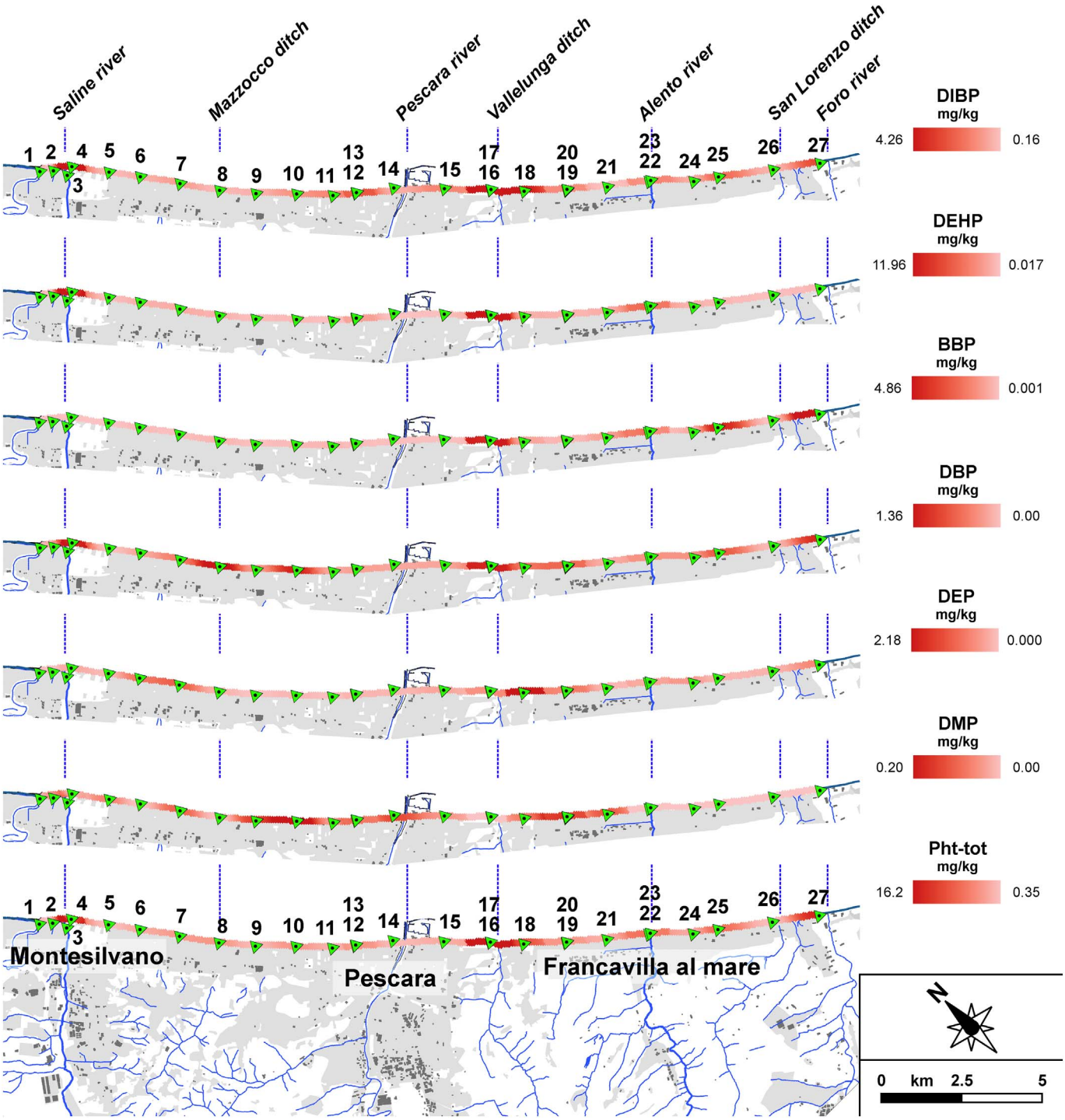

Fig. 5. Single type phthalate content measured from twenty-three sites along the central coast of Abruzzo, from the Saline River (Montesilvano) to the Foro River (Francavilla al Mare). Select sites were sampled twice, yielding twenty-seven viable measurements.

$$\begin{aligned}
HI &= CRS * \left[\frac{EM * 10^{-6}}{RfD}\right] && \text{ingestion or dermal adsorption;}\\
HI &= CRS * \left[\frac{EM * PEF * ADF}{RfD}\right] && \text{particulate inhalation;}\\
R &= CRS * [SF * EM * 10^{-6}] && \text{ingestion or dermal adsorption;}\\
R &= CRS * [SF * EM * PEF * ADF] && \text{particulate inhalation;} \qquad (1)
\end{aligned}$$

where the following acronyms are used:

CRS: analytically determined, in situ, dry soil contaminant concentration (mg/kg);

EM: effective exposure dosage (mg/kg/day);

SF: slope factor representing the carcinogenic potential of a contaminant (mg/kg/day);

PEF: outdoor particulate emission factor (mg/m^3)/(mg/kg);

RfD: reference dose (mg/kg/day) (2)

Of the above quantities, CRS is analytically determined through on site measurements, while all others are default, tabulated values that depend on the specific contaminant. Note that the EM defined above combines several carcinogenic and/or toxic factors for non-volatile substances, such as average exposure time, age and body weight, duration and frequency of exposure, exposed skin surface, dermal adherence factor, dermal absorption factor, fraction and rate of

Table 2
Heavy metal content in two samples of natural rocks taken from the Pescara River basin and two sediment samples taken from the Pescara beach. Samples GRA 01 and GRA 02 were measured in this work and are calcarenites collected from the Pescara River basin. Their mineralogical composition is similar to beach sand. Sand sediment samples MS 10 = 01 and MS 10 = 02 were similarly collected in this work at the Pescara beach. All others are sand and silt sediments collected at the Pescara port. The data is publicly available from ARTA's public database (*Agenzia Regionale per la Tutela dell'Ambiente*, 2009). The letters D; C; V pertain to unique locations with measurements conducted in various years. Standard analyses of heavy metals were conducted following the EPA Method 6010C 2007. bdl = below detection limit.

Sample	Al2O3	Cr	Ni	Cu	Zn	Cd	Hg	Pb	As
	wt%	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.	mg/kg s.s.
GRA01	0.44	9.60	4.0	3.0	12	< 0.1	< 0.1	< 0.5	1.00
GRA02	0.36	10.0	3.0	6.0	7	< 0.1	< 0.1	< 0.5	1.00
MS_10/01	n.a.	5.90	6.5	3.3	20	< 0.1	< 0.1	< 0.5	5.40
MS_10/02	n.a.	15.6	7.9	4.0	19	< 0.1	< 0.1	1.94	7.00
D_2011[a]	1.90	32.0	26.0	24.0	72	0.18	0.20	15	9.66
D_2012[a]	1.65	23.0	37.0	25.0	52	0.11	0.20	12	8.99
D_2013[a]	n.a.	17.0	24.0	22.0	62	0.15	0.20	10	11.8
C_2009[a]	2.18	36.0	18.0	16.0	58	0.21	0.20	10	8.16
C_2011[a]	2.91	26.0	33.0	35.0	106	0.21	1.50	26	9.31
C_2012[a]	3.21	71.0	45.0	29.0	100	0.45	1.20	36	7.57
C_2013[a]	n.a.	25.0	30.0	28.0	109	0.26	0.60	18	8.53
V_2013[a]	n.a.	30.0	23.0	20.0	71	0.18	0.20	14	9.43

n.a. = not analyzed.
[a] database from: http://www.artaabruzzo.it/caratterizzazione_porto_pe.php?id_page=0

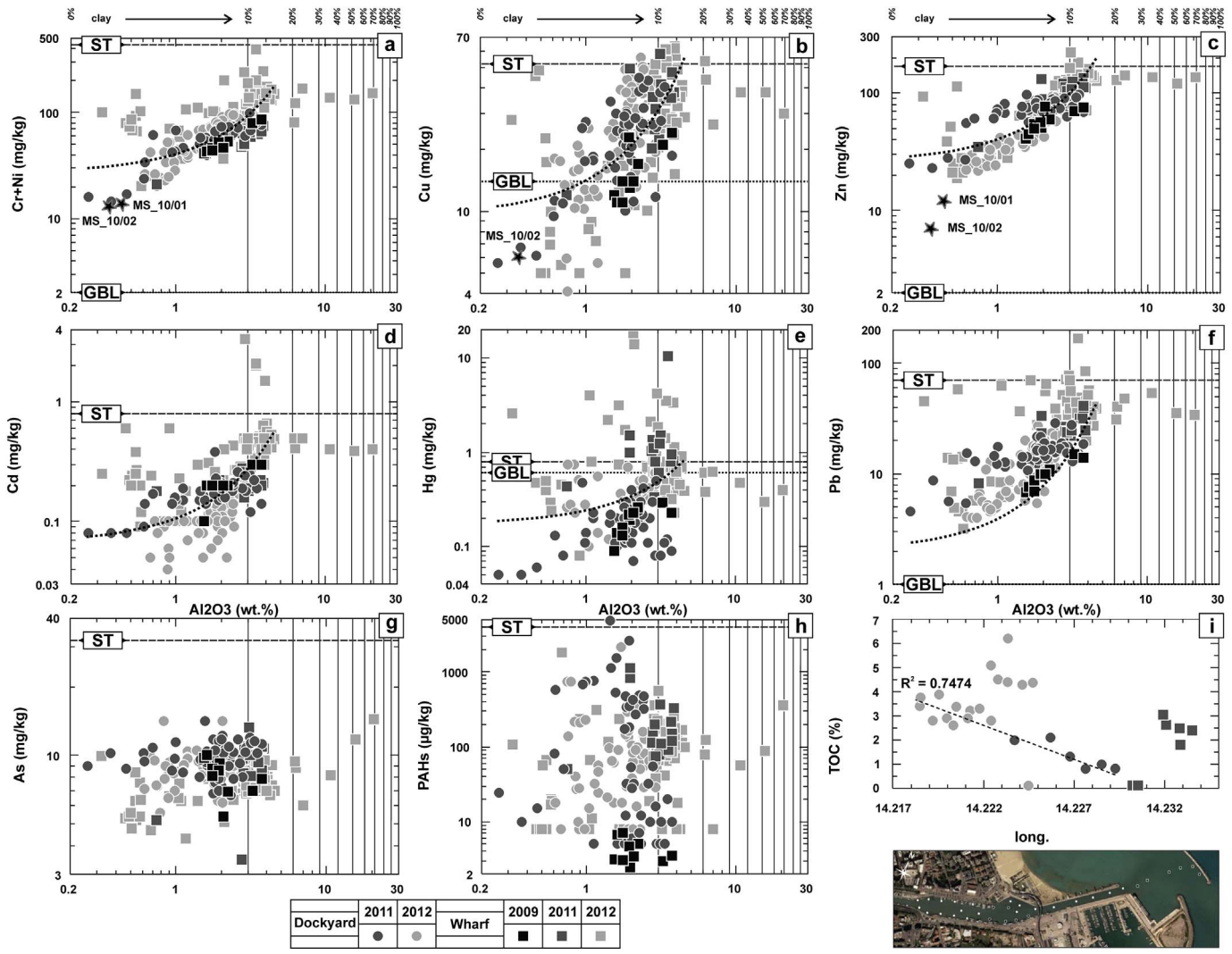

Fig. 6. Distribution of heavy metals, total organic carbon and other pollutants. Sediments collected at the Pescara port (*Agenzia Regionale per la Tutela dell'Ambiente*, 2009) are compared with two samples from the current study taken at the Pescara beach: MS 10 = 01 and MS10 02 and depicted as stars (Table 1). Safety threshold and baseline values for each contaminant are shown by a dashed and a dotted line, respectively. The composition trend is approximated by a best-fit curve.

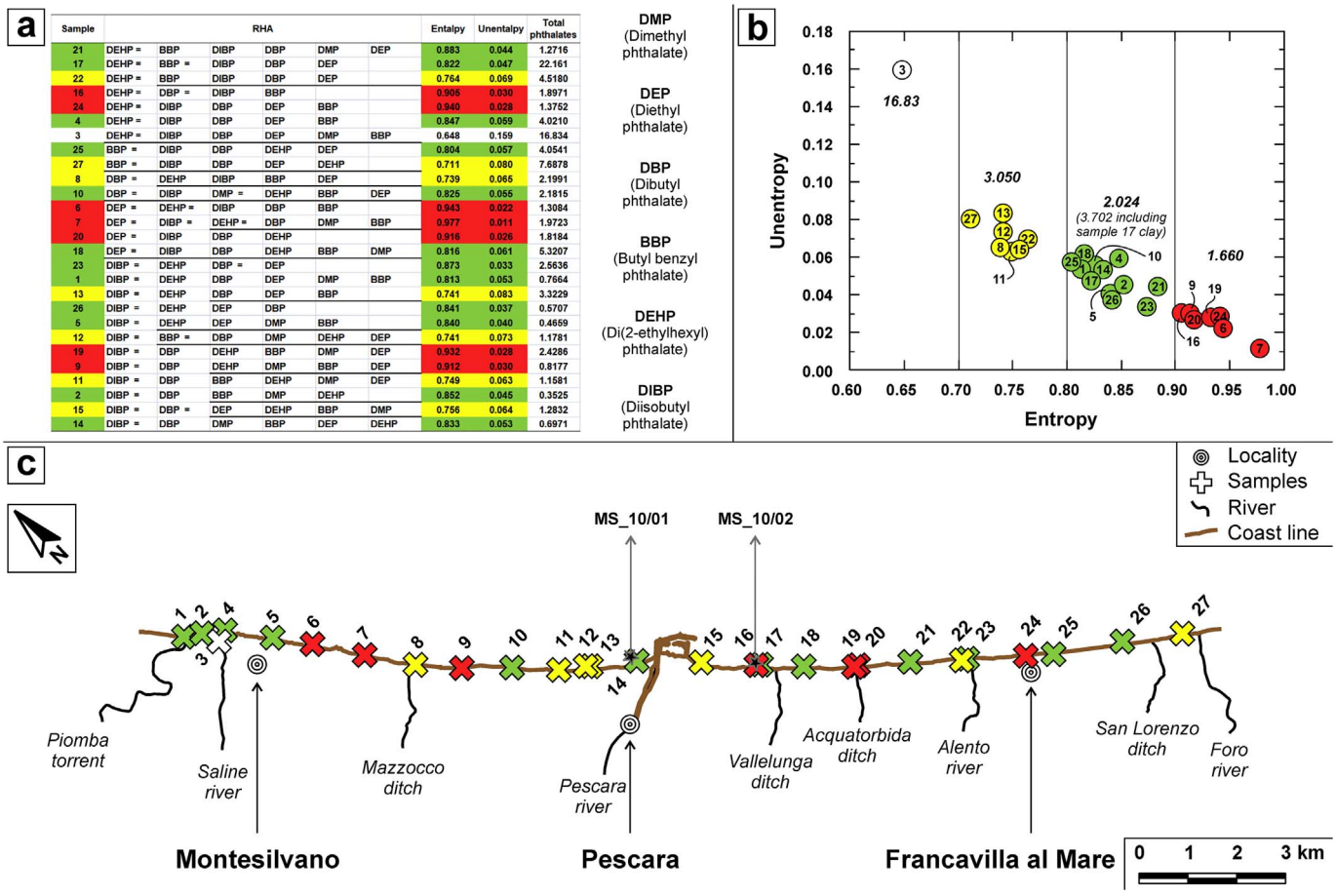

Fig. 7. (a) Phthalate rank formula in terms of abundance; (b) Anentropy and entropy diagrams showing three main groups and an outlier; (c) Spatial distribution of the entropy-anentropy groups. Data was analyzed and visualized using the Petros 3 software (Petrov and Moshkin, 2015).

particulate ingested. Also note that for a given dosage, the slope factor SF represents the corresponding likely increase of cancer incidence over the average life expectancy. The RfD represents the maximum tolerable daily dose of the toxic contaminant. The results of our calculations are listed in Table 3 and in Section III of the Supplementary Files for all twenty-seven sampled sites. Data were cross validated using Risk-net software 2.1 (Verginelli, 2016) which was developed according to the APAT-ISPRA procedure for risk calculation (Agenzia per la Protezione dell'Ambiente e del Territorio (APAT), 2008) in accordance with Italian law (Decreto Legislativo 3 aprile 2006, n. 152, 2006; Decreto Legislativo 16 gennaio 2008, n. 4, 2008). The Italian Higher Institute of Health tabulates safety threshold risks for any type of phthalate exposure, whether by dermal contact, inhalation, or ingestion, as $R = 10^{-6}$ for the carcinogenicity of a single chemical substance and $R = 10^{-5}$ for the cumulative carcinogenicity of a pollutant mixture. Similarly, the amount of contaminants adsorbed via ingestion, inhalation or through dermal contact, expressed by the numerators in the expressions for HI, must not exceed the RfD tolerable daily intake so that the HI threshold for toxicity is unity. These thresholds are discussed in Annex 1 of the Legislative Decree 152/06 (Decreto Legislativo 3 aprile 2006, n. 152, 2006).

Upon analyzing all twenty-seven samples, we found that the measured HI and R for the three direct exposure routes under investigation (ingestion, via dermal contact and inhalation) are well within the toxicity and carcinogenic safety thresholds (up to one order of magnitude less for ingestion). We therefore do not proceed to the `second level', more in-depth analysis as prescribed by Italian law. However we note that two critical locations emerge from our analysis, in vicinity of the Saline and Alento Rivers. Marine sediments collected in these areas, from sites 3 and 17, were marked by phthalate concentrations lower, but of the same order of magnitude, of the safety CSR for carcinogenic risk. Using the procedure described in the APAT guidelines (Agenzia per la Protezione dell'Ambiente e del Territorio (APAT), 2006; Agenzia per la Protezione dell'Ambiente e del Territorio (APAT), 2008) we determine the latter to be 38.12 mg/kg for adults and 23.28 mg/kg for children under the assumption of residential and recreational use, and exposure through dermal contact. Ingestion thresholds are set at 152 and 65 mg/kg for adults and children, respectively. As can be seen from Table 1, the observed value of 16.83 mg/kg for phthalate concentration at site 3 and 22.16 mg/kg at site 17 are 44% (site 3) and 72% (site 17) of the CSR risk threshold concentration for dermal contact for adults and 58% (site 3) and 95% (site 17) for children. These two sites should thus be carefully monitored especially in critical conditions such as during the summer months when phthalate concentrations in the environment are likely to increase. Further analysis of fluvial sediments would be also required upstream from these rivers. An additional line of investigation would be to monitor the concentration of low molecular phthalates (BBP, DEHP, DIBP, and DBP) that have been banned by the European Union in 2015, to determine adherence to the law and whether unknown sources of low molecular phthalates still persist in the area.

The widespread presence of endocrine disruptor agents, including phthalates, in over-populated environments has been linked to increases in metabolic diseases, gonadal abnormalities, decreasing fertility and cancer incidence world-wide. Given the stakes and the ubiquitous presence of plastic consumer products, there is a pressing need for medical research to determine the exact relationship between phthalates and these diseases, as well as possible mechanisms of action

Table 3
Toxicologic and carcinogenic risk calculation for various exposure routes, shown for cumulative phthalate concentrations. Danger index [HI] and Risk values [R] derived from the sum of individual phthalates per site.

Risk	Dermal contact		Soil ingestion		Inhalation of particulates			
Land use	Resident		Resident		Resident		Recreatonal	
Target	Adult	Child	Adult	Child	Adult	Child	Adult	Child
[HI]	Non-carcinogenic		Non-carcinogenic		Non-carcinogenic		Non-carcinogenic	
1	2.09E-04	1.37E-03	5.25E-04	4.90E-03	3.91E-12	1.42E-10	1.74E-12	4.82E-12
2	9.63E-05	6.31E-04	2.41E-04	2.25E-03	1.80E-12	6.53E-11	8.00E-13	2.22E-12
3	4.60E-03	3.01E-02	1.15E-02	1.08E-01	8.59E-11	3.12E-09	3.82E-11	1.06E-10
4	1.10E-03	7.20E-03	2.75E-03	2.57E-02	2.05E-11	7.45E-10	9.12E-12	2.53E-11
5	1.27E-04	8.34E-04	3.19E-04	2.98E-03	2.38E-12	8.63E-11	1.06E-12	2.93E-12
6	3.58E-04	2.34E-03	8.96E-04	8.36E-03	6.68E-12	2.42E-10	2.97E-12	8.22E-12
7	5.39E-04	3.53E-03	1.35E-03	1.26E-02	1.01E-11	3.65E-10	4.47E-12	1.24E-11
8	6.01E-04	3.94E-03	1.51E-03	1.41E-02	1.12E-11	4.07E-10	4.99E-12	1.38E-11
9	2.23E-04	1.46E-03	5.60E-04	5.23E-03	4.17E-12	1.51E-10	1.86E-12	5.14E-12
10	5.96E-04	3.90E-03	1.49E-03	1.39E-02	1.11E-11	4.04E-10	4.95E-12	1.37E-11
11	3.16E-04	2.07E-03	7.93E-04	7.40E-03	5.91E-12	2.15E-10	2.63E-12	7.28E-12
12	3.22E-04	2.11E-03	8.07E-04	7.53E-03	6.01E-12	2.18E-10	2.67E-12	7.40E-12
13	9.08E-04	5.95E-03	2.28E-03	2.12E-02	1.70E-11	6.16E-10	7.54E-12	2.09E-11
14	1.91E-04	1.25E-03	4.77E-04	4.46E-03	3.56E-12	1.29E-10	1.58E-12	4.38E-12
15	3.51E-04	2.30E-03	8.79E-04	8.20E-03	6.55E-12	2.38E-10	2.91E-12	8.07E-12
16	5.18E-04	3.40E-03	1.30E-03	1.21E-02	9.68E-12	3.51E-10	4.30E-12	1.19E-11
17	6.06E-03	3.97E-02	1.52E-02	1.42E-01	1.13E-10	4.11E-09	5.03E-11	1.39E-10
18	1.45E-03	9.52E-03	3.64E-03	3.40E-02	2.72E-11	9.86E-10	1.21E-11	3.34E-11
19	6.64E-04	4.35E-03	1.66E-03	1.55E-02	1.24E-11	4.50E-10	5.51E-12	1.53E-11
20	4.97E-04	3.25E-03	1.25E-03	1.16E-02	9.28E-12	3.37E-10	4.12E-12	1.14E-11
21	3.48E-04	2.28E-03	8.71E-04	8.13E-03	6.49E-12	2.36E-10	2.88E-12	7.99E-12
22	1.23E-03	8.09E-03	3.09E-03	2.89E-02	2.31E-11	8.37E-10	1.02E-11	2.84E-11
23	7.01E-04	4.59E-03	1.76E-03	1.64E-02	1.31E-11	4.75E-10	5.82E-12	1.61E-11
24	3.76E-04	2.46E-03	9.42E-04	8.79E-03	7.02E-12	2.55E-10	3.12E-12	8.64E-12
25	1.11E-03	7.26E-03	2.78E-03	2.59E-02	2.07E-11	7.51E-10	9.20E-12	2.55E-11
26	1.56E-04	1.02E-03	3.91E-04	3.65E-03	2.91E-12	1.06E-10	1.29E-12	3.59E-12
27	2.10E-03	1.38E-02	5.27E-03	4.91E-02	3.92E-11	1.42E-09	1.74E-11	4.83E-11
[R]	Carcinogenic		Carcinogenic		Carcinogenic		Carcinogenic	
1	2.01E-08	3.29E-08	5.04E-09	1.18E-08	1.13E-14	1.02E-13	5.01E-15	3.47E-15
2	9.25E-09	1.51E-08	2.32E-09	5.41E-09	5.18E-15	4.70E-14	2.30E-15	1.60E-15
3	4.42E-07	7.23E-07	1.11E-07	2.58E-07	2.47E-13	2.25E-12	1.10E-13	7.62E-14
4	1.05E-07	1.73E-07	2.64E-08	6.17E-08	5.91E-14	5.36E-13	2.63E-14	1.82E-14
5	1.22E-08	2.00E-08	3.06E-09	7.15E-09	6.85E-15	6.21E-14	3.04E-15	2.11E-15
6	3.43E-08	5.62E-08	8.60E-09	2.01E-08	1.92E-14	1.75E-13	8.55E-15	5.92E-15
7	5.17E-08	8.47E-08	1.30E-08	3.03E-08	2.90E-14	2.63E-13	1.29E-14	8.93E-15
8	5.77E-08	9.45E-08	1.45E-08	3.37E-08	3.23E-14	2.93E-13	1.44E-14	9.95E-15
9	2.15E-08	3.51E-08	5.38E-09	1.25E-08	1.20E-14	1.09E-13	5.34E-15	3.70E-15
10	5.72E-08	9.37E-08	1.43E-08	3.35E-08	3.21E-14	2.91E-13	1.43E-14	9.87E-15
11	3.04E-08	4.97E-08	7.61E-09	1.78E-08	1.70E-14	1.54E-13	7.57E-15	5.24E-15
12	3.09E-08	5.06E-08	7.75E-09	1.81E-08	1.73E-14	1.57E-13	7.70E-15	5.33E-15
13	8.72E-08	1.43E-07	2.18E-08	5.10E-08	4.88E-14	4.43E-13	2.17E-14	1.50E-14
14	1.83E-08	2.99E-08	4.58E-09	1.07E-08	1.02E-14	9.30E-14	4.55E-15	3.15E-15
15	3.37E-08	5.51E-08	8.44E-09	1.97E-08	1.89E-14	1.71E-13	8.38E-15	5.81E-15
16	4.98E-08	8.15E-08	1.25E-08	2.91E-08	2.79E-14	2.53E-13	1.24E-14	8.59E-15
17	5.81E-07	9.52E-07	1.46E-07	3.40E-07	3.26E-13	2.96E-12	1.45E-13	1.00E-13
18	1.40E-07	2.29E-07	3.50E-08	8.16E-08	7.82E-14	7.10E-13	3.48E-14	2.41E-14
19	6.37E-08	1.04E-07	1.60E-08	3.73E-08	3.57E-14	3.24E-13	1.59E-14	1.10E-14
20	4.77E-08	7.81E-08	1.20E-08	2.79E-08	2.67E-14	2.43E-13	1.19E-14	8.23E-15
21	3.34E-08	5.46E-08	8.36E-09	1.95E-08	1.87E-14	1.70E-13	8.31E-15	5.75E-15
22	1.19E-07	1.94E-07	2.97E-08	6.93E-08	6.64E-14	6.03E-13	2.95E-14	2.04E-14
23	6.73E-08	1.10E-07	1.69E-08	3.93E-08	3.77E-14	3.42E-13	1.67E-14	1.16E-14
24	3.61E-08	5.91E-08	9.04E-09	2.11E-08	2.02E-14	1.83E-13	8.98E-15	6.22E-15
25	1.06E-07	1.74E-07	2.67E-08	6.22E-08	5.96E-14	5.41E-13	2.65E-14	1.83E-14
26	1.50E-08	2.45E-08	3.75E-09	8.76E-09	8.39E-15	7.61E-14	3.73E-15	2.58E-15
27	2.02E-07	3.30E-07	5.05E-08	1.18E-07	1.13E-13	1.03E-12	5.02E-14	3.48E-14

(Pant et al., 2008; McLachlan et al., 2006). The current study reveals a serious carcinogenic risk owing to phthalates combining in large percentages with heavy metals and PAHs in the greater Pescara-Chieti area, with two specific sites marked by phthalate concentrations of the same order of magnitude as risk threshold concentrations. A correct approach to public health would require the implementation of specific measures to ensure drastic reduction of phthalate risk before toxicity and carcinogenicity thresholds can be reached. It is particularly important to preserve environmental hygiene in areas used by the general public for leisure such as beaches and outdoor areas. Appropriate awareness campaigns should be set in place to inform residents of phthalate exposure in their communities. The hospitality and fishing industries should be provided with mitigation tools aimed at ensuring the quality and health safety of their services and products. These

would include guidelines to eliminate the use of unnecessary and unsustainable phthalate-containing materials, and to help better streamline their disposal, avoiding uncontrolled release to the environment. Chemometric maps would help identify the areas at greatest risk and possible phthalate sources. They could also be useful for future correlation studies linking epidemiological data to phthalate geographical distribution.

Several findings emerge from this pilot study:

1. Analyzes of phthalates in intertidal and emerged beach sediments revealed unsuspected phthalate contamination along the coastline of the greater Pescara-Chieti area. Samples show various phthalate mixtures and concentrations that typically depend on sediment type and proximity to river mouths. We found high concentrations of pollutant species in fine-grained sediments, but unexpectedly, in gross ones as well. This may be due to sand particle porosity favoring absorbance and retention of phthalates and other pollutants including micro-plastics.
2. The observed spatial distribution and componentometry of phthalates provides a good indicator of environmental risk due to human activities, as it may help infer likely point sources and dispersion mechanisms and pathways.
3. Surfactant proprieties of phthalates suggest that they may be easily transported from sea surfaces to beach sediments via marine particulate such as aerosols and brines.
4. The moderate risks posed by current levels of phthalates, combined with the presence of other pollutants such as heavy metals and PAHs along the Pescara-Chieti coastline, underscore the need for mitigation and remediation measures to ensure safe use of land and sea. The effects of phthalate contaminated marine aerosols should be included in future studies. Mitigation and remediation strategies are more effective if undertaken before risk thresholds have been reached. At the moment it appears that all combined pollutant concentrations are increasing.
5. Untreated landfill material and civil sewage should be removed and treated appropriately. Current approaches to storage or dispersal of dredged sediments must be thoroughly re-evaluated and if necessary, altered, to protect resident health. The benefits of tackling phthalate contamination would extend beyond hygiene and environmental health to encompass tourism and fisheries.
6. A large-scale awareness campaign should be set in place to inform the general public and sectors of the economy of the adverse effects of phthalate pollution to the larger Pescara-Chieti area. Phthalate contamination is not confined to the Abruzzo coastline; rather other beach communities throughout the world are similarly affected. The plastic industry should be pressured to find new plasticizers based on vegetable oils as alternatives to phthalates. Only long-term corporate profits will drive any decision to find safer and sustainable plasticizers instead of phthalates.
7. The next research goal for the larger Pescara-Chieti area should be to evaluate phthalate risk in a more comprehensive manner, including the creation of seasonal risk maps over the course of a representative numbers of years, between ten and fifteen. Global threshold concentrations for all pollutants should be calculated. This is an ambitious project, which would require substantial funding. Finally, it would be useful to relate epidemiological data to risk in patients who experience symptoms associated with phthalate exposure. Samples should be taken from those who habitually frequent the Pescara-Chieti coast.

Acknowledgements

We are grateful to Prof. Werther Damonti and Prof. Nicola d'Alessandro for their kind assistance while performing routine phthalate analytical tests and to Dr. Marco Sborgia for assisting us in the preliminary phases of this work. We thank Prof. Piero di Carlo who provided invaluable help in calculating phthalate transportation factors. We are grateful for fruitful discussions with Prof. Andrea Ledda and Prof. Giuseppe Di Giovacchino from the Multidisciplinary Italian Academy for Territorial Urology, their appreciation of our work and future collaboration offers. The research was funded with a departmental (DiSPUTer) grant from the G. d'Annunzio University of Chieti Pescara and by ARO grants W1911NF-14-1-0472 and W1911NF-16-1-0165.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2017.08.008.

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