

# Inputs of chemicals from recreational activities into the Norwegian coastal zone

K. H. Langford\* and K. V. Thomas

Received 11th April 2008, Accepted 2nd June 2008

First published as an Advance Article on the web 17th June 2008

DOI: 10.1039/b806198j

Wastewater treatment works effluent is often considered to be one of the most important point sources of a wide range of anthropogenic contaminants to aquatic systems, however, this paper discusses other potential sources. With the aim of establishing the important sources of UV filters, insect repellent and biocides to the aquatic environment, samples were collected from sites with direct (bathing areas and marinas) and indirect (sites receiving wastewater effluent) human influences. Sunscreens containing UV filters are used in large volumes during the summer months and often applied shortly before a person enters the water for swimming activities. The results presented here demonstrate that washing directly from the skin is an important point source of 4 UV filters to the Oslofjord. The insect repellent, diethyl toluamide, was also measured and it was concluded that washing from the skin was not such an important point source into the fjord. Concentrations of the biocide Irgarol 1051 were also measured and were elevated in the small boat marina and surrounding enclosed area. This work demonstrates that mans recreational water-based activities are a diffuse source of some contaminants into coastal and fjord environments and this study provides an initial assessment of the levels being released.

## Introduction

During the summer months many of Norway's fjords are used extensively for recreational activities such as sailing and swimming. There is very little information available on the inputs and impacts of chemicals to the Norwegian coastal zone from these activities. Oslofjord is 110 km long with a 19 m sill separating the outer and inner fjord. This sill acts as a natural barrier against water replacement in the inner fjord.<sup>1</sup> The surface water exchange in the inner fjord is limited and results mainly from estuarine circulation and freshwater from rivers entering and mixing with the fjord, resulting in the brackish water surface layer.<sup>2</sup>

It has been reported that boating activities can be an important source of biocides to the aquatic environment<sup>3,4</sup> but for many other compounds, wastewater effluent is the most frequently considered source of contamination. Insect repellents<sup>5,6</sup> and UV filters<sup>7,8</sup> have been measured in wastewater effluents and surface waters receiving effluent. Inputs directly from chemicals washing off the skin during swimming have rarely been considered. Due to the large quantities of compounds used and the large numbers of people swimming in enclosed coastal areas during summer months, it is an important source that should also be considered when assessing the sources of insect repellents and UV filters.

The insect repellent, diethyl toluamide (DEET), and its replacement, Bayrepe1®, have already been widely detected in the environment (e.g. in Germany, USA and the North Sea). In Tromsø-Sound, Norway, where wastewater treatment works effluent is directly discharged, DEET was detected at elevated levels despite dilution and tidal currents.<sup>9</sup>

Concerns have also been raised over UV filters used in sun protection creams entering the environment due to their potential impacts on the environment. For example, benzophenone-2 has shown significant estrogenic effects on vitellogenin induction, secondary sex characteristics, gonadal development and reproduction in fish<sup>10</sup> and previous studies identified synergistic estrogenic effects with a range of UV filters.<sup>11</sup> 3-Benzylidene-camphor and 3-(4'-methylbenzylidene)-camphor also showed significant impact on reproduction and on the development of aquatic invertebrates.<sup>12</sup>

With a ban on the use of tributyl tin (TBT) containing antifouling paints, there has been concern over the replacements which contain mainly copper metal oxides with the addition of organic biocides to increase the effectiveness of the paint and prevent the growth of copper resistant fouling organisms.<sup>13</sup> Previous studies on the environmental concentrations of biocides have detected elevated concentrations in areas of increased yachting activity. There are currently approximately 18 compounds in use as antifouling biocides.<sup>14</sup> Two of the most frequently used, Irgarol 1051 and diuron are persistent in surface waters and another such as ZPT degrades quickly.<sup>4,13</sup> Irgarol 1051 and diuron have been detected in Swedish<sup>15</sup> and Dutch<sup>16</sup> waters and ZPT has been monitored but found to be below limits of detection in UK marinas.<sup>17</sup>

It is obvious that chemical substances are entering the coastal zone; however, the input mechanism has received little attention to date. The seasonal affects this may have on areas where recreational use is intense may potentially be high. This is particularly true for fjords where there is limited water exchange. With this in mind, the aim was to establish the importance of direct inputs of contaminants resulting from human recreational activities.

Norwegian Institute for Water Research, 0349 Oslo, Norway. E-mail: kla@niva.no; Fax: +47 22185200; Tel: +47 22185100

## Materials and methods

### Materials

Standards of diethyl toluamide (DEET), Irgarol 1051, 4-methylbenzylidene camphor (4 MBC), ethylhexyl methoxycinnamate (EHMC), octocrylene (OC), benzophenone-3 (BP3) and chrysene-d12 were purchased from Sigma–Aldrich (Germany). No commercial preparation of Bayrepel® was available so the compound was isolated from Autan® insect cream for analyte identification purposes without quantification.

### Sample collection

Water samples were collected at a depth of 50 cm. Triplicate samples were collected in the peak of summer on a weekend in July when recreational activities were at a high with extensive boating and swimming activity. Many of the sampling points are frozen over during winter, so a winter sampling campaign was not possible. Sampling was again completed in May, before the summer, as the ice melted and before the small boats were back in the water and before any swimming activity.

Sample locations are displayed in Fig. 1. The Sandvika beach and marina samples, Kalvøya and Ostøya Channel are all enclosed areas with very limited exposure to currents, wind or freshwater inputs. The VEAS and fjord samples are in the middle of the fjord, resulting in more tidal and weather influence. The VEAS sample point is in close proximity to the discharge point of a wastewater treatment serving the west of Oslo city and surroundings. The beach at Huk faces the inner Vestfjord so has more exposure to water exchange than the other beach locations. Samples from Sandvika beach 1 and 2 were collected off the beach amongst approximately 200 swimmers, the majority being children, with sample 1 being the most densely populated with children.

### Sample extraction

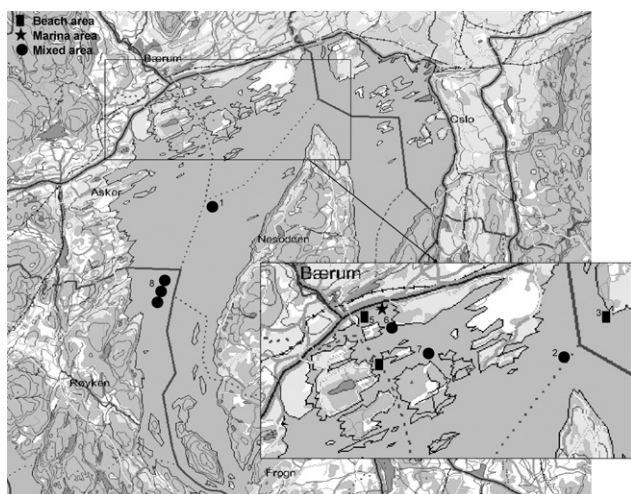
Samples (1 L) were extracted using a generic extraction method to allow for the screening of a broad range of compounds and

resulted in recoveries of over 60% for all compounds. StrataX solid phase extraction (SPE) cartridges (Phenomenex, UK) were washed with 6 mL ethyl acetate and conditioned with 6 mL methanol and 6 mL water before sample application. After sample application, SPE cartridges were rinsed with water to remove excess salts and then dried. Analytes were eluted with 6 mL ethyl acetate and 3 mL DCM and eluants combined and dried over anhydrous sodium sulfate before evaporation to approx 200  $\mu$ L and reconstitution to 1 mL with cyclohexane for gas chromatography-time of flight-mass spectrometric (GC-ToF-MS) analysis. 10 ng of chrysene-d12 was added to each extract as an instrument injection standard.

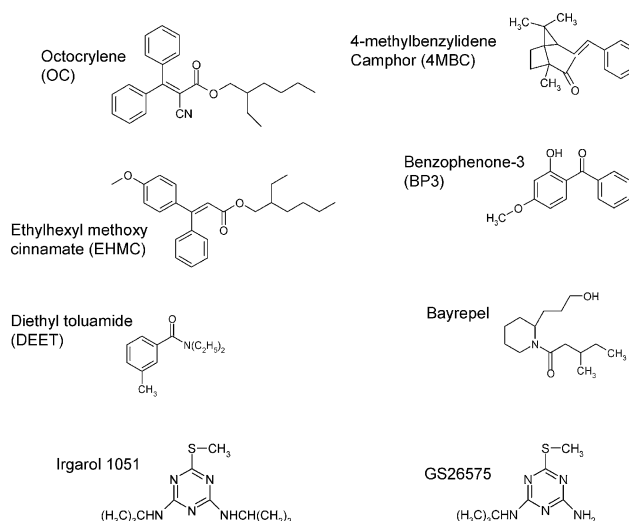
### Compound determination

GC-ToF-MS (GCT-Premier, Micromass,) analysis was performed in electron impact mode (70 eV) using full scan ( $m/z$  50–1000 mD) and a source temperature of 180 °C. The accurate masses used for compound determination are as follows DEET; 119.038 + 190.117 (0.8 mD), Bayrepel®; 128.194 + 184.258, BP3; 151.038 + 227.070 (0.2 mD), 4 MBC; 254.157 (1.6 mD), EHMC; 161.055 + 178.052 (1.7 mD), OC; 249.077 + 204.08 (2.6 mD), Irgarol 1051; 182.051 + 253.135 (1.8 mD), with acceptable mass errors noted in brackets (structures shown in Fig. 2). Gas chromatographic separation was carried out using a DB-5 MS column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) (J&W Scientific, UK). The temperature program was as follows: 60 °C for 2 min, 20 °C min<sup>-1</sup> to 150 °C, held for 5 min, 3 °C min<sup>-1</sup> to 220 °C and held for 10 min, and 20 °C min<sup>-1</sup> to 280 °C and held for 2 min. Splitless mode injection at 240 °C was used. Detection limits were in the range of 1–5 ng L<sup>-1</sup> for all compounds quantified.

EHMC and 4 MBC form geometrical isomers (*Z*- and *E*-), the ratios of which may vary in environmental samples and commercial formulations, therefore a response factor of 1 is assumed for each and the isomers were summed and reported as total concentrations for each compound. The chromatogram of a sample (Fig. 3) shows the separation of all the analytes and the EHMC and 4 MBC isomers.



**Fig. 1** Sample locations. Location numbers correspond to location numbers in Table 1.



**Fig. 2** Structures of compounds investigated.

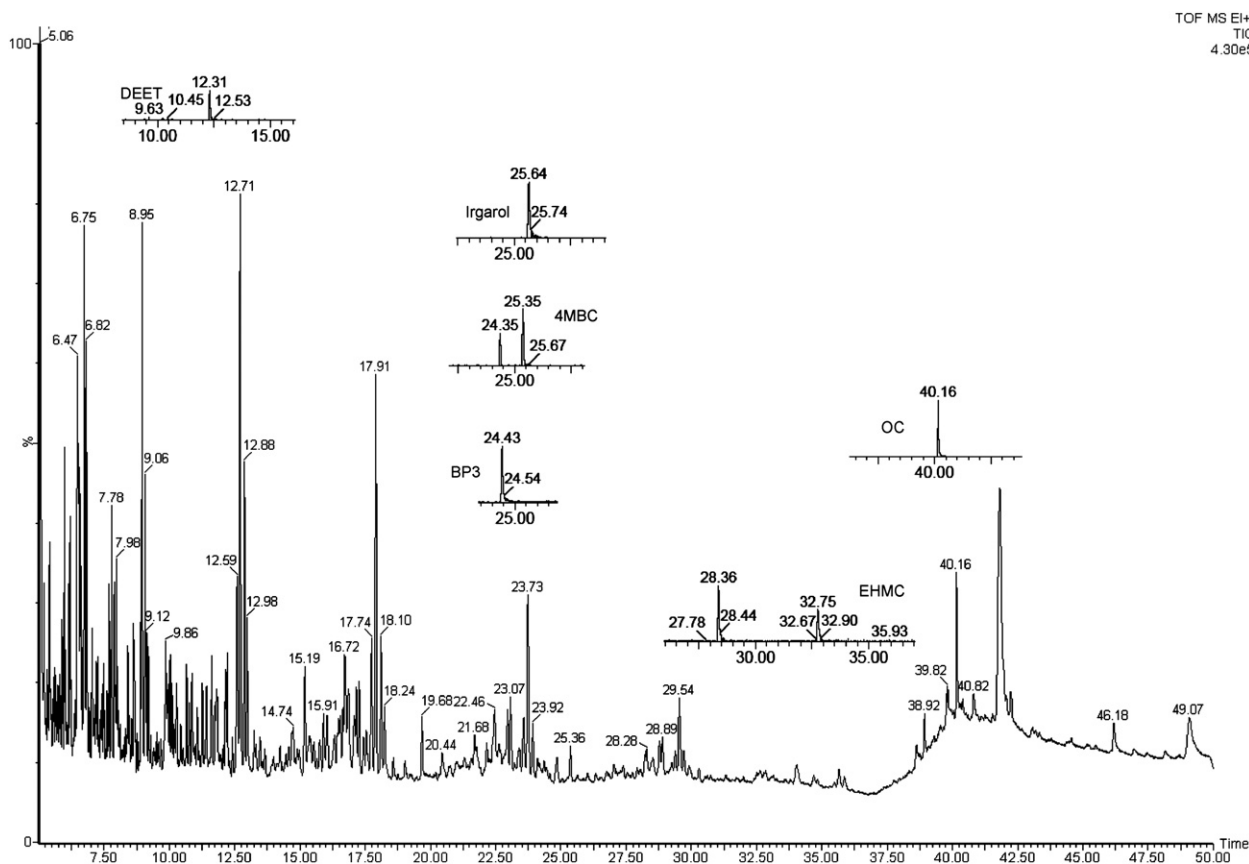


Fig. 3 GC-ToF-MS chromatogram of a bathing area sample with extracted ion chromatograms inset.

2-Methylthio-4-tert-butylamino-6-amino-s-triazine (M1 or GS26575), a transformation product of Irgarol 1051 and caffeine were also identified with  $m/z$  ratios of 269.4143 and 194.0804, respectively.

## Results and discussion

Concentrations of all compounds were less before summer than in the peak summer period (Table 1). During the peak season, in all except 3 samples, all compounds measured were identified. The 3 samples that did not contain some of the UV filters were samples taken in the open fjord where dilution and the distance from the point sources are greatest.

Irgarol 1051 shows some persistence with elevated concentrations in the samples collected before summer in the marina and enclosed areas, and higher concentrations measured in the summer samples. This seasonal variation has been seen in other studies.<sup>18,19</sup> Summer concentrations in European marinas were of comparable concentrations to those in this study with concentrations of 8–90 ng L<sup>-1</sup>, 11–440 ng L<sup>-1</sup> and up to 1421 ng L<sup>-1</sup> reported,<sup>16,18,13</sup> compared to 183–254 ng L<sup>-1</sup> in the proximity of the Sandvika marina in this study. One of Irgarol 1051's environmental transformation products, GS26575, was detected in all of the samples containing Irgarol 1051 and the summer samples demonstrated higher concentrations than those collected in May. An additional transformation product, 3-[4-tert-butylamino-6-methylthiol-s-triazin-2-ylamino] propanal, previously identified by Lam *et al.*,<sup>20</sup> was not detected in the Oslofjord

samples and the production by-product *N,N'*-di-tert-butyl-2,4-diamino-6-methylthiol-s-triazine<sup>21</sup> was also not detected.

DEET shows a relatively constant distribution in all samples indicating that washing from the skin is not an important point source in the Oslofjord area. Biting insects are not a problem in the fjord area but are a problem in the mountain areas. Therefore it is possible that concentrations in the mountain lakes could be elevated due to more insect repellent potentially being used and less dilution occurring in lakes because of smaller water volumes. In Northern Norway DEET was measured<sup>22</sup> in seawater in the range 0.5–13 ng L<sup>-1</sup>, which is the same order of magnitude as the off season samples in this study, with concentration ranges of up to 10.4 ng L<sup>-1</sup>. 14.1–240.8 ng L<sup>-1</sup> measured during the peak season in this study is higher than that reported elsewhere. Bayrepel<sup>®</sup> has been identified in other work in wastewater influent<sup>5,23</sup> but not in lakes<sup>6</sup> which supports this work in Oslofjord where no Bayrepel<sup>®</sup> or its metabolite Bayrepel<sup>®</sup>-acid were detected. These results could also be due to poor analyte recovery as the extraction method used was not optimised for Bayrepel<sup>®</sup> and no method validation was completed for this compound.

The UV filter compounds also demonstrate reduced concentrations in winter compared to summer and the very high levels measured in the bathing areas show that washing directly from the skin is an important point source. The two samples with the highest concentrations were taken where children were swimming, so this high level was expected and concentrations decreased further from the swimming area. The concentrations detected in Oslofjord are of the same order of magnitude as other

**Table 1** Concentrations of compounds measured (ng L<sup>-1</sup>), nd denotes less than detection limits and ns denotes that no sample was collected. Numbers in brackets correspond to sample locations in Fig. 1

	DEET		BP3		4MBC		Irgarol		EHMC		OC	
	May	July	May	July	May	July	May	July	May	July	May	July
Innerfjord 1 (1)	nd	27.0	19.5	5.4	nd	nd	3.6	29.0	19.6	159.2	nd	12.5
Innerfjord 2 (2)	nd	18.6	nd	16.3	nd	nd	12.6	45.9	17.6	57.7	nd	nd
Huk (3)	nd	14.1	nd	165.5	1.1	9.8	10.8	40.3	30.6	44.9	nd	29.9
Kalvøya (4)	nd	31.9	nd	24.0	nd	40.7	24.3	294.2	20.1	63.1	nd	105.1
Sandvika Beach 1 (5)	ns	240.8	ns	439.9	ns	798.7	ns	183.3	ns	389.9	ns	7301.0
Sandvika Beach 2	ns	48.0	ns	89.1	ns	262.1	ns	198.1	ns	168.8	ns	2780.7
Sandvika Beach 3	10.4	18.5	nd	13.4	nd	25.4	37.1	218.1	nd	60.4	nd	65.3
Sandvika Marina (6)	10.1	23.6	nd	15.8	nd	38.2	39.9	245.0	nd	70.8	nd	90.1
Off Sandvika Marina	4.2	16.8	nd	20.1	nd	31.8	60.6	254.5	23.2	74.7	24.8	71.2
Sandvika Mid channel		22.9	ns	32.1	ns	28.4	ns	212.5	ns	38.6	ns	63.2
Ostøya Channel (7)	nd	25.6	37.0	21.6	2.2	20.1	20.0	142.8	nd	93.6	nd	58.5
0 m off VEAS (8)	5.0	53.2	nd	nd	nd	nd	nd	21.5	32.6	164.1	nd	nd
10 m off VEAS	nd	34.6	22.5	15.5	nd	17.2	nd	30.5	nd	189.3	nd	31.2
100 m off VEAS	nd	22.3	35.5	13.7	2.6	5.3	nd	24.9	nd	178.9	nd	24.8

work. Selected Swiss lakes contained up to 35, 28, 7 and 5 ng L<sup>-1</sup> of BP3, 4 MBC, EHMC and OC, respectively, during summer<sup>8</sup> and slightly lower concentrations were reported in an earlier study with concentrations less than the detection limit for BP3 and OC.<sup>24</sup> The samples collected amongst the swimmers in this study demonstrated very high concentrations of 439.9, 798.7, 389.9 and 7301 ng L<sup>-1</sup> of BP3, 4 MBC, EHMC and OC, respectively. Excluding these samples, the concentration range for BP3 was nd–165.5 ng L<sup>-1</sup> in summer and nd–19.5 ng L<sup>-1</sup> during off peak. 4 MBC was detected at higher concentrations than BP3 in summer (nd–262.1 ng L<sup>-1</sup>) but lower in winter (nd–2.6 ng L<sup>-1</sup>). The concentration range for EHMC in summer was 38.6–189.3 ng L<sup>-1</sup> in summer and nd–32.6 ng L<sup>-1</sup> in winter. Excluding the two samples with exceptionally high concentrations due to washing directly from the skin of swimmers, the range was nd–105.1 ng L<sup>-1</sup> in summer and nd–24.8 ng L<sup>-1</sup> during off peak.

Using calculations used by Poiger *et al.*,<sup>24</sup> and assuming the same factors, 1.5 applications per day at 1 mg cm<sup>-2</sup> over 1 m<sup>2</sup> of body, assuming the same sunscreen products and sun protection factor are used, and assuming a conservative 80% of the swimmers were using sun protection, an input of approximately 208 g of UV filters per day was calculated for just the Sandvika beach area. Swimmers were not counted at the other bathing areas but were less than at the Sandvika sampling point.

The concentrations that were measured in Oslofjord are below the concentrations where acute toxic effects have been observed. However, risks through chronic exposure have not yet been reported so this mechanism should be assessed before any risk can be ruled out.

Around the fjord coastline there are numerous bathing points and small boat marinas which will all input UV filters, insect repellents and biocides into the fjord environment. Most risk assessments concentrate on inputs from point sources such as wastewater effluent but it is clear that for some groups of compounds, such as UV filters and biocides, there are other point sources to consider.<sup>25,26</sup> This study clearly shows that recreational water-based activities are a diffuse source of some contaminants into coastal and fjord environments and provides an initial assessment of the levels being released. The risk

associated with antifouling paint biocides is currently being assessed as part of the EU's Biocidal Products Directive, however, less is known about the potential risks posed by insect repellents and sunscreens to the aquatic environment.

## Acknowledgements

The Research Council of Norway is acknowledged for funding (Ref. 173461/S40).

## References

- 1 T. Pinturier-Geiss, L. Mejanelle, B. Dale and D. A. Karlsen, *J. Microbiol. Methods*, 2002, **48**, 329.
- 2 H. G. Gade, *Helgol. Mar. Res.*, 1968, **17**, 462.
- 3 N. Voulvoulis, M. D. Scrimshaw and J. N. Lester, *Chromatographia*, 1999, **50**, 353.
- 4 K. V. Thomas, M. McHugh and M. J. Waldock, *Sci. Total Environ.*, 2002, **293**, 117.
- 5 T. Knepper, *Water Sci. Technol.*, 2004, **50**, 301.
- 6 S. Weigel, J. Kuhlmann and H. Huhnerfuss, *Sci. Total Environ.*, 2002, **295**, 131.
- 7 H.-R. Buser, M. E. Balmer, P. Schmid and M. Kohler, *Environ. Sci. Technol.*, 2006, **40**, 1427.
- 8 T. Kupper, C. Plagellat, R. C. Brandli, L. de Alencastro, D. Grandjean and J. Tarradellas, *Water Res.*, 2006, **40**, 2603.
- 9 S. Weigel, U. Berger, E. Jensen, R. Kallenborn, H. Thoresen and H. Huhnerfuss, *Chemosphere*, 2004, **56**, 583.
- 10 C. J. Weisbrod, P. Y. Kunz, A. K. Zenker and K. Fent, *Toxicol. Appl. Pharmacol.*, 2007, **225**, 255.
- 11 P. Y. Kunz and K. Fent, *Toxicol. Appl. Pharmacol.*, 2006, **217**, 86.
- 12 C. Schmitt, M. Oetken, O. Dittbener, M. Wangner and J. Oehlmann, *Environ. Pollut.*, 2007, **152**, 322.
- 13 K. V. Thomas, T. W. Fileman, J. W. Readman and M. J. Waldock, *Mar. Pollut. Bull.*, 2001, **42**, 667.
- 14 I. K. Konstantinou and T. A. Albans, *Environ. Int.*, 2004, **30**, 235.
- 15 B. Dahl and H. Blanck, *Mar. Pollut. Bull.*, 1996, **32**, 462.
- 16 M. H. Lamoree, S. P. Stewart and B. Van der Hattum, *J. Chromatogr. A*, 2002, **970**, 183.
- 17 K. V. Thomas, *J. Chromatogr. A*, 1999, **833**, 105.
- 18 S. Biselli, K. Bester, H. Huhnerfuss and K. Fent, *Mar. Pollut. Bull.*, 2000, **40**, 233.
- 19 J. C. Bowman, J. W. Readman and J. L. Zhou, *Mar. Pollut. Bull.*, 2003, **46**, 444.
- 20 K. H. Lam, H. Y. Wai, K. M. Y. Leung, V. W. H. Tsang, C. F. Tang, R. Y. H. Cheung and M. H. W. Lam, *Chemosphere*, 2006, **64**, 1177.

- 
- 21 K. H. Lam, Z. W. Cai, H. Y. Wai, V. W. H. Tsang, M. H. W. Lam, R. Y. H. Cheung, H. X. Yu and P. K. S. Lam, *Environ. Pollut.*, **136**, 221.
- 22 M. W. Sandstrom, D. W. Kolpin, E. M. Thurman and S. D. Zaugg, *Environ. Toxicol. Chem.*, 2005, **24**, 1029.
- 23 T. Knepper, *J. Chromatogr., A*, 2004, **1046**, 159.
- 24 T. Poiger, H.-R. Buser, P.-A. Bergquist and M. D. Muller, *Chemosphere*, 2004, **55**, 951.
- 25 A. Standler, A. Schatzl, C. W. Klampfl and W. Buchberger, *Microchim. Acta*, 2004, **148**, 151.
- 26 M. E. Balmer, H.-R. Buser, M. D. Muller and T. Poiger, *Environ. Sci. Technol.*, 2005, **39**, 953.