

A Study on the Measurement of Time-Weighted Average Value of Benzo (a) pyrene in Surface-Water without Power Supply

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Abstract

We attempted to estimate one-week average value of a water pollutant, benzo (a) pyrene (BaP), with a new sampling method in a laboratory. In result, it was considered that the sampling method was useful for the estimation of time-weighted average value for 7 days on surface-water contained BaP of ppb level.

However, it was difficult to apply the sampling method in field, because concentrations of BaP in water of river, lake and sea were too low, namely ppt level, to detect by this sampling procedure.

1. Introduction

There are many reports on examination of mutagenicity and/or levels of polycyclic aromatic hydrocarbons (PAHs) in natural water such as rivers and lakes. Their results are usually represented at the time of the sampling, namely spot-sampling. A frequent spot-sampling of water at the same site is often required to obtain objective estimation, with much time and efforts.

In our previous report¹⁾, the mutagenicity and BaP pollution of the seawater were monitored for one day by hanging blue rayon (BR), that adsorbs specifically PAHs with three or more fused rings²⁾. In addition, we reported a method to obtain one day-TWA of PAHs using solid phase extraction cartridges and a portable pump³⁾.

This time, we set up a sampler to obtain one week-TWA of BaP in surface-water without power supply: a modified sampler reported by us previously⁴⁾. Then we tested its performance using experimental aquarium with BaP dosing column.

2. Materials and Methods

The experimental apparatus used here was a modification of a system reported

previously⁵⁾. We prepared a laboratory glass aquarium, 65(w)×30(d)×35(h) cm in size containing 30 L water at the start of the experiment. The water containing BaP (Tokyo Kasei Co., Tokyo, Japan) was continuously supplied from a dosing column at a flow rate of 20-30 mL/min (Fig. 1).

When the BaP concentration of test water became constant, the water was sampled continuously with TWA-sampler shown in Fig. 2 within a certain period of time. The water was slowly sucked up from the bottom end of the sampling pipe filled 0.5 g BR (Funakoshi Chemicals, Tokyo, Japan) due to the capillary potential. The water volume passed through the sampling pipe was estimated by the weight-difference of silica gel in airtight box (chamber).

BaP in the aquarium water was quantified from spot-samples obtained periodically by extraction with petroleum ether⁶⁾. Procedures for BaP extraction from BR were described in a previous report⁷⁾.

For the analysis of BaP with HPLC (Tosoh Co., Tokyo, Japan), a column of

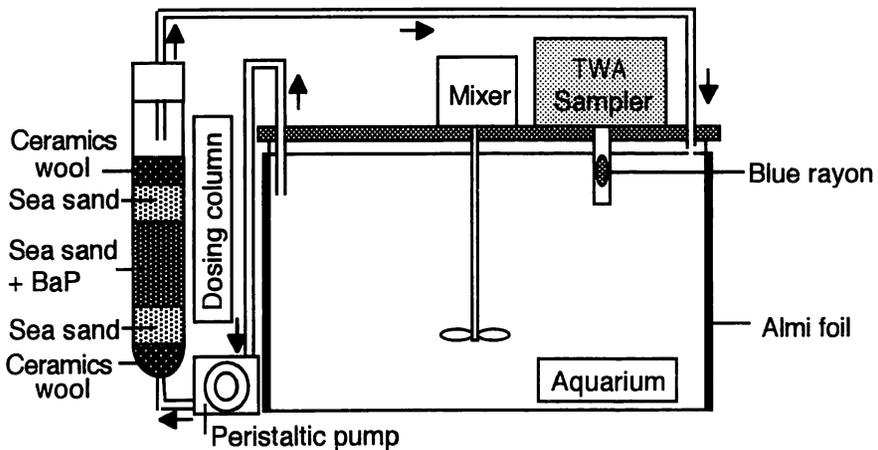


Fig. 1 A schematic diagram of experimental system

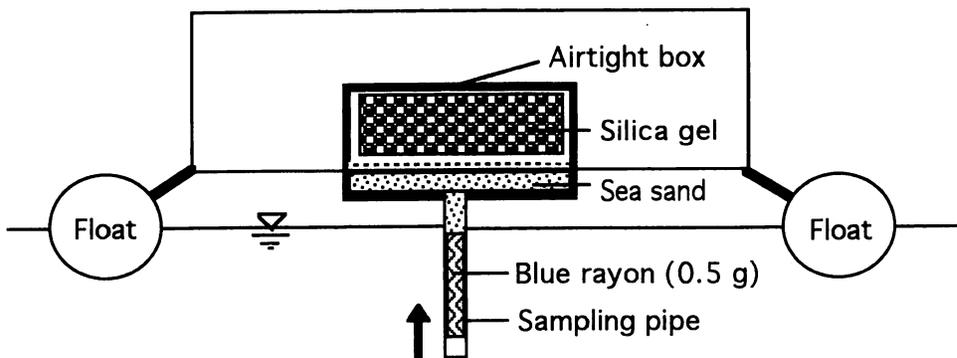


Fig. 2 A schematic diagram of TWA Sampler
(Theoretical vapor-area of sea sand is 113 cm².)

Nova-Pak C18, 4 micrometer, 150×3.9 mm (Waters, Millipore Co.) coupled with fluorometric detection was used. The column, which was maintained at 40 degree by use of an oven, was eluted with acetonitrile-water (65:35) at a flow rate of 1 mL/min. The fluorometer was set at 365 nm for excitation and at 405 nm for emission.

3. Results and Discussion

BaP-concentration in aquarium

Fig. 3 shows an example of time course of BaP concentration in the glass aquarium. The concentration was stable after 4 days and the BaP level was maintained at about 0.2 ppb, regardless of the operation condition such as a size of dosing column and flow rate of the water. Thereafter it was difficult to obtain a desired level of BaP with the experimental apparatus.

Water-volume passed through the sampling pipe

At first, we confirmed that the increase of weight of silica gel in the box (chamber) was water-volume passed through the sampling pipe in a sampling period (Table 1). The increase of weight of silica gel was proportional nearly with days of sampling, though the increase-rate decreased gradually with the lapse of sampling days (Fig. 4).

When we placed 200 g silica gel in the box, the increase rate was constant during about for 10 days. Though a little effect of water temperature on the increase in the rate was observed, the amount of water passed through the sampling pipe was within the limit of error of repeat-measurement.

Recovery rate of BaP from BR

We examined recovery rate of BaP from BR as follows. That is, BaP solution of a constant volume was added to BR, and the BaP adsorbed to BR was eluted with

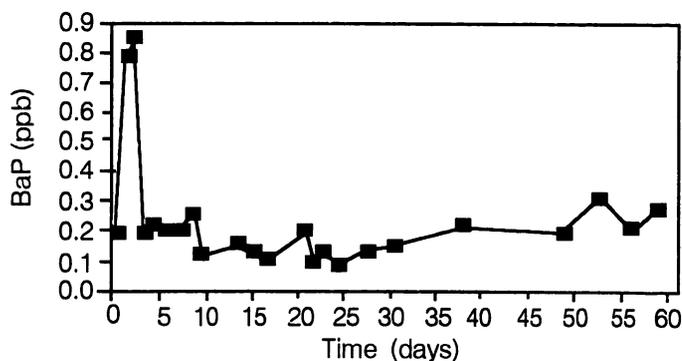


Fig. 3 Time course of BaP concentration in aquarium

Table 1 Examination on leak of air into airtight box filled with silica gel

time elapsed (days)	3	5	7	10
increase of silica gel (g)	1.26	1.68	2.02	2.43
rate of increase of silica gel (g/d)	0.42	0.34	0.29	0.24

methanol-concentrated ammonia (50:1). The recovery rate of BaP from BR was about 40 % by the single extraction (Table 2).

TWA during one week

Table 3 shows some examples of BaP amount obtained by continuous sampling during one week. TWAs during one week (TWA-7d) were estimated from their data. Their values were near to average concentration of BaP during sampling period in the aquarium. Then, we considered that the sampling method was useful for estimation of

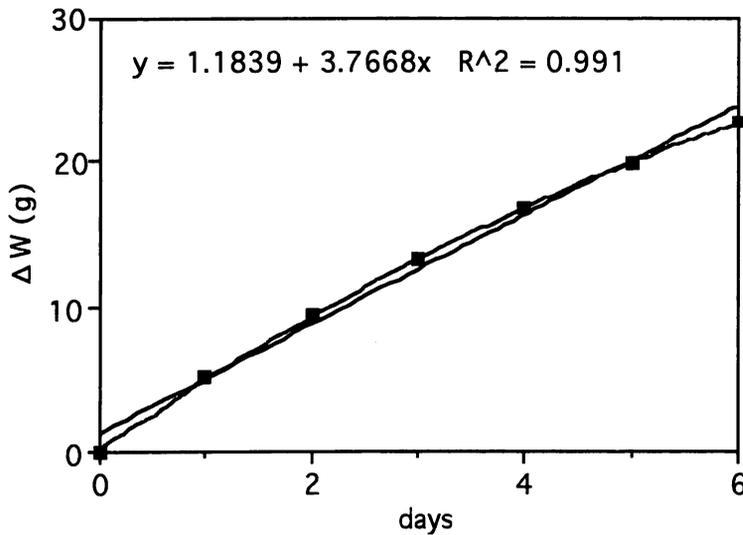


Fig. 4 Time course of weight of silica gel in airtight box during sampling period

Table 2 Recovery rate of BaP from blue rayon

amount adsorbed, ng	8	8	8	50	50	50
amount dissolved, ng	3.5	3.5	3.6	24	16.9	17.0
Recovery rate, %	44	44	45	48	34	34 (41.5)

() : average value of recovery rate

Table 3 One-week TWAs obtained with TWA sampler

Run No.	1	2	3
(a) Amount of BaP eluted from BR, ng	1.98	1.01	1.19
(b) Value corrected (a), ng*	4.95	2.52	2.98
(c) Water volume passed through, mL**	26	22	23
(d) Estimated TWA of one week, ppb	0.19	0.11	0.13
(e) BaP concentration in aquarium, ppb	0.14	0.19	0.18

* value of (a) was divided by 0.4 of recovery rate of BaP from BR

** estimated from weight-increase of silica gel

Table 4 Relationship between sampling period and TWA

Sampling period (days)	1	3	5	10
Conc. of BaP in aquarium (ppb)	0.18	0.18	0.17	0.20
TWA estimated (ppb)	0.25	0.27	0.14	0.09

TWA-7d of BaP in water at ppb level. However, we did not examine the relationship between BaP concentration in water and TWA-7d because it was difficult to adjust the BaP level as desired for the experiment.

Relationship between sampling period and TWA

A relationship between sampling period and TWA was examined in the test water of constant BaP concentration (Table 4). TWA-10d was lower than average value of BaP in the aquarium. On the other hand, the TWAs obtained in the sampling of a few days were higher than the average value of BaP in the aquarium. The phenomenon may be explained that the water in the sampling pipe does not contain BaP at the beginning of sampling, and the diffusion of BaP occurs in the sampling pipe simultaneously. Namely, the amount of BaP transferred with diffusion exceed the one transferred with water movement. In the course of time, transfer of BaP with diffusion decreases and the BaP in test water is transferred constantly. It is considered that a moderate sampling period may be necessary in use of the TWA sampler.

4. Conclusion

To evaluate the impact of pollutants in water to the ecosystem, we need to estimate the amount of pollutants exposed to aquatic biota. We tried to estimate one-week average value of exposure to mutagenic chemical, BaP, with a new sampling method in our laboratory. In conclusion, it was considered that the sampling method was useful for estimation of TWA-7d on water contained BaP of ppb level.

However, it was difficult to test the TWA sampler in field, because the BaP concentrations of river, lake and sea were too low, at ppt level, to quantify by our proposed sampling system.

Acknowledgements

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