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Measurement of a Time-Weighted Average Concentration of Polycyclic Aromatic Hydrocarbons in Aquatic Environment Using Solid Phase Extraction Cartridges and a Portable Pump

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There have been several different methods of measurement for waterborne pollutants. The most frequently utilized method for sample preparation has been a liquid-to-liquid partition or a liquid-to-solid partition. In these methods, pollutants such as polycyclic aromatic hydrocarbons (PAHs) are extracted to organic solvents directly from the sample water, or the pollutants are once adsorbed to solid phase adsorbent, and subsequently eluted with organic solvents. In either case, the measured level represents at the time of the sampling, namely a spot-sampling. On the other hand, a time-weighted average concentration (TWA) has been used as a determinant to evaluate an atmospheric environment. But it has been an elaborated work for us to estimate TWA of pollutants in water, since a frequent spot-sampling of water is required at a field site. Further no data on the TWA of PAHs in the field water has been published, however the TWA of pollutants could be an important factor for a chronic effect on biota.

In our previous report (Kira et al., 1996), we set up a continuous sampling device, using Sep-Pak C18 cartridge and a peristaltic pump, which enabled us to measure a TWA of benzo(a)pyrene in an experimental water system. The present paper describes a portable sampling device that can continuously sample PAHs in water. We have evaluated basic characteristics of the sampling device in the laboratory, and optimized chromatographic detection of 4 PAHs, fluoranthene, perylene, benzo(b)-fluoranthene (BbF) and benzo(a)pyrene (BaP). After these procedures, we have brought this sampling device to field water sites to verify its performance. The levels of PAHs was calculated as TWA for 24 hr period of time in water at a site.

MATERIALS AND METHODS

Figure 1 shows the block diagram of a portable device that was designed to sample PAHs in the water continuously for 24 hr. A peristaltic pump with three channels (SJ-121lHS, Atto, Tokyo, Japan), and two batteries than 24 hr (12V-6.5 ampere-

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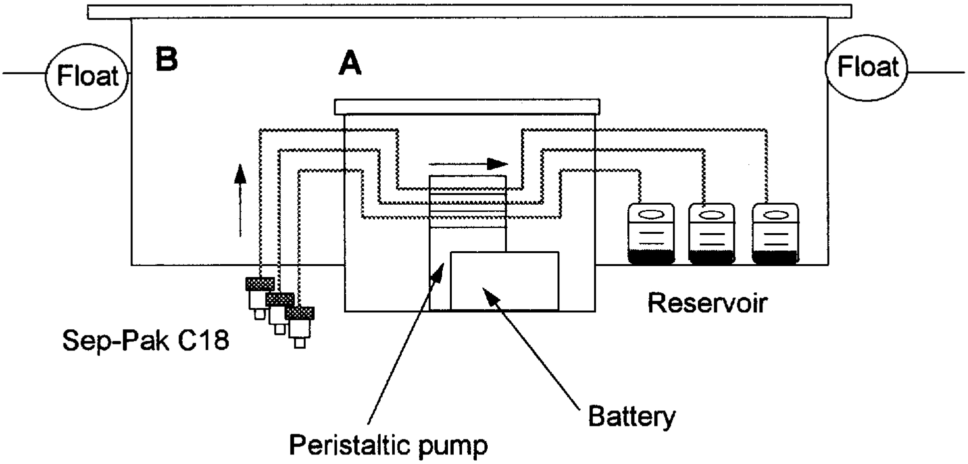

Figure 1. A block diagram of the portable sampler.
A: A stainless steel container that holds a peristaltic pump and batteries, B: a plastic case that holds the stainless steel container (A), tubing, and reservoir bags. See text for details.

hour, Nihon Battery, Tokyo, Japan) were sealed in a waterproof stainless steel container (A in Figure 1). The batteries had enough capacity to drive the pump for more more than 24 hr without significant decline in the power output. Each of three solid phase extraction cartridges (Sep-Pak C18 Plus Environmental, Waters, Massachusetts, USA) was connected to tubing (ID 3.20 mm, OD 6.00 mm), which passed through one of the three channels of the pump. The other end of the tubing was connected to a reservoir bag (urine collection bags for clinical use). The stainless steel container and the three reservoir bags were placed on the bottom of a plastic case (42 x 60 x 20 cm; B in Figure 1). The cartridge-side of the tubing penetrated the bottom of the case, and the cartridge was hanging into the water. Empty plastic bottles were attached to the plastic container as floats. The dry weight of the sampling device was less than 10 kg. During the sampling procedure, water was continuously passed through the cartridge, and stored in the reservoir bag, while PAHs were adsorbed to the cartridge. The flow-rate was initially set to be about 1 ml/min.

Collection of samples was carried out 6 times during the period from March 9, 1994 to January 7, 1995 at two sampling sites in the Seto Inland sea of Japan. One of the sampling site was at an industrial area (Site 1: Mizushima Port, Okayama, Japan), which is surrounded by petrochemical factories and power plants. The other sampling site was a resort area (Site 2: Ushimado, Okayama, Japan), which is remote from the industrial region. The portable sampling device was moored on the sutiace of the sea water at each sampling site for 24 hr. The volume of sea water that was stored in the reservoir bags was measured immediately after the sampling. Then, the TWA of PAHs was calculated according to previous reports (Ashton and Gill, 1992; Kira et al., 1996).

The extraction cartridges were then brought back to our laboratory, and the adsorbed fluoranthene, perylene, BbF and BaP were recovered according to our previous report (Kira et al., 1996). Briefly these PAHs were eluted together from extraction cartridge with 2 ml, l-3 ml portion, of tetrahydrofurane; the eluate was evaporated to dryness under a stream of nitrogen, then the residue was dissolved in 0.2 ml of methanol to obtain the final sample for analysis of PAHs.

For the analysis of each PAH, we used a Waters 600E system with a Roedyne 7125 injector. A Nova-Pak Cl8 column (ϕ−3.9 x 150 mm, mesh 4µm, Waters, Millipore) was coupled with fluorometric detection. The column was kept at 40 ° C and was eluted with acetonitrile/water (65/35) at a flow rate of 1.0 ml/min. The fluorospectrophotometer (F-1080, Hitachi, Tokyo, Japan) was set at suitable excitation (EX) and emission (EM) wavelengths for detecting each PAH; fluoranthene (EX: 289 nm, EM: 438 nm), perylene (EX: 407 nm, EM: 438 nm), BbF (EX: 300 nm, EM: 43lnm), BaP (EX: 365 nm, EM: 405 nm). The peak area of the spectra was recorded with an integrator (Hitachi D-2500). All solvents used for elution and HPLC analysis were of HPLC grade purchased from Wako Pure Chemicals (Osaka, Japan).

A preliminary study on the levels of PAHs in field water using Sep-Pak C18 was done. Then we predicted l-5 ng of PAH to be recovered after passing 1.5 L water, and day-to-day variance was observed (unpublished data). Therefore the recovery of each PAH was tested after spiking 5 ng (0.05 ml of 100 ng/ml methanol solution) of them each into the top layer of a Sep-Pak Cl8 cartridge followed by passing distilled water (1443+/-241 ml, n=3) for 24 hr in our laboratory. The results were 79.2+/-13.8% for fluoranthene, 104.4+/-6.3% for perylene, 80.0+/-6.6% for BbF and 107.0+/-5.8% for BaP. All PAHs used were purchased from Nakalai Co, Tokyo, Japan.

RESULTS AND DISCUSSION

The main purpose of this project was to develop a new system that can measure TWA of waterborne PAHs at low level. The device was brought to previous sampling sites (Kira et al., 1989; Kira et al., 1995) to evaluate its performance. Six experiments were carried out, and 12 out of 18 cartridges passed more than 600 ml of water without pre-filteration during 24 hr period of time. Based on the sampling volume of 600 ml, practical detection limits calculated for 4 PAHs were 0.17, 0.03, 0.13 and 0.05 ng/L for fluoranthene, perylene, BbF and BaP respectively. The results of the present experiment were summarized in Table 1. All TWAs of 4 PAHs measured here were lower than 10 ng/L and the data were agreeable to the published one that was performed by the Environmental Protection Agency of Japan in 1993 (Environment Agency, 1994): the agency reported “not detected or less than 10 ng/L”, however the survey monitored PAH levels by a “spot-sampling” at a time.

Table 1. Time weighted average concentration of PAHs in two sampling sites in Seto Inland Sea of Japan

date and site	sampled water (ml/day)	fluoranthene (TWA [c] ng/L)	perylene (TWA [c] ng/L)	BbF [a] (TWA [c] ng/L)	BaP [b] (TWA [c] ng/L)
Site 1 (Mizushima)					
9-Mar-94	1160	3.72	0.18	0.17	0.34
9-Mar-94	1400	5.84	0.09	0.14	0.17
9-Nov-94	820	3.34	1.36	0.60	1.82
9-Nov-94	650	3.50	1.83	0.52	3.12
7-Jan-95	1270	3.63	0.24	0.16	0.59
7-Jan-95	1070	1.12	0.28	ND [d]	0.15
Site 2 (Ushimado)					
9-Mar-94	640	1.16	0.10	ND [d]	0.16
1-Jun-94	1520	1.13	0.21	0.43	0.42
1-Jun-94	600	1.40	0.11	ND [d]	0.23
1-Jun-94	680	1.38	0.13	ND [d]	0.41
18-Oct-94	720	1.77	0.61	0.23	1.07
18-Oct-94	950	1.32	0.38	0.14	0.65

[a] BbF: benzo(b)fluoranthene, [b] BaP: benzo(a)pyrene, [c] Time-weighted average for 24 hr period, [d] ND: not detected

Previously reported solid phase extraction-HPLC analysis methods (Lai and White, 1995; Fladung, 1995) use small amount of water sample. These methods could monitor the level of PAHs for a designated interval with automated equipments, including adsorption, extraction and HPLC analysis procedure. So that these sophisticated methods may require more power supply for the operation and these devices may be heavier than ours. Hence their methods and devices may not be necessarily suitable for on-site sampling in the field water.

Comparing the TWA levels of PAHs monitored at 2 sites in the present study, all of them at site 1 showed higher level than those at site 2. This tendency was in accordance with our previously reported results (Kira et al., 1995) obtained by hanging blue rayon (Hayatsu, 1992), which is another time-weighted measurement that can be used for waterborne polycyclic mutagens. At site 1, our previous results show BaP level within 0.9-12.0 ng / g Blue Rayon Equivalent (BRE) for 24 hr, and 0.8-10.2 ng /g BRE at site 2, respectively. While the data that are obtained by the blue rayon hanging method are affected by the intensity of ambient water movement as was indicated in our previous study (Kira et al., 1996), such an influence of water movement was negligible with the proposed method under a normal condition at sea shores or lakes. Therefore, we consider that our device could be used to calibrate measurements by blue rayon hanging method or any other methods that can measure TWA of low level pollutants. Ongoing experiment that would prove this hypothesis will be reported shortly.

In addition, the present sampling procedure has several advantages over conventional methods. The target substances are not limited to PAHs, and other classes of pollutants in water could be easily sampled and be calculated TWAs of these pollutants. For example, it may be possible to monitor pesticides simply by changing the elution methods. By using several different kinds of extraction cartridges with solid phase adsorbent, simultaneous measurement of different substances is also possible. There are many types of cartridges that could be used for this purpose, which are commercially available. In fact, extraction cartridges with a new material such as blue chitin (advanced version of blue rayon, Hayatsu et al, 1996) are available, and the cartridge may collect PAHs and other polycyclic mutagens, as well as blue rayon, simultaneously. This possibility is currently under investigation.

There are, however, several disadvantages of our system that might have to be improved. First, water-flow may become unstable when the water contains many suspended particulates that would be trapped in the extraction cartridge. This problem occurs when water is cloudy and the capacity of the battery is small, even if a pre-filter was connected to the cartridge serially. To prevent the problem, we have tried parallel connection of batteries. Second, the power supply and the pump costs more than the normal running cost of conventional method. However, if we compare the time- and chemical-consuming nature of the conventional method with the convenience of the proposed method, the initial cost for the proposed method seemed acceptable.

In conclusion, we have reported new sampling device that can measure a TWA of waterborne PAHs. The application of the device in the Seto Inland Sea has shown that levels of four different PAHs were in less than 10 ng/L range in this area.

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