

# Laboratory and Field Testing on an INFILTREX 100 Pump

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## ABSTRACT

Low levels of contaminants in coastal waters present an enormous challenge to water quality monitoring efforts. The collection, transport, and processing of the large volumes of water required to achieve the necessary detection limits are tedious, and samples are vulnerable to cross-contamination. The INFILTREX 100 pumping system has the capability to filter particulates and extract filtrates simultaneously from a large quantity of water, thus attaining ultra-low detection limits without the potential for cross-contamination. However, the reliability and feasibility of using INFILTREX 100 have not yet been fully examined. This study was conducted to assess the performance of the INFILTREX 100 from four different operational perspectives: (1) on-column elution, (2) retainability, (3) overall efficiency, and (4) field deployment. The first test, which evaluated the efficiency of recovering analytes adsorbed on the extraction column, obtained a range of recoveries of 60 to 100%, 40 to 93%, and 83 to 100% for polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides (DDTs), and polychlorinated biphenyls (PCBs), respectively. The second test, which was designed to estimate the degree of loss of sorbed analytes after long-term pumping, achieved average recoveries of  $80\pm 35\%$  and  $61\pm 16\%$  for PAH and PCB surrogate standards after 623 L of tap water was pumped through the column. The third test recovered from 32 to 85%, 31 to 100%, and 42 to 100% of PAHs, DDTs, and PCBs, respectively, from tap water; and 29 to 97%, 22 to 100%, and 36 to 100% of PAHs, DDTs, and PCBs, respectively, from sea water. Field deployment was conducted at Station 7C (heavily contaminated) near the outfall of the County Sanitation

Districts of Los Angeles County (CSDLAC), Station T1 (moderately contaminated) near the outfall of the County Sanitation Districts of Orange County (CSDOC), and Station R52 (reference) off Dana Point. At Station 7C, total concentrations of up to  $10.4\pm 2.9$  ng/L,  $11.7\pm 3.6$  ng/L, and  $4.3\pm 2.1$  ng/L were obtained for PAHs, DDTs, and PCBs, respectively. At Station T1, total concentrations of  $4.1\pm 4.7$  ng/L and  $0.30\pm 0.14$  ng/L were found for PAHs and DDTs, respectively, but no PCBs were detected. At Station R52, only DDTs were detected ( $0.200\pm 0.001$  ng/L). These contaminant concentrations were similar to the concentrations obtained for the surface sediments collected at the same locations. Collectively, the results validate the use of INFILTREX 100 in coastal water sampling.

## INTRODUCTION

Monitoring water quality in the coastal environment is important, since monitoring provides valuable information on the impacts of contaminated sediments on the water column and on the bioavailability of contaminants to marine species. The generally low concentrations of many chemicals in sea water, however, require a monitoring system capable of attaining ultra-low detection limits. Sampling and analysis of very large volumes of water are often required to achieve the necessary detection sensitivity. Collecting, transporting, and processing these large volumes of water are labor-intensive efforts prone to cross-contamination.

Alternatively, living organisms are often used as long-term samplers to collect compounds that bioaccumulate. For example, transplanted mussels have been successfully utilized to concentrate water-borne organics (Farrington *et al.* 1983 and references therein), since they are widespread, sessile, and unlikely to metabolize the contaminants (Kennish 1997). However, the use of living organisms in field sampling has several drawbacks, such as long deployment time (1+ months); restricted habitats (e.g., mussels can only survive in certain areas); and variation in bioaccumulation with sex, body



size, and season (Hofelt and Shea 1997).

A second option is to use nonliving monitoring systems. One of the frequently used samplers is the semipermeable membrane device (SPMD). An SPMD consists of a thin-walled, layflat tubing of polymer (polyethylene, polypropylene, or silicone) containing a thin film of lipophilic material such as triolein (Huckins *et al.* 1993, Petty *et al.* 1995). Although the membrane is composed of nonporous or dense polymers, random thermal motion of the polymer chains allows the formation of transient cavities with diameters up to 10 Å, enabling dissolution of organic compounds into the membrane and diffusional jump transfer of contaminants to the lipophilic layer (Huckins *et al.* 1993, and references therein). While the SPMD has been considered as a supplementary biomonitoring tool, several limitations must be considered (Huckins *et al.* 1993). For example, chemicals are concentrated only when they are in the dissolved phase. Second, the transport corridors on the semipermeable membrane severely limit the molecular sizes of permeate pollutants that can enter. This sampling method consequently does not permit the quantification of total concentrations for many targeted analytes (Huckins *et al.* 1993).

A third alternative is to use the INFILTREX 100 water sampler (Figure 1, Axy's Environmental Systems Ltd., Sidney, British Columbia, Canada), which is a device analogous to the mussel in many functional aspects, but not subject to geographical restrictions. The physical dimensions of an INFILTREX 100 sampler are: overall length, 78 cm; maximum width, 21 cm (with disk filter); and maximum thickness, 19 cm. This system features a water pump, a filter assembly housing up to 8 GF/F 142 mm glass fiber filters in parallel (one sample), a Teflon column (2.0 cm in diameter, 37 cm in length with end caps), and a microprocessor that records the sampling volume from the preset flow rate and sampling time. Water is pumped into the filter assembly, where the particulates are retained. The filtrate is then directed to the Teflon column packed with resins of choice; e.g., Amberlite XAD-II for extracting hydrophobic organics. These features permit collection of contaminants in dissolved and particulate phases. The fast flow rate (up to 0.5 L/min) allows sampling of a large volume of water in a relatively short period of time.

The *in-situ* filtration and extraction method provided by the INFILTREX 100 sampler has become increasingly popular in recent years (Green *et al.* 1986, Ehrhardt and Burns 1990, Nichols and Espey 1991) due to its apparent advantages. Tests on the efficiency of the INFILTREX samplers for extracting trace organics from water have also been conducted (Green and Kowalski 1984, Sojo and Miega 1994). Relatively high column efficiency in the extraction of trace organics from sea water using XAD-II resin was

reported: 91±8 (alkanes), 104±10 (PAHs), and 94±14 (organochlorines) (Green and Kowalski 1984). In these tests, 14 chlorinated pesticides were included. However, for other types of organic pollutants, less than 10 compounds in each class were selectively tested. Before an INFILTREX 100 can be used routinely, its performance and feasibility for offshore deployment must be extensively tested under controlled laboratory conditions as well as in open waters. This article reports results from such a comprehensive evaluation.

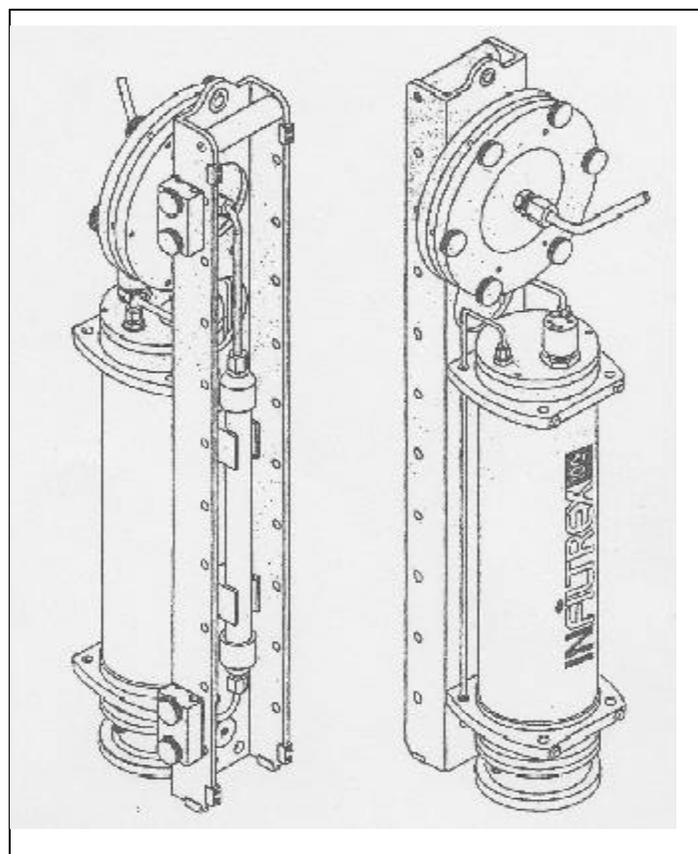
## MATERIALS AND METHODS

### Approach

In this study, the performance of an INFILTREX 100 was evaluated from four operational perspectives: (1) on-column elution; (2) retainability; (3) overall efficiency; and (4) field deployment. The target compounds in all the tests were polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (DDTs).

In the first test, the recommended elution procedure (Sojo and Miega 1994) to recover analytes sorbed onto a resin column was tested. This procedure was accomplished by directly spiking target compounds (and surrogate standards) onto the column. The column was then eluted

FIGURE 1. Schematic drawing of an INFILTREX 100 water sampler.



using the procedure described below. The spiking quantity was 2 µg for PAH compounds (and related surrogates) and 400 ng for PCB and DDT compounds (and surrogates).

The second test assessed the magnitude of losses of target analytes sorbed onto a resin column after long-term pumping. In this test, a total of 623 L of tap water were pumped through the column that was previously spiked with PAH and PCB surrogate standards (2 µg and 400 ng, respectively). The recoveries of the representative surrogate standards provided an evaluation of the retainability of the analytes on the column.

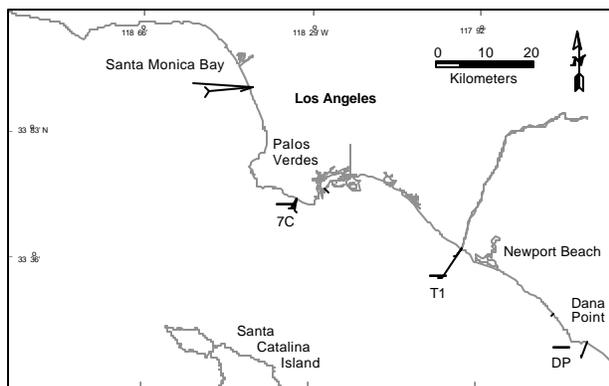
The third test examined the overall performance of the INFILTREX 100 in terms of extracting target compounds from various sample matrices and recovering them from the column. To accomplish this goal, spiked samples (5 L each) were prepared by spiking PAH, PCB, and DDT standards into tap water and sand-filtered sea water (collected from an intake of Southern California Edison, Redondo Beach, California) in precleaned glass bottles. Sea water was prefiltered with GF/F 47 mm glass fiber filters before spiking. The spiking concentrations were 0.4, 0.06, and 0.06 µg/L for individual PAH, PCB, and DDT components, respectively (0.4 and 0.08 µg/L for PAH and PCB surrogate standards, respectively). These spiked samples were allowed to equilibrate at room temperature for at least 12 hours before being pumped through resin columns.

In Tests 1 through 3, PCBs and DDTs were prepared and analyzed separately to eliminate any possible chromatographic interference from each other. In addition, unspiked water was also extracted with clean columns and processed as samples (three replicates). No detectable PAH or organochlorine compounds were found in these samples, indicating no interference from the column, packing resins, or sample matrices.

The fourth test evaluated the field performance and reliability of the INFILTREX 100 by deploying it at different locations where sediments are known to contain various levels of organic contaminants. Field deployments were conducted in October and November of 1995 and April and May of 1996. Three stations were selected (Figure 2): Station 7C (33°42.31'N/118°20.90'W) near the Joint Water Pollution Control Plant (JWPCP) outfall of the CSDLAC, Station T1 (33°34.67'N/118°00.63'W) near the CSDOC outfall, and one reference station, Station R52 (33°23.79'N/117°39.98'W), off Dana Point. Station R52 was sampled only in April and May 1996.

At all of the stations, the sampling device was deployed at a water depth of 60 m. The device was held in the vertical position by iron links (total weight of approximately 200 lbs) attached to the bottom end of the pump by a rope approximately 1 m in length; and by a set of buoys

**FIGURE 2. Field deployment locations near the outfalls of the County Sanitation Districts of Los Angeles and Orange Counties and a reference station off Dana Point, California.**



attached to the top end of the pump near the water inlet. Since the overall length of the pump is 80 cm, the water inlet is approximately 2 m above the sea floor. A releasing device was also attached between the links and the pump. At the end of each sampling, a remote signal was sent to the releasing device to disengage this unit and the pump from the links. The pump and the releasing device then surfaced together by the force of buoyancy.

Before every long-term deployment, a one-hour pumping operation was conducted to determine total suspended solids (TSS) concentrations. Two replicates were taken from Station 7C during both sampling periods and from Stations R52 and T1 during the April and May 1996 sampling period. Additionally, three replicates were sampled at Station T1 (272, 288, and 1,732 L of water were sampled, respectively) during the October and November 1995 sampling period. Upon retrieval of the pump, the filters were removed and placed in petri dishes wrapped in aluminum foil. The Teflon column was also detached from the system and wrapped in aluminum foil. The filters and column were immediately transported to the laboratory in an ice chest.

As part of the QA/QC program, for each field deployment one resin column that underwent all the laboratory procedures was processed as a procedural blank and a second resin column was carried to the sampling site (uncapped during the on-board servicing of the pump) and processed as a field blank. No organochlorine compounds were detected in the blanks. However, naphthalene was detected in these samples. Although the resin columns were repeatedly washed with organic solvent, naphthalene appeared to persist and its concentration varied from column to column. The prepurified Amberlite XAD-II resins used in the spiking experiments and field measurements were purchased on different dates from the same supplier (Alltech Associates, Inc., Deerfield, Illinois). Close inspection revealed that only the XAD-II resins used

in the field measurements contained high levels of naphthalene. Therefore, naphthalene was excluded from the field measurements, but remained in the laboratory spiking data.

The target compounds and surrogate standards reported in Tables 1 through 6 are arranged by increasing retention times, which are generally proportional to the molecular weights.

#### *Sample Processing and Extraction*

Each Teflon column was spiked with the appropriate surrogate standards (field samples only) and eluted consecutively with 200 mL of methylene chloride and methanol at a flow rate of 5 mL/min. The methanol fraction was extracted three times with methylene chloride (50 mL each). The methylene chloride extracts were combined, concentrated, and solvent exchanged to hexane using a rotary evaporator at 30°C and 650 mmHg vacuum pressure. For field samples, activated copper granules were added to the extract and the container was placed in the dark overnight to remove sulfur from the extract. The extract was further concentrated to 1 mL under gentle nitrogen flow, then loaded onto a 1:2 alumina/silica gel glass column for clean-up/fractionation. The column was first eluted with 15 mL of dry hexane. The PAHs, PCBs, and DDTs were then eluted from the column with 5 mL of dry hexane and 30 mL of a 30/70 mixture of methylene chloride/hexane. The combined extract was concentrated to 1 mL using a Zymark TurboVap 500 (Zymark Corporation, Hopkinton, Massachusetts). Appropriate amounts of internal standards were added to the extract prior to instrumental analysis.

A set of eight filters from each sample were placed in two centrifuge bottles and spiked with surrogate standards. The filters were extracted three times (16, 6, and 16 h) with methylene chloride (100 mL each) using a roller table. The three extracts, taken from the same sample, were combined and processed following the same procedure used for the column extracts.

Filters from the one-hour pumping operation were dried in an oven (105°C) for approximately one hour or until their weights were constant. The TSS concentration in each one-hour pumping operation was used to approximate the concentration in the sample collected in the subsequent pumping operation.

#### *Instrumental Analysis*

PAHs were measured using a Hewlett Packard (HP) 5890 II gas chromatograph (GC) with a 5970 mass selective detector. The PCBs and DDTs were measured using an HP 5890 II GC equipped with a <sup>63</sup>Ni electron capture detector. The concentrations were determined using the internal calibration method. For PAHs, nitrobenzene-d<sub>5</sub>, 2-fluorobiphenyl, p-terphenyl-d<sub>14</sub>, and dibenzo[a,h]-

anthracene-d<sub>14</sub> were used as internal standards. For PCBs and DDTs, 2,4,6-trichlorobiphenyl (PCB Congener 30) and 3,3',4,4',5,5'-hexachlorobiphenyl (Congener 169) were used as internal standards. The detection limits for individual PAHs and organochlorines were 200 ng/g and 10 ng/mL, respectively, for 1 g of solid sample or 1 mL of liquid sample. The details of the experimental conditions have been described elsewhere (Zeng and Khan 1995).

#### *Materials*

Trace organic standards, PAHs, PCBs, and DDTs were purchased from AccuStandard, Inc. (New Haven, Connecticut) or Ultra Scientific, Inc. (North Kingstown, Rhode Island). Pesticide-grade hexane, methylene chloride, and methanol were used as supplied from Fisher Scientific, Inc. (Pittsburgh, Pennsylvania).

Empty Teflon columns were soaked overnight consecutively in methylene chloride, methanol, and methylene baths. Prepurified XAD-II resins (Alltech Associates, Inc.) were suspended in methanol and passed through a Teflon screen with 0.5 mm mesh size. After being packed into a Teflon column, the resins were washed with 200 mL of methanol and methylene chloride, respectively, and soaked in methanol until use. GF/F glass fiber filters with 47 mm and 142 mm diameters (Whatman International Ltd., Maidstone, England) were baked at 420°C for at least 4 h prior to use.

## **RESULTS**

#### *Laboratory Spiking Experiments*

*Test 1.* The recoveries of PAHs generally increased with the number of aromatic rings. For example, the average recovery of naphthalene was 59±2%, whereas that of anthracene was 84±24%. On the other hand, no notable difference between the recoveries of unalkylated and alkylated PAHs was observed (Table 1).

The recoveries of organochlorine pesticides ranged from 39 to 93%, with an average of 70±20%. The lowest recovery was with o,p'-DDD (39±3%); and the highest recovery was with o,p'-DDE (93±1%). The recoveries appeared to decrease with increasing retention time (Table 2), although the retention times of DDTs are not necessarily proportional to their molecular weights.

The recoveries were excellent for all PCB components in the on-column test and were not dependent up on their retention times or molecular weights (Table 3). The average recovery was 102±7%, with a minimum of 83±10% (PCB Congener 52) and a maximum of 109±8% (PCB Congener 200).

*Test 2.* Moderate to good recoveries were obtained for PAH surrogate standards (Table 4). Similar recoveries were also obtained for chlorinated hydrocarbon surrogates.

**TABLE 1. Recoveries (%) of PAHs in laboratory spiking experiments (Tests 1 and 3).**

PAH Compound	On-Column Elution Ave. (n=3)	Fresh Water Ave. (n=3)	Sea Water Ave. (n=3)
Naphthalene	59.0±2.0	54.0±6.9	61.0±3.6
2-Methylnaphthalene	57.8±3.6	58.9±4.9	73.9±6.7
1-Methylnaphthalene	58.4±4.2	59.3±4.4	74.3±5.7
Biphenyl	56.8±1.5	61.7±5.7	74.5±6.1
2,6-Dimethylnaphthalene	58.1±1.7	51.6±1.0	76.0±5.6
Acenaphthylene	55.3±4.5	33.5±7.4	74.4±5.4
Acenaphthene	55.7±4.3	40.3±6.0	76.3±6.3
2,3,6-Trimethylnaphthalene	58.2±7.2	45.5±6.3	78.2±2.7
Fluorene	55.5±7.3	62.4±6.1	75.7±5.6
Phenanthrene	89.6±27.8	77.9±10.0	84.6±8.7
Anthracene	84.4±23.6	59.1±43.8	75.6±5.5
2-Methylphenanthrene	77.6±15.2	72.0±7.3	79.3±8.4
1-Methylphenanthrene	91.0±20.2	79.8±6.7	91.0±9.2
3,6-Dimethylphenanthrene	87.6±14.5	82.0±2.7	97.5±9.9
Fluoranthene	84.2±7.1	85.0±6.7	94.5±6.2
Pyrene	89.7±5.9	49.4±1.9	93.8±6.6
2,3-Benzofluorene	81.0±3.5	69.1±2.7	67.6±10.8
Benzo[a]anthracene	95.3±9.8	50.4±14.5	66.5±10.2
Chrysene	92.9±11.6	82.0±2.1	53.2±7.4
Benzo[b]fluoranthene	96.9±23.5	75.7±5.3	60.6±5.0
Benzo[k]fluoranthene	88.3±20.3	59.8±3.5	36.7±9.3
Benzo[e]pyrene	98.8±32.2	63.7±5.2	48.9±5.3
Benzo[a]pyrene	100.3±28.5	32.2±3.7	39.0±3.3
Perylene	102.3±32.0	41.6±1.7	29.1±2.8
<u>Surrogates</u>			
Naphthalene-d <sub>8</sub>	54.4±1.0	54.9±6.6	61.8±2.3
Acenaphthene-d <sub>10</sub>	58.1±5.9	45.4±7.8	79.4±3.4
Phenanthrene-d <sub>10</sub>	85.7±16.6	75.4±6.4	81.3±8.0
Chrysene-d <sub>12</sub>	90.5±8.2	71.7±1.1	50.0±8.9
Perylene-d <sub>12</sub>	92.7±27.3	44.1±4.8	27.9±4.8

No PAH or chlorinated hydrocarbon target analytes were detected, indicating no noticeable level of background interference from the tap water matrix.

*Test 3.* The recoveries of 2- to 3-ring PAHs in both tap water and sea water generally increased with retention time and molecular weight (Table 1), similar to the results from Test 1. The recoveries of pyrene (2,3-benzofluorene for sea water) and heavier PAHs did not show any consistent trend.

Similar to the results obtained in Test 1, the recoveries of DDTs tended to decrease with increasing retention time for both tap water and sea water experiments (Table 2). In these two experiments, mirex had the lowest recoveries (31±3 and 22±1%, respectively).

In both tap water and sea water spiking experiments, the PCB recoveries increased slightly with the degree of chlorination for relatively low molecular weights. However, the PCB recoveries decreased substantially with an increase in molecular weight for four or more chlorine substituted compounds (Table 3).

In Tests 1 and 3, surrogate standards were also spiked into the samples prior to extraction. The recoveries of the

surrogate standards were all consistent with those of the target analytes (Tables 1 through 3), attesting to the value of surrogate standards in monitoring the performance of the sampler in field sampling.

### Field Deployments

During the October to November 1995 sampling period, most of the samples were taken using a one-day pumping operation. After assessing the preliminary results from samples collected at Station T1, another sampling was conducted with a longer pumping time to increase the sample volume and thus lower the detection limits. For the same reasons, the pumping rate set at 200 mL/min in the preliminary test at Station T1 was increased to 500 mL/min in the extended run (three days) at Station T1, in the one-day runs at Station 7C, and for the subsequent samplings during the April to May 1996 period.

In one four-day deployment, the INFILTREX 100 system (equipped with two internal lantern cells and an external battery unit packed with 27 D-size batteries) pumped through 2,012 L of water and stopped as the battery power

fell below an operational level. This volume represents approximately the maximum water sample that can be filtered and extracted by the INFILTREX 100 system with maximum power supply.

*PAHs.* At Station 7C, particulate PAHs were not detected and only low molecular weight dissolved PAHs were found in the samples collected in October and November 1995. However, the samples collected in April and May 1996 contained particulate and dissolved PAHs (Table 5). This difference can be attributed to the higher volumes of sea water pumped in April and May 1996 (1,592 and 2,012 L) than in October and November 1995 (468 and 523 L). Overall, the filtrates were dominated with alkylnaphthalenes and other low molecular weight PAHs. However, the particulates contained abundant PAHs with four or five aromatic rings. In addition, the total dissolved PAH concentrations were essentially the same in both sampling seasons: 7.5±3.3 ng/L in October and November 1995 and 8.8±2.4 ng/L in April and May 1996 (Table 5).

At Station T1, the concentrations of most PAHs were below the detectable levels (Table 5). Only the filtrates

**TABLE 2. Recoveries (%) of organochlorine pesticides in laboratory spiking experiments.**

Compound	On-Column Elution Ave. (n=3)	Fresh Water Ave. (n=3)	Sea Water Ave. (n=3)
g-BHC	81.5±8.9	74.3±1.3	83.4±8.8
Heptachlor	91.7±5.8	53.3±2.9	81.3±10.3
Aldrin	76.5±5.6	53.1±3.3	52.8±6.5
Heptachlor epoxide	89.8±7.5	83.1±3.8	88.8±7.7
o,p'-DDE	92.8±1.2	69.1±5.2	67.6±7.6
a-Chlordane	85.5±8.4	73.9±4.8	79.9±7.9
trans-Nonachlor	84.8±8.1	70.2±4.7	71.7±8.6
p,p'-DDE	81.5±4.7	55.8±4.4	49.6±7.0
Dieldrin	40.1±3.6	77.2±3.5	84.9±7.2
o,p'-DDD	38.6±2.8	71.2±1.6	77.1±9.0
Endrin	71.5±1.4	103.3±2.0	108.0±7.4
p,p'-DDD	61.1±1.3	75.8±4.9	79.7±7.1
o,p'-DDT	46.1±1.0	70.6±6.6	63.9±8.8
p,p'-DDT	60.9±3.6	73.4±9.7	66.1±9.0
Mirex	39.7±1.8	31.1±2.8	22.1±1.2
<u>Surrogates</u>			
PCB 65	95.2±2.1	76.4±1.1	77.5±8.3
PCB 189	56.2±5.0	40.8±1.4	25.6±0.8

**TABLE 3. Recoveries (%) of PCBs in laboratory spiking experiments.**

PCB Congener	On-Column Elution Ave. (n=2) <sup>a</sup>	Fresh Water Ave. (n=3)	Sea Water Ave. (n=3)
8	107.9±18.3	91.3±34.6	81.6±12.5
18	107.1±6.1	102.6±9.2	123.8±7.1
29	112.5±17.5	103.3±10.8	117.8±18.3
50	108.1±15.5	90.5±11.0	99.4±8.6
28	92.5±18.1	93.7±8.3	101.9±14.4
52	82.7±9.5	82.9±5.9	82.3±6.2
104	99.9±13.2	90.2±7.7	75.5±10.3
44	99.4±12.8	95.2±9.7	99.3±12.5
66	103.1±7.6	88.9±11.3	89.4±13.2
101	102.3±11.8	76.1±8.6	71.1±7.1
87	104.1±7.1	76.9±10.5	73.0±9.5
77,154	101.3±9.6	74.8±6.6	69.3±7.5
118	99.6±12.3	69.2±10.0	61.8±6.5
188	107.5±11.1	56.1±8.6	48.3±3.3
153	104.8±11.6	62.3±9.8	54.5±2.2
126	103.8±13.6	75.2±13.9	68.7±4.1
187	106.4±10.6	57.5±10.1	47.9±2.0
128	101.1±10.0	61.2±10.3	54.4±1.9
200	109.2±7.9	51.8±6.3	45.3±3.3
180	103.0±10.3	50.8±7.6	42.4±1.7
170	98.7±9.5	49.0±7.8	41.7±0.7
195	97.6±9.3	45.5±7.8	39.4±2.4
206	94.4±8.9	43.4±8.7	39.9±4.5
209	92.3±7.5	42.2±7.2	35.7±1.7
<u>Surrogates</u>			
65	87.2±10.1	82.4±6.1	87.8±8.9
189	87.5±7.0	43.5±3.9	35.2±0.8

<sup>a</sup>One replicate was partially lost during column elution.

**TABLE 4. Recoveries (%) of PAH and PCB surrogate standards in the retainability test.**

Surrogate Standard	Recovery (%)
PAHs:	
naphthalene-d <sub>3</sub>	42
acenaphthalene-d <sub>10</sub>	78
phenanthrene-d <sub>10</sub>	117
chrysene-d <sub>12</sub>	114
perylene-d <sub>12</sub>	50
PCB congeners:	
65	72
189	50

contained a few detectable PAHs with relatively low molecular weights. The samples collected from Station R52 in April and May 1996 contained no detectable PAHs.

*DDTs.* Among 15 chlorinated pesticides measured, only 7 were detected at least once in the field samples (Table 6). The total concentration was highest at Station 7C and lowest at Station R52, when the samples collected in April and May 1996 were compared (Table 7). The concentrations of detectable p,p'-DDT were substantially lower than most of its metabolite products (Table 6). The average concentration of total DDTs at Station 7C was 8.4±4.5 ng/L, comparable to the concentration of 3.8±1.9 ng/L determined by Green *et al.* (1986) in 1984 using an *in situ* water sampler deployed at a depth of 20 m near one of the unused JWPCP outfalls.

*PCBs.* Only a few PCB congeners were detected in the filtrates collected from Station 7C in April and May 1996, where large volumes of sea water were pumped (1,592 and 2,012L). The concentration of total PCBs was 4.3±2.1 ng/L (Table 7). It should be noted that the previous study by Green *et al.* (1986) did not report any PCBs with an average sample volume of 94±10 L of water (n=7).

## DISCUSSION

The results of the laboratory spiking experiments from this study suggest that the performance of the INFILTREX 100 sampler was satisfactory. In addition, the INFILTREX 100 sampler was capable of filtering and extracting trace chemicals from more than 2,000 L of sea water in a single deployment without encountering significant background interference. The large volumes of water sampled utilizing this instrument enabled the detection of many trace organics, including PAHs, DDTs, and PCBs, that were nondetectable with lower sample volumes. Several issues relative to the performance of the

**TABLE 5. Concentrations of PAH compounds in southern California coastal waters.<sup>a</sup>**

PAH Compound	7C				T1			
	Oct/Nov 95		Apr/May 96		Oct/Nov 95		Apr/May 96	
	Filtrate (ng/L)	Particulate (ng/g)						
2-Methylnaphthalene	2.3±0.8	ND	1.5±0.5	ND	ND to 1.6	ND	ND to 0.13	ND
1-Methylnaphthalene	1.7±0.6	ND	1.1±0.4	ND	ND to 1.1	ND	ND	ND
Biphenyl	0.57±0.22	ND	3.3±0.5	ND	ND to 0.51	ND	ND	ND
2,6-Dimethylnaphthalene	0.92±0.24	ND	0.70±0.26	ND	ND to 0.78	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND to 0.10	ND	ND	ND	ND	ND
2,3,6-Trimethylnaphthalene	ND	ND	0.22±0.10	ND	ND	ND	ND	ND
Fluorene	ND	ND	0.19±0.08	ND	ND	ND	ND	ND
Phenanthrene	0.69±0.31	ND	0.30±0.10	ND	ND to 0.14	ND	ND	ND
Anthracene	ND to 0.50	ND	0.17±0.09	ND	ND	ND	ND	ND
2-Methylphenanthrene	ND to 0.58	ND	0.26±0.07	ND	ND	ND	ND	ND
1-Methylphenanthrene	ND to 0.40	ND	0.17±0.04	ND	ND	ND	ND	ND
3,6-Dimethylphenanthrene	ND to 0.48	ND	0.20±0.04	ND to 8.4	ND	ND	ND	ND
Fluoranthene	ND	ND	0.14±0.01	6.1±0.3	ND	ND	ND	ND
Pyrene	ND	ND	0.28±0.11	11.0±0.4	ND	ND	ND	ND
2,3-Benzofluorene	ND	ND	ND to 0.18	ND to 6.3	ND	ND	ND	ND
Benzo[a]anthracene	ND	ND	ND to 0.15	ND to 6.0	ND	ND	ND	ND
Chrysene	ND	ND	ND to 0.17	ND to 8.7	ND	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND	9.6±1.6	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND	10.2±0.9	ND	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND	11.5±1.1	ND	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	ND to 10.3	ND	ND	ND	ND
Perylene	ND to 0.67	ND	ND	ND to 15.1	ND	ND	ND	ND
Total PAHs (ng/L or ng/g dry wt.)	7.5±3.3	ND	8.8±2.4	75.8±21.8	ND to 4.1	ND	ND to 0.13	ND
<b>Surrogate Recoveries (%)</b>								
Naphthalene-d <sub>8</sub>	43.7±5.7	29.3±4.3	45.2±6.2	29.5±9.1	23.8±13.4	23.5±5.4	44.1±4.1	28.6±4.0
Acenaphthene-d <sub>10</sub>	70.1±1.1	52.2±8.0	71.2±8.2	66.1±3.6	55.8±9.0	37.1±9.4	61.2±2.2	47.7±5.3
Phenanthrene-d <sub>10</sub>	94.4±5.0	74.8±9.8	71.1±3.8	71.0±0.1	87.3±6.9	47.2±11.0	73.3±2.1	64.3±9.1
Chrysene-d <sub>12</sub>	88.6±11.4	79.2±8.8	83.2±10.3	86.5±3.9	94.9±37.3	54.6±9.9	70.6±0.6	58.3±9.5
Perylene-d <sub>12</sub>	99.7±5.2	55.3±9.9	93.4±12.3	103.6±4.8	116.9±36.0	44.8±7.5	60.5±6.6	55.6±7.4

<sup>a</sup> PAHs were not detectable in the R52 samples collected in April 1996.  
 ND = Not detected.

INFILTREX 100 sampler in laboratory spiking experiments and off-shore deployments are discussed below.

*Recovery Efficiency and Retainability*

The efficiency of the INFILTREX 100 in recovering trace organics is governed by several physiochemical processes, such as the affinity of the organic compounds to the packing resins and their desorption from the column by solvent elution. As presented previously, the recoveries from the on-column elution (Test 1) were excellent for PCBs, generally increased with the retention times of PAHs, and decreased with the retention times of DDTs (Tables 1 through 3). The low recovery rates for low molecular weight PAHs most likely resulted from losses incurred during the evaporation steps required to concentrate the

samples (Zeng and Khan 1995, Kootstra *et al.* 1995), rather than the low efficiency of desorption from the column. The low recovery rates for some chlorinated pesticides (e.g., dieldrin, mirex, o,p'-DDD, and o,p'-DDT) in the on-column elution (Table 2) are not yet understood. In summary, the results from the on-column elution experiments suggest that the elution method using methanol and methylene chloride at an eluting rate of 5 mL/min was extremely effective in recovering PAHs and PCBs from the Amberlite XAD-II resins; the elution of chlorinated pesticides was moderately effective. These results ensured that the subsequent experiments (Tests 2 and 3) were generally not affected by the solvent elution.

The results from Test 2 (Table 4) indicated that the low to middle molecular weight PAH and PCB compounds were

well retained in the resins-packed column during long-term pumping (623 L of water). However, the heavy PAHs and PCBs (perylene-d<sub>12</sub> and PCB Congener 189 as representatives) did not fare as well as the lighter compounds. The limited capacity of the column to retain high molecular weight organic compounds may also have partially caused low recoveries to retain high molecular weight PAHs and PCBs in the overall efficiency test (Test 3), in addition to other factors discussed below.

#### *Overall Laboratory Performance*

Overall laboratory performance is a product of recovery efficiency, retainability, matrix effect, and interference from sample containers, etc. As shown in Tables 1 and 3, the recoveries of PAHs and PCBs from tap water and sea water were consistent in both experiments; however, they were not as efficient as those obtained by on-column elution. Sample matrices were excluded as a negative factor. The recovery efficiency was also not a factor, since efficient recoveries were generally obtained for all the target compounds considered (especially PAHs and PCBs). As discussed above, the high molecular weight PAHs and PCBs may not have been efficiently retained by the resins-packed column. However, only 5 L of water were used in Test 3 compared to the large quantity of water (623 L) used in Test 2. Hence, retainability should account for some but not all of the losses.

In Test 3, the targeted analytes were spiked into a clean glass bottle filled with prefiltered tap water or sea water. Due to the low solubility of some compounds, particularly those of relatively high molecular weights, an organic solvent such as methanol or acetone was added to solubilize the organics. The solution was then equilibrated overnight before being pumped through the column. Nevertheless, we suspect that adsorption of the organic compounds to the glass bottle may have occurred and resulted in reduced concentrations of the analytes in the water compared to the initial spiking concentrations used to calculate the recoveries. The losses of spiked hydrophobic organics due to adsorption to the glass wall containers have been documented. In general, the adsorption of many targeted analytes including PAHs, PCBs, and DDTs were found to increase with their corresponding molecular weights as found in a recent related study (Tran and Zeng, unpublished results). Previously published results also showed that high molecular weight PAHs generally experienced higher losses to glass containers than their low molecular weight counterparts (Zeng and Khan 1995, Fladung 1995).

#### *Field Application*

The field data (Tables 5 through 7) indicated that sampling a large volume of water was necessary to concen-

trate many trace organics in the open waters to currently detectable levels. For example, no PCB congeners were detected in the samples collected in October and November 1995 when less than 500 L were filtered. However, a concentration of  $4.3 \pm 2.1$  ng/L was obtained for total PCBs in the samples collected in April and May 1996 when 1,800 L were filtered. Similarly, no PAHs were found in the particulate samples of October and November 1995, while a few PAHs were detected in the April and May 1996 samples. Thus, the extended pumping capability of the INFILTREX 100 equipped with an external battery package allowed detection of many trace organic contaminants at ultra-low concentrations in the southern California coastal environment.

Since no comparable results have been obtained using alternative sampling techniques, the field data from this study could not be verified directly. However, the spatial differences in these concentrations can be compared against the sediment contaminations at the same locations. The dry weight-based concentrations of p,p'-DDE in the surficial sediments collected from Stations 7C, T1, and R52 in April and May 1996 (the same period in which the water column samples were collected) were  $7,880 \pm 930$ ,  $1.50 \pm 0.26$ , and  $5.28 \pm 0.67$  ng/g, respectively (Tran and Zeng, unpublished results). By comparison, the p,p'-DDE concentrations in the water column particulates at Stations 7C, T1, and R52 were  $174.3 \pm 5.0$  ng/g,  $0.74 \pm 0.15$  ng/g, and  $0.90 \pm 0.66$  ng/g, respectively (Table 7), consistently reflecting these trends.

The filter assembly component of the INFILTREX 100 was designed to retain particulates only. However, Osterroht (1974) reported that the microglass filters might also retain dissolved organic contaminants in addition to particles and thus reduce the concentrations of dissolved organics extracted by the resin column. Although further investigations into this operational effect are beyond the scope of this study, caution should be exercised if results obtained with this technique are to be used to derive partitioning coefficients.

#### **LITERATURE CITED**

- Ehrhardt, M.G. and K.A. Burns. 1990. Petroleum-derived dissolved organic compounds concentrated from inshore waters in Bermuda. *Journal of Experimental Marine Biology and Ecology* 138:35-47.
- Farrington, J.W., E.D. Goldberg, R.W. Risebrough, J.H. Martin and V.T. Bowen. 1983. U.S. "Mussel Watch" 1976-1978: An overview of the trace-metal, DDE, PCB, hydrocarbon, and artificial radionuclide data. *Environmental Science and Technology* 17:490-496.
- Fladung, N.C. 1995. Optimization of automated solid-phase extraction for quantitation of polycyclic aromatic hydrocarbons

**TABLE 6. Concentrations of organochlorine pesticide compounds in southern California coastal waters.**

Compound	7C				T1			
	Oct/Nov 95		Apr/May 96		Oct/Nov 95		Apr/May 96	
	Filtrate (ng/L)	Particulate (ng/g)						
g-BHC	0.12±0.04	ND	0.12±0.02	ND	0.059±0.002	ND	0.0902±0.0004	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND to 0.009	ND
o,p'-DDE	0.52±0.02	3.1±0.7	0.90±0.29	31.7±3.4	ND	ND	0.020±0.009	ND
p,p'-DDE	2.5±0.7	26.0±5.1	4.5±2.4	174.3±5.0	ND to 0.045	ND to 0.19	0.15±0.08	0.74±0.15
o,p'-DDD	0.17±0.04	0.77±0.07	0.31±0.16	8.5±0.5	ND	ND	0.0092±0.0007	ND
p,p'-DDD	0.62±0.20	2.1±0.2	0.75±0.39	14.8±0.7	ND	ND	0.0084±0.0030	ND
p,p'-DDT	0.028±0.000	1.1±0.3	0.28±0.11	4.0±0.5	ND	ND		ND
Total	3.9±0.5	33.0±5.7	6.8±3.3	233.4±7.8	0.074±0.024	ND to 0.19	0.28±0.10	0.74±0.15
<u>Surrogate Recoveries (%)</u>								
TCX	25.7±11.5	34.8±0.7	18.2±5.0	20.0±9.9	39.2±19.7	50.6±36.1	17.7±10.9	34.4±7.0
PCB 65	55.0±22.7	69.9±15.1	87.1±4.3	70.3±3.4	63.0±7.5	89.6±30.8	68.8±27.6	68.3±3.3
PCB 189	57.1±47.8	79.2±11.6	70.4±1.9	66.0±13.8	74.1±5.6	90.6±34.2	57.3±33.0	61.3±1.4

ND = Not detected.

in aqueous media by high-performance liquid chromatography. *Journal of Chromatography A* 692:21-26.

Green, D.R. and D. Kowalski. 1984. Amberlite XAD-2 resin columns - Documentation of their performance in the extraction of organics from water. Axys Environmental Systems Ltd., Sidney, B.C. 71 p.

Green, D.R., J.K. Stull and T.C. Heesen. 1986. Determination of chlorinated hydrocarbons in coastal waters using a moored *in situ* sampler and transplanted live mussels. *Marine Pollution Bulletin* 17:324-329.

Hofelt, C.S. and D. Shea. 1997. Accumulation of organochlorine pesticides and PCBs by semipermeable membrane devices and *Mytilus edulis* in New Bedford Harbor. *Environmental Science and Technology* 31:154-159.

Huckins, J.N., G.K. Manuweera, J.D. Petty, D. Mackay and J.A. Lebo. 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environmental Science and Technology* 27:2489-2496.

Kennish, M.J. 1997. Practical handbook of estuarine and marine pollution. CRC Press, Boca Raton, Florida. 524 p.

Kootstra, P.R., M.H.C. Straub, G.H. Stil, E.G. van der Velde, W. Hesselink and C.C.J. Land. 1995. Solid-phase extraction of polycyclic aromatic hydrocarbons from soil samples. *Journal of Chromatography A* 697:123-129.

Nichols, P.D. and Q.I. Espey. 1991. Characterization of organic matter at the air-sea interface, in subsurface water, and in bottom sediments near the Malabar sewage outfall in Sydney's

coastal region. *Australian Journal of Marine and Freshwater Research* 42:327-348.

Osterroht, C. 1974. Development of a method for the extraction and determination of non-polar, dissolved organic substances in sea water. *Journal of Chromatography* 101:289-298.

Petty, J.D., J.N. Huckins, C.E. Orazio, J.A. Lebo, B.C. Poulton, R. W. Gale, C.S. Charbonneau and E.M. Kaiser. 1995. Determination of waterborne bioavailable organochlorine pesticide residues in the lower Missouri River. *Environmental Science and Technology* 29:2561-2566.

Sojo, L.E. and D.J. Miege. 1994. Test of Infiltrax II linearity for hexachlorocyclohexane pesticides in Patricia Bay, Sidney, British Columbia. Axys Environmental Systems Ltd., Sidney, B.C. 10 p.

Southern California Coastal Water Research Project. 1986. Characteristics of municipal wastewater in 1984 and 1985. pp.1-5 in J. Anderson (ed.), Southern California Coastal Water Research Project Annual Report 1986. Long Beach, CA.

Young, D.R., T.C. Heesen and D.J. McDermott. 1976. An offshore biomonitoring system for chlorinated hydrocarbons. *Marine Pollution Bulletin* 7:156-160.

Zeng, E.Y. and A.R. Khan. 1995. Extraction of municipal wastewater effluent using 90-mm C-18 bonded disks. *Journal of Microcolumn Separations* 7:529-539.

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R52	
Apr/May96	
Filtrate (ng/L)	Particulate (ng/g)
0.070±0.003	ND
ND	ND
0.0085±0.0008	ND
0.085±0.011	0.90±0.66
ND to 0.0054	ND
ND to 0.0067	ND
ND	ND
0.17±0.02	0.90±0.66
10.5±3.5	9.49±1.11
84.3±5.9	64.5±0.3
70.8±19.3	56.9±0.9

**TABLE 7. Total concentrations (ng/L) of trace organics in southern California coastal waters.**

Ave. Vol., L	7C		T1		R52	
	Oct/Nov 95 496	Apr/May96 1802	Oct/Nov 95 764	Apr/May96 1691	Oct/Nov 95 NA	Apr/May96 1667
PAHs	7.5±3.3	10.4±2.9	4.1±4.7	ND	NA	ND
DDTs	5.4±0.1	11.7±3.6	0.10±0.01	0.30±0.14	NA	0.200±0.001
PCBs	ND	4.3±2.1	ND	ND	NA	ND

ND = Not detected.  
NA = Not available.