Table 1
Water and air sampling

Sample	Date	Station	Volume (L)	Temperature (°C)	Wind speed ($m\,s^{-1}$)	Salinity (‰)
Water						
W1	29/2/2004	3–4	38	4.3	9.0	28.5
W2	1/3/2004	4–6	174	4.5	8.7	30.4
W3	1/3/2004	6–8	82	3.8	10.0	27.8
W4	2/3/2004	10–13	175	4.5	10.0	30.1
W5	3/3/2004	16–19	254	6.0	6.8	34.1
W6	4/3/2004	23–25	410	6.7	14.0	34.9
W7	5/3/2004	22–36	381	6.3	11.6	34.6
W8	6/3/2004	29, 30, 36	335	6.2	4.3	34.5
W9	7/3/2004	35–37	201	6.0	4.2	34.5
W10	8/3/2004	33–34	162	5.3	7.2	32.2
W11	9/3/2004	34–39	81	4.8	11.4	31.6
Air			(m^3)			
A1-1[a]	29/2–2/3/2004	1–11	494			
A1-2[a]			549			
A2-1	2/3–6/3/2004	11–25–36	1147			
A2-2			927			
A3-1	6/3–9/3/2004	33–39	670			
A3-2			589			

[a]Parallel air samples were collected simultaneously using two high volume pumps.

2.2. Chemical analysis

2.2.1. Chemicals and materials

Phthalates (DMP, DEP, DBP, BBP, DEHP and DOP), deuterated di-(2-ethylhexyl) phthalate 3,4,5,6 (DEHP D4) and Surrogate standard mix 5 (Dibenzyl phthalate, Diphenyl phthalate, Diphenyl isophthalate) were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Their physicochemical properties are listed in Table 2. Solvents (methanol, acetone, n-hexane, dichloromethane (DCM) and diethyl ether) were pico grade (Promochem GmbH, Germany) and were distilled prior to use. The glass pipettes, vials and ampoules were initially rinsed with Milli-Q water and acetone, then baked out at 450 °C in a muffle furnace prior to use. All handling of samples was performed under clean-room conditions (positive pressure, carbon and HEPA filtered air) to minimize contamination.

2.2.2. Extraction and clean-up

The PUF/XAD-2 columns were spiked with 50 μL of 650 ng mL^{-1} DEHP D4 as internal standard and extracted for 16 h using 300 mL of 10% (v/v) diethyl ether in n-hexane solution with modified Soxhlet extractor. The PAD-2 columns were extracted for 16 h using 250 mL DCM with modified Soxhlet extractor after spiked with the same internal standards. Both air and water filter samples were extracted for 16 h using 150 mL of DCM with Soxhlet extractor. Prior to the extraction for PAD-2 columns and filter samples, 50 μL of 650 ng mL^{-1} DEHP D4 were added into the solvent as internal standard.

All the extracts were purified through a 5% H_2O deactivated silica gel column (2.5 g silica gel packed in a 15 cm × 1 cm i.d. glass column). The silica gel (0.063–0.200 mm, Merck, Darmstadt, Germany) was prepared as follows: extracted using acetone and baked out at 450 °C for 12 h to remove organic contaminations and deactivated by addition of 5% (w/w) of milli-Q water (purified by PAD-2 resins). After the extracts were transferred into the column, their purification was performed by passing 10 mL hexane through the column in order to remove non-polar compounds. The column was then eluted with 30 mL of n-hexane and diethyl ether (3:1 v/v) for the phthalate fraction. The elution was reduced in volume by rotary evaporation and subsequently concentrated via N_2 evaporator up to 100 μL. Hundred microlitre of N,O-bis(trimethylsilyl)-trifluoroacetamide and 1% trimethylchlorosilane (BSTFA, Part No. 701 490.201, Macherey-Nagel GmbH, Dueren, Germany) was added into the vial containing the extracts in order to determine the alkylphenols simultaneously. The mixture was allowed to react for 1 h at 70 °C. After cooling for 5 min, the final sample volume was adjusted to 200 μL using n-hexane. One microlitre of the solution was subsequently injected to the GC–MS without further treatment.

2.2.3. Gas chromatogram–mass spectrometry

The quantification of phthalates was performed with an Agilent 6890 N capillary gas chromatograph coupled

Table 2
Physicochemical properties of phthalates

Phthalate	DMP	DEP	DBP	BBP	DEHP
Formula	$C_{10}H_{10}O_4$	$C_{12}H_{14}O_4$	$C_{16}H_{22}O_4$	$C_{19}H_{20}O_4$	$C_{24}H_{38}O_4$
Molecular weight	194.2	222.2	278.4	312.4	390.6
Boiling point (°C)	282.4[a]	297.8[a]	340.0[b]	387.45[b]	384.0[b]
Le Bas Molar volume ($mL\,mol^{-1}$)[c]	206.4	254.0	342.8	364.8	520.4
S_W ($mg\,L^{-1}$)[c]	5200	591	9.9	3.8	0.0025
V_P (Pa)[c]	0.263	6.48×10^{-2}	4.73×10^{-3}	2.49×10^{-3}	2.52×10^{-5}
H_0 ($Pa\,m^3\,mol^{-1}$)[c]	9.78×10^{-3}	2.44×10^{-2}	0.133	0.205	3.95
Log K_{OW}[c]	1.61	2.54	4.27	4.70	7.73
Log K_{OA}[c]	7.01	7.55	8.54	8.78	10.53
$\Delta H_{V,B}$ ($kJ\,mol^{-1}$)[b,d]	—	—	61.95	58.80	67.20
ΔH_V ($kJ\,mol^{-1}$)[e]	—	—	84.13	84.32	92.47

[a]Buckingham and Donaghy (1982).
[b]California EPA (2001).
[c]Cousins and Mackay (2000).
[d]Enthalpy of vapourization at boiling point.
[e]Estimated enthalpy of vapourization at 25 °C.

to an Agilent 5973 quadrupole mass selective detector (GC–MS). Ions detected were generated by electron impact ionization and monitored in the selective mode (EI-SIM) and total ions scan mode by two injections. A 30 m × 0.25 mm fused silica capillary column (95%, dimethyl-5%-diphenylpolysiloxan, HP-5ms) with 0.25 μm film thickness was used for the separation. The flow rate of the carrier gas helium was kept constant at $1.0\,mL\,min^{-1}$. The temperature program was as follows: 80 °C for 1 min, 30 °C min^{-1} to 150 °C, 5 °C min^{-1} to 300 °C, then 300 °C for 5 min. The transfer line and the ion source temperature were maintained at 280 and 230 °C, respectively. One microlitre of the sample was injected into GC–MS by pulse splitless mode with a pulse pressure of 20 psi for 2 min and inlet temperature of 300 °C.

For the quantification, the GC–MS was operated in the selective ion monitoring mode detecting the following masses: $m/z = 163$, 149 (DMP); $m/z = 177$, 149 (DEP); $m/z = 149$, 167 (DBP, BBP); $m/z = 167$, 149 (DEHP); $m/z = 171$, 153 (DEHP D4); $m/z = 225$, 149 (surrogate standard mix 5). Phthalates were quantified by comparing the responses of analytes to that of internal standard of DEHP D4. The quantification was performed with calibration curves for analytes using standards with concentrations ranging from 0.1 to $2.5\,\mu g\,mL^{-1}$.

2.2.4. Quality control

Matrix spikes, breakthrough check, field blanks, and method detection limits (MDLs) were applied for quality assurance and control purposes. Recoveries for phthalates in water samples were evaluated by spiking surrogate standard mix 5 to the PAD-2 column, which are in the range of 58–91%. The recovery of phthalate on PUF/XAD-2 column was tested by spiking DEHP D4 on the PUF prior to use. The average recovery of DEHP D4 was 79 ± 3% ($n = 3$). Extraction recoveries averaged more than 75% in all matrixes. Concentrations of phthalate in dissolved and vapour phase samples were corrected by the individual recoveries. However, no recovery corrections were done for the phthalates in particle and TSM phases. Breakthrough was tested previously at the GKSS Research Centre and on board using two PUF/XAD-2 columns connected in series. The first column retained 70–94% ($n = 5$, 433–966 m^3) of the masses in the samples, which indicated that no significant breakthrough occurred during the sampling.

Laboratory and field blanks were incorporated in the analytical analysis to quantify possible contamination due to collection, transport and extraction, which were shown in Table 3. Field blanks of water samples were obtained by attaching PAD-2 column spiked with surrogate standard mix 5 to the water pump and putting a glass fibre filter on the filter plate, followed by passing 100 ml sea water through the column. Field blanks of air samples were prepared by putting a glass fibre filter on the filter frame and attaching a PUF/XAD-2 column to the pump. These field blanks were stored together with other samples and transported back to the laboratory. There was no significant difference between field and laboratory blanks. It was shown in Table 3 that DEP and DEHP were found in all of materials with high blank values, and masses of BBP were consistently lower in the field blanks. The mean mass found in the field blanks was subtracted from the samples.

Instrumental detection limits were determined by signal to noise ratio of 10, which were ranging from 1