Supporting Information

Determination of Polycyclic Aromatic Hydrocarbons in Sediment by Using

Pressure-Balanced Cold Fiber SPME

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Table of Contents

Section S1 Supplementary materials and reagents.

Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene were purchased from Supelco (Oakville, ON, Canada). HPLC-grade methanol and diethylamine were purchased from BDH (Toronto, ON, Canada). Ultrapure water, used for preparation of the sample matrix, was obtained from a Barnstead/Thermodyne NANO pure water system (Dubuque, IA, USA). Stock standard solutions of all PAHs (1000 mg/L) were prepared in methanol, and working standard solutions were prepared by appropriate dilutions of standard stock solutions with methanol. All standard solutions were stored at 4 °C. The sand matrix was purchased from EM Science (NJ, USA). All gases were supplied by Praxair (Kitchener, Canada). CRM 104 certified reference sediment was purchased from Sigma-Aldrich. Syringes (30 mL) and sample vials (10 mL) with magnetic crimp caps and PTFE coated silicone septa were provided by Supelco (Oakville, ON, Canada).

Section S2 Model of in-vial pressure with addition of diethylamine

In this section, the effect of diethylamine and water vapor on vial pressure was presented theoretically. Pressure inside the vial headspace is affected by two factors: the expansion of air inside the vial stemming from the change in temperature from ambient temperature (25 °C) to 200 °C, and the vapor pressure of diethylamine and water vapor. According to Gay-Lussac's law and Boyle's law, the partial pressure for expansion of air in vial (P_1) can be deduced by equation 1:

$$P_1 = \left(\frac{P_0 V_0}{V_0 + V_W} \right) \left(\frac{T_2}{T_0} \right) \qquad (1)$$

Where P_0 is the standard atmospheric pressure (101325 Pa), V_0 is the volume of the vial (10 mL), V_W is the volume withdrawn from the vial, T_0 is the ambient

temperature ($\approx$ 298.15 K), and T_2 is the final temperature of the vial (473.15 K).

For the vapor pressure in the sampling vials, the ideal gas law can be used to estimate the partial pressure of diethylamine vapor (P_2) and water vapor (P_3), following the assumption that diethylamine and water in vial at 200 °C is an ideal gas.

$$P_2 = \left(\frac{\rho_D V_D}{M_D} \right) \left(\frac{RT_2}{V_0} \right) \tag{2}$$

$$P_3 = \left(\frac{\rho_L V_L}{M_L} \right) \left(\frac{RT_2}{V_0} \right) \tag{3}$$

Where ρ_D and ρ_L is the density of diethylamine (0.71 g/mL) and water (1.00 g/mL), V_D is the liquid volume of diethylamine added to samples, V_L is the water content in the samples, M_D and M_L is the molar mass of diethylamine (73.14 g/mol) and water (18.02 g/mol) respectively, and R is the ideal gas constant (8.3145 $\times$ 10^{-2} L bar/K mol).

According to Dalton's law, the pressure (P) in vial at 200 °C after addition of a specific amount of diethylamine is equal to the sum of the partial pressures:

$$P_3 = \left(\frac{P_0 V_0}{V_0 + V_W} \right) \left(\frac{T_2}{T_0} \right) + \left(\frac{\rho_D V_D}{M_D} \right) \left(\frac{RT_2}{V_0} \right) + \left(\frac{\rho_L V_L}{M_L} \right) \left(\frac{RT_2}{V_0} \right) \tag{4}$$
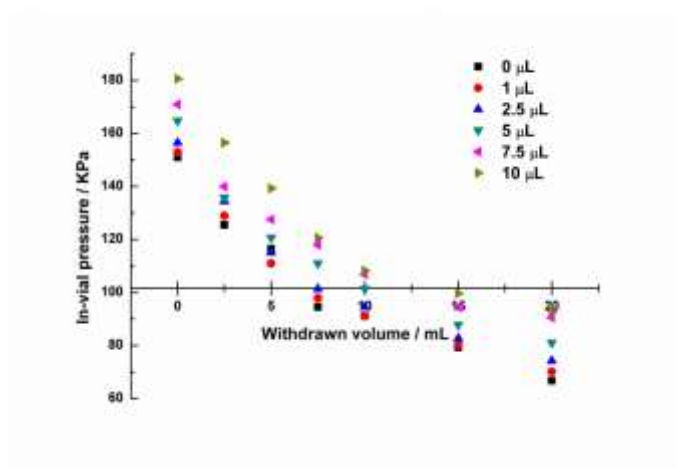

Figure S1 In vial pressure after addition of diethylamine at 200 °C.

In order to obtain the relationship between the amount of liquid volume of diethylamine added into samples (V_D) and the volume to be withdrawn from vials (V_W), the pressure conditions of the in vial headspace were investigated, with various volumes amounts being withdrawn from vials after different amounts of diethylamine were added into samples. Results are shown in Figure S1.

Section S3 Quantification of PAHs in vials after heating to 200 °C

In order to verify that there was a loss for PAHs from the vial during the heating process, quantification of PAHs in vials was carried out after heating to 200 °C at both regular procedure and pressure-balanced procedure. A 10 mL of vial containing 1 g sand sample spiked by 200 ng PAHs was assembled with CF-SPME device without coating and cooling, and then was placed into the heater keeping 30 min at 200 °C. Then took out the vial from the heater. After cooling down to ambient temperature, removed the CF-SPME device. Added 0.5 mL dichloromethane into the vial using 1 mL syringe, and put it on the vortex for 5 min. For the pressure-balanced procedure, 7 mL of air was withdrawn from the vial before spiked PAHs. Finally, the amount of PAHs in vial was determined using GC/FID.
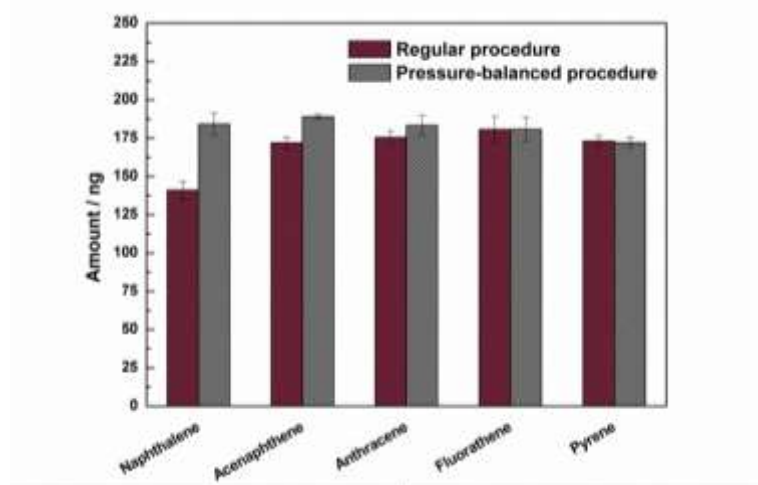

Figure S2 PAHs amounts in vials after heated to 200 °C for 30 min

Figure S2 showed that comparing to pressure-balanced procedure, amounts of naphthalene, acenaphthene and anthracene decreased with regular procedure during the heating process, while there was no evident difference for fluorathene and pyrene. This phenomenon demonstrated that some analytes escaped from sampling vial into ambient through the tiny hole made by CF-SPME needle due to its higher volatility. pressure-balanced procedure reduced the loss of analytes and air exchange during heating process.

Section S4 Effect of change in pressure as a function of in vial air volume

The effect of reduced and increased pressure on CF-SPME sampling from spiked sand samples was also investigated (Figure S3). A 30 mL syringe was used to change the in vial headspace pressure by withdrawing or injecting a specified volume of air. The pressure conditions inside the vial headspace were 211.64, 150.97, 95.12, and 66.78 KPa at 200 °C for injections of 5 mL of air into sample vial, and withdrawals of 0 mL (regular CF-SPME sampling), 7 mL, and 20 mL of air from sample vials, respectively, wherein the withdrawal of 7 mL of air from the vial was considered as a pressure-balanced state. The obtained results, as seen in Figure S3-a, showed that reduced pressure in the vial headspace enhanced extraction efficiency as expected, while increased pressure decreased the extracted amount of PAHs and yielded poor RSD values, especially for the higher volatility analytes naphthalene and acenaphthene. In comparison to pressure-balanced extraction, sampling under sub-ambient pressure conditions, accomplished by withdrawing 20 mL of air from the vial, yielded almost the same extraction efficiency for naphthalene, acenaphthene and anthracene, while obtained a little increasing for fluorathene and pyrene. However, extraction under sub-ambient pressure conditions could also lead to ambient air

entering the vial headspace due to pressure differences, and as such, influence the accuracy and precision of the method. It is worth noting that pressure-balanced extraction achieved the best RSD results among the tested conditions (Figure S3-b).
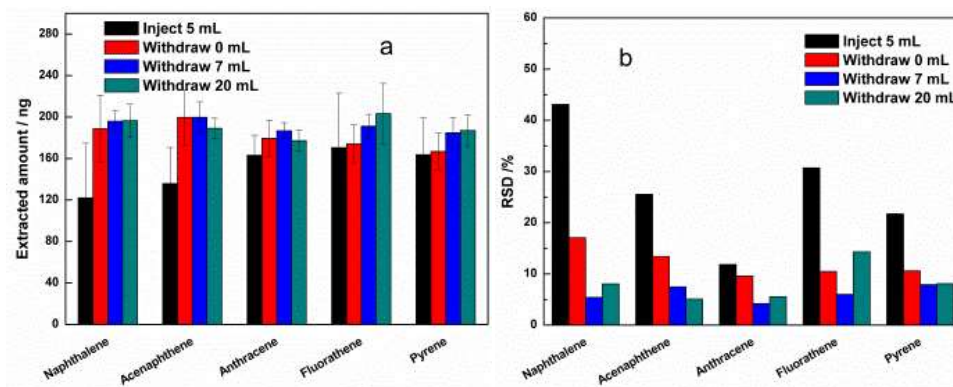

Figure S3 Comparisons of extracted amounts (a) and RSD values (b) from spiked sand samples for different withdrawn volumes of air from vial headspace. Extractions were carried out for 30 min under temperatures of 200 °C for samples and 30 °C for coatings.
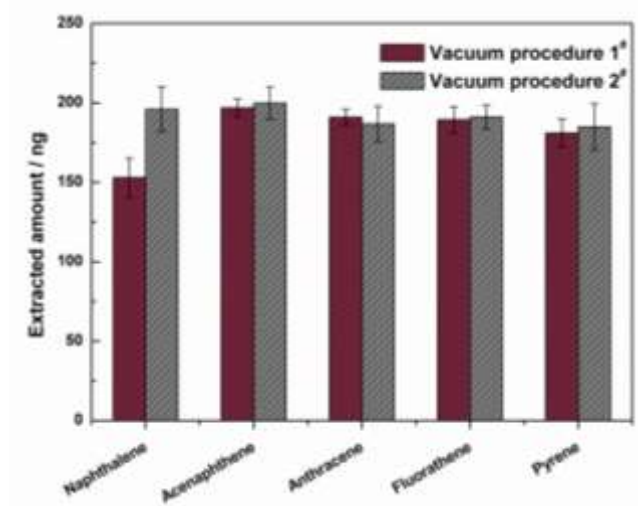

Figure S4 Extracted amounts of 5 PAHs in sand samples with different vacuum procedure for pressure-balanced CF-SPME. Vacuum procedure 1#-withdraw 7 mL air from vials with spiked sand samples; Vacuum procedure 2#-spike PAHs after withdrawing 7 mL air from vials with sand. The sample temperature and coating

temperature were 200 and 30 °C respectively, and extraction time was 30 min.

Section S5 Effect of air withdrawal on naphthalene loss in different matrix

In order to verify the effect of vacuum procedure on the extraction of volatile compounds from real samples, empty vial, sand sample and sediment sample spiked with 200 ng naphthalene were used for experiment. First, spiked 1 μL 200 μg/mL naphthalene solution into 10 mL empty vial, vial containing 1 g sand sample and 1 g sediment sample, respectively, then added 0.5 mL dichloromethane into the vial using 1 mL syringe after withdrawing 7 mL of air or without withdrawing. Put the vial on the vortex for 5 min. The amount of naphthalene in dichloromethane was determined using GC/FID.

As Figure S5 shown, naphthalene was lost with withdrawing air procedure from the vial for empty vial and sand sample. However, there was no loss for naphthalene in sediment sample when withdrawing 7 mL of air at ambient temperature (≈25 °C), due to its high affinity and adsorption.
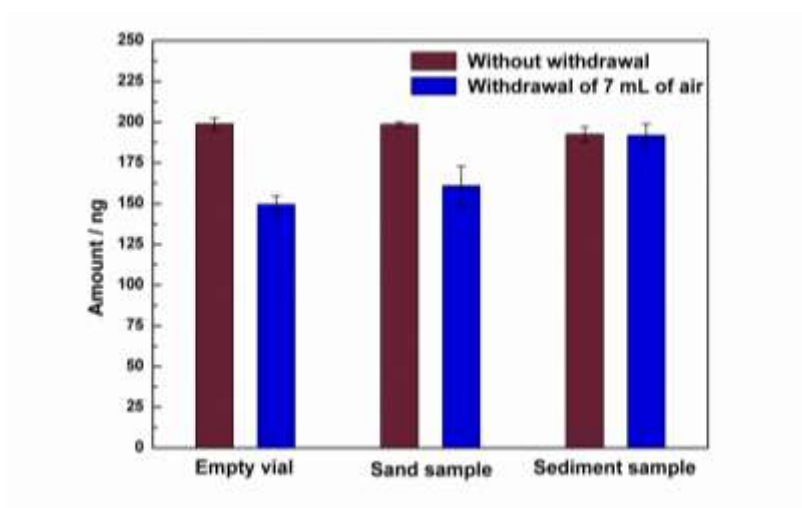

Figure S5 Effect of air withdrawal on naphthalene amount in different matrix.

10 samplings of sand samples spiked with 200 ng of 5 PAHs were studied to evaluate the analytical precision of pressure-balanced CF-SPME in comparison to regular CF-SPME (as shown in Table S1). Extractions were carried out for 30 min, with set temperatures for sample and coating of 200 °C and 30 °C, respectively.

Table S1 RSD results for regular CF-SPME and pressure-balanced CF-SPME

regular CF-SPME												
	1	2	3	4	5	6	7	8	9	10	average / ng	RSD / %
naphthalene	221.41	224.76	199.19	178.81	226.47	115.63	202.02	181.63	162.65	174.57	188.72	18
acenaphthene	202.01	223.05	210.33	201.08	219.46	150.66	216.08	204.61	177.68	191.39	199.64	11
anthracene	182.82	205.14	187.49	156.04	186.42	146.77	198.03	178.73	172.27	181.05	179.48	10
fluorathene	169.54	191.22	179.59	161.46	170.88	164.01	186.16	171.98	171.80	173.71	174.04	5
pyrene	153.14	193.37	173.71	142.94	171.33	148.90	191.87	173.27	153.55	165.07	166.72	10
pressure-balanced CF-SPME												
	1	2	3	4	5	6	7	8	9	10	average / ng	RSD / %
naphthalene	200.39	198.30	206.54	190.44	190.27	221.71	196.28	203.77	181.25	170.41	195.94	7
acenaphthene	194.84	203.45	201.46	184.62	182.79	209.50	206.96	212.88	202.27	199.29	199.81	5
anthracene	184.40	185.72	182.90	172.06	166.87	203.91	194.28	197.48	193.22	186.43	186.73	6
fluorathene	199.19	194.24	194.13	182.58	181.87	188.80	185.45	190.75	205.08	189.22	191.13	4
pyrene	185.01	196.87	164.99	163.50	166.43	194.03	186.01	195.42	201.99	194.10	184.84	8