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Distribution and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Household Drinking Water

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Water pollution has become an important problem for public health. Among polluting compounds, polycyclic aromatic hydrocarbons (PAHs) represent an important class, and their widespread distribution has raised global concerns. The bioconcentration factor (BCF) of PAHs in aquatic organisms typically ranges between 100 and 2000, and it is increasing with the molecular size of PAHs. Many PAHs have deleterious effects in mammals due to their carcinogenic potential because PAH product intermediates (DNA-adducts) covalently bind with cellular DNA (Aas et al., 2000). The US Environmental Protection Agency (USEPA) has promulgated 16 unsubstituted PAHs in its list of 129 priority pollutants. Six PAHs including benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[k]fluoranthene, chrysene, dibenzo[a]nthracene and indeno[1,2,3-cd]pyrene have been classified as potential carcinogens to human (IARC 1987). Thus, their occurrence in the aqueous environment poses a potential threat to human health.

The PAHs are ubiquitous pollutants found in various environments, such as atmosphere, water bodies, and sediments (Fernandez et al., 2000). Pathways for PAHs to entering surface water bodies include atmospheric fallout, urban run-off, municipal effluents, industrial effluents, and oil spillage or leakage. Atmospheric fall-out occurs upon dry and wet deposition of particles and vapors (Baker et al., 1990; Leister et al., 1994). PAHs, as semi-volatile organic compounds, exit in both the gaseous and particulate phase in air, and are subject to both vapor and particle washout from the atmosphere during precipitation. Atmospheric deposition has been regarded as the main pathway for PAHs to enter water bodies (McVeety et al., 1988; Dickhut et al., 1995; Malik et al., 2004).

Taiwan's petrochemical industry has grown vastly; it currently generates approximately one-third of Taiwan's total industrial profits, and employs over 1.5 million people (Yang et al., 2002). Petrochemical industries have been recognized as an effective way of promoting technology development, urban renewal, and economical growth. However, the petrochemical industry's manufacturing processes are complex and involve many different types of raw materials. Petrochemical industries that use oil or coal produce effluents with high concentrations of PAHs (Doong and Lin, 2004). A level of PAH (300-20000 μg/L) has been observed in the effluents of industries producing organic compounds and plastics, and in the effluents of iron and petrochemical factories. An important source of PAHs in the surface water bodies of southern Taiwan is industrial effluents (EPA Taiwan, 2005). Due to the tendency of PAHs to accumulate in the food chain, their release during dredging operations, episodes of high scouring, or leaching from confined facilities poses a threat to aquatic ecosystems, and a potential threat to human health (Tabak et al., 2003). In a study evaluating the behavior of PAHs in aquatic systems, we found that the level of PAHs in Cheng-Ching Lake (a reservoir neighboring a petrochemical industry area in southern Taiwan) were 0.84–1.23, 0.91–1.32, 0.18–0.35 μg/L, for pyrene, benzo[ghi]perylene, benzo[a]pyrene, respectively (Chen, 2004). The latter value exceeded the European Union for drinking water standards, which states that the maximum concentration for benzo[a]pyrene is 100 ng/L (European Economic Community, 1998). It is suspected that household drinking

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water could be contaminated with PAHs via industrial effluents (Chen, 2004). Contaminated drinking water may pose a threat and health risk to people living nearby. However, there is no data evaluating the level of PAHs in household drinking water, and it is therefore difficult to demonstrate this risk. This study was undertaken to determine the distribution of PAHs in household drinking water in Taiwan, and presents preliminary information on the assessment of health risks for residents consuming household drinking water. The current study was performed so that a database could be established for the government to develop new regulations for drinking water.

Materials and Methods

The study was performed in three major cities of Taiwan: Kaoshiung, Taipei, and Taichung. The total population of these three areas constitutes nearly 25% of Taiwan's total population. The water samples were taken randomly from various city districts in each of the three cities (Kaoshiung, 10 districts; Taipei, 12 districts; Taichung, 10 districts). 40 samples were collected from each area (120 samples total) during June 2005. Samples were collected in 250-mL amber glass bottles with Teflon lined tops to prevent reaction. All glassware was previously cleaned with acetonitrile and hexane to the remove any polar and non-polar compounds, and rinsed with de-ionized water (>18.2 MΩ). The faucet was run for ten minutes before the tap water was collected to ensure consistency. Ascorbic acid (10 mg/L) was added to each sample bottle in order to prevent the confounding reaction with residual chlorine. Each sample was stored in a cooler at 4°C for transportation to the laboratory and analyzed within 24 hours of collection. The procedure for pretreatment and analysis of each sample was based on solid phase microextraction-liquid chromatography, as described in our previous study (Chen, 2004). Approximately 10 mL of household drinking water sample was extracted with a solid phase microextraction (SPME) device (Supelco Corporation, Bellefonte, Pen). The operating conditions for the SPME device were 1.5 M sodium monochloroactate, 80°C, pH 6.0, 900 rpm for a duration of 35 minutes. The fiber assembly was used with 30 µm of polydimethylsiloxane for nonpolar semivolatiles (PDMS, Supelco Corporation, Bellefonte, PA). Samples were analyzed with a high performance liquid chromatography (HPLC) system (Model LC-6B, Shimadzu, Kyoto, Japan) equipped with a six-port valve (M7125, Rheodyne, Calif) adapted with a reverse-phase Supelcosil LC-PAH analytical column (150 × 4.6 mm I.D.; Bellefonte, PA). A programmable fluorescence detector (FLD-6A, Shimadzu, Kyoto, Japan) was used to detect the signals from PAH-containing compounds, and data was treated by a Chem. Win 1.0 data system (Taipei, Taiwan). All samples were analyzed three times. The operating conditions were as follows: the flow rate of mobile eluent (80% acetonitrile + 20% 0.01 M sodium mono-chloroacetate) was 1.0 mL/min and the oven temperature was 45°C.

Analytical-reagent grade acetonitrile (Fisher, Springfield, Mo, USA) was used as solvent. The standard mixtures of 16 PAHs at a concentration of 2000 µg/mL in methylene chloride-benzene (1:1 v/v) were purchased from Supelco (Bellefonte, PA). Pyrene-d_{10} (Pyr-d_{10}), internal standards for PAHs, was purchased from Wako Pure Chemicals (Osaka, Japan). These standards were stored at 4°C and were used for the preparation of working solutions. A working standard (20 µg/mL in acetonitrile) was prepared every week. Calibration curves were plotted from the concentrations (5–100 ng/L) of 16 PAHs standards. The recovery yields of the 16 PAHs were 88–98%. The detection limits of the 16 PAH compounds were all < 2 ng/L.

To test for significant differences between cities on the distribution and risk of total PAHs (including Kaoshiung, Taipei and Taichung), analysis of variance (F) and Kruskal-Wallis test were performed. Statistical analyses were conducted using SPSS/PC$^+$ (SPSS, Inc., Chicago, Ill). All tests were regarded as significant when $p < 0.05$.

Results and Discussion

Household drinking water from three major metropolitan areas of Taiwan was evaluated for PAH levels. Table 1 shows the mean concentration of PAHs (ng/L) in the three metropolitan areas. Each figure represents the average value of all sampling sites. Total average concentrations of PAHs were different in the three areas, with the highest in Kaohsiung and the lowest in Taichung. The level of PAH in tap water samples was 1452.9 ± 204.2, 94.6 ± 18.6, and 85.2 ± 17.6 ng/L for Kaohsiung, Taipei, and Taichung, respectively. The level of PAHs in Kaohsiung tap water was approximately 15 and 17 times that of Taipei and Taichung, respectively. Concentrations were compared between areas to look for significant differences. The results showed that the level of PAHs was significantly higher in Kaohsiung ($p < 0.05$) than in Taipei or Taichung. Except for DBA, BghiP, and IDP, the other 13 PAHs species were all consistently found in these three areas. The most abundant PAHs were NaP, BaP, and PhA in Kaohsiung. Nap, FL, and AcP were the most abundant PAH species in Taipei and Taichung, while the less abundant PAHs in these areas were the 5–6 ring PAHs, due to lower water solubility. The solubility of PAHs in water is low and it decreases with molecular

Table 1 Concentrations of PAHs in household drinking water from three metropolitan areas (ng/L; mean ± SD)

PAH	Kaoshiung (1) (*n* = 40)	Taipei (2) (*n* = 40)	Taichung (3) (*n* = 40)
NaP	330.0 ± 18.5	27.9 ± 2.7	22.7 ± 3.4
AcPy	110.2 ± 12.6	4.3 ± 1.6	5.8 ± 2.9
AcP	95.6 ± 22.3	6.3 ± 1.5	8.6 ± 2.3
An	35.0 ± 18.9	5.9 ± 0.9	3.0 ± 1.5
F	112.9 ± 18.6	7.2 ± 1.2	8.4 ± 2.0
PhA	149.0 ± 10.0	6.7 ± 2.4	6.3 ± 0.8
FL	32.5 ± 12.7	8.6 ± 1.4	15.7 ± 1.2
BaA	92.4 ± 19.1	2.5 ± 0.8	2.6 ± 0.8
Chr	88.5 ± 18.4	5.4 ± 1.6	3.5 ± 0.6
Pyr	91.2 ± 17.1	6.0 ± 1.5	2.0 ± 0.5
BbF	63.1 ± 8.6	5.0 ± 1.2	3.0 ± 0.8
BkF	54.0 ± 6.2	5.2 ± 0.7	2.2 ± 0.5
BaP	156.7 ± 12.2	2.4 ± 0.9	1.4 ± 0.3
DBA	8.0 ± 2.3	1.2 ± 0.2	ND
BghiP	20.0 ± 3.5	ND	ND
IDP	13.8 ± 3.2	ND	ND
Total PAHs	1452.9 ± 204.2	94.6 ± 18.6	85.2 ± 17.6
P value	$p < 0.05$ for (1) vs (2) and (1) vs (3); $p > 0.05$ for (2) vs (3)		

NaP, Naphthalne; AcPy, Acenaphthylene; AcP, Acenaphthene; An, Abthracene; F, Fluorene; PhA, Phenanthrene; FL, Fluoranthene; BaA, Benzo[a]anthracene; BbF, Benzo[b]fluoranthene; BkF, Benzo[k]fluorathene; BaP, Benzo[a]pyrene; DBA, Dibenzo[a,h]anthracene; BghiP, Benzo[ghi]perylene; IDP, Indeno[1,2,3-cd]pyrene

weight. Because PAHs are hydrophobic (log Kow = 5–7, 5–7ring) their concentration in water is very low. Similar results were also observed in Finland (Manoli and Samara, 1999). The concentration of PAHs in Kaohsiung tap water in our study (1452.9 ng/L) was higher than that from Nova Scotia (Canada; 134 ng/L) (Goodarzi and Mukhopadhyay, 2000), Helsinki (Finland; 150.3 ng/L) and Horsholm (Denmark; 106.5ng/L) (Manoli and Samara, 1999). The allowable level of PAHs in European Union's drinking water standards are 10 ng/L for benzo(a)pyrene and 100 ng/L for total PAHs (European Economic Community, 1998). In Kaohsiung household drinking water, these levels were 156.7 ng/L for benzo[a]pyrene and 1452.9 for total PAHs. The results for Kaohsiung drinking water exceeded the EU standards, while the results for Taipei and Taichung were in compliance with these standards. The high degree of PAHs pollution in Kaohsiung drinking water can be associated with the presence of petrochemical industries in this area. The presence of PAHs in the Kao-Ping River (1.0–12.7 μg/L) and in the Cheng-Ching Lake Reservoir (3.0–4.3 μg/L) in Kaohsiung are consistent with the findings (Doong and Lin, 2004; Chen, 2004).

Table 2 Source of PAHs in household drinking water from three metropolitan areas based on species ratio

Ratio/source	R1	R2	R3	R4
Cheng 2001				
Gasoline engines	0.2–0.4	0.4–0.6	0.1–1.5	0.2–0.3
Diesel engines	0.6–0.9	0.6–0.9	1.5–3.0	0.3–0.4
Factories	0.4–0.6	0.2–0.3	3.0–5.0	-
Petroleum refineries	-	-	5.0–10.0	0.4–0.9
This study				
Kaoshiung	0.51	0.26	7.84	0.41
Taipei	0.32	0.59	-	-
Taichung	0.43	0.89	-	-

R1 = [BaA]/([Chr]+[BaA]), R2 = [FL]/([FL]+[Pyr]), R3 = [BaP]/[BghiP], R4 = [IDP]/([IDP]+[BghiP])

Many studies have suggested that the ratios between various PAH compounds may be used for source identification. The estimated values for the most common ratios of PAHs from diesel engines, gasoline engines, factories, and petroleum refineries are present along with previous reports in Table 2. The ratios R1 = [BaA]/([Chr]+[BaA]) = 0.51 and R2 = [FL]/([FL]+[Pyr]) = 0.26 tend to indicate that PAH contamination of Kaohsiung household drinking water is from factories. The other ratios R3 = [BaP]/[BghiP] = 7.84 and R4 = [IDP]/([IDP]+[BghiP]) = 0.41 are similar to those reported for areas affected by petroleum refineries. These results demonstrate that the major source of PAH pollution in drinking water are petroleum refineries pollutants, which are introduced in raw water and tap water by industrial effluents and emission air fallout. The R1 and R2 ratios in Taipei household drinking water were 0.32 and 0.59, respectively. The source of PAHs in Taipei drinking water is most likely gasoline engine emissions. The R1 and R2 ratios in Taichung household drinking water were 0.43 and 0.89, respectively. The presence of PAHs in Taichung drinking water is most likely due to the emissions of both diesel engines and factories. These results are in agreement with previous principal component analysis (Yang et al., 2002) that has shown some correlations between 2–4 rings PAHs (such as NaP, AcP, FL, and Pyr) and gasoline-engine or diesel-engine vehicles. There is also a strong correlation between PAHs with 4–5-rings or more (BaP, BghiP) and factories and petroleum refineries.

An island-wide analysis of cancer mortality showed that the southern region including Kaoshiung city had the highest mortality (Yang et al., 2002). Two possible factors for high cancer mortality in the southern region are due to its vicinity to Taiwan's petrochemical industry and to poor drinking water. The increase in cancer risk due to the ingestion of PAHs in contaminated household drinking water was calculated using contaminated average concen-

Table 3 Estimates of cancer risk in household drinking water from three metropolitan areas

PAH	TEF[a]	Cancer risk (10^{-6})		
		Kaoshiung (1)	Taipei (2)	Taichung (3)
NaP	0.001	0.079	0.007	0.005
AcPy	0.001	0.026	0.001	0.001
AcP	0.001	0.023	0.002	0.002
An	0.01	0.084	0.014	0.007
F	0.001	0.027	0.002	0.007
PhA	0.001	0.036	0.002	0.002
FL	0.001	0.008	0.002	0.002
BaA	0.1	2.218	0.060	0.377
Chr	0.01	0.212	0.013	0.006
Pyr	0.001	0.022	0.001	0.001
BbF	0.1	1.512	0.120	0.072
BkF	0.1	1.296	0.125	0.053
BaP	1	37	0.576	0.360
DBA	1	1.920	0.288	0
BghiP	0.01	0.048	0	0
IDP	0.1	0.331	0	0
Total risks		44.842	1.213	0.895
p value	$p < 0.05$ for (1) vs. (2) and (1) vs. (3); $p > 0.05$ for (2) vs. (3)			

TEC, toxic equivalent factor; NaP, Naphthalne; AcPy, Acenaphthylene; AcP, Acenaphthene; An, Abthracene; F, Fluorene; PhA, Phenanthrene; FL, Fluoranthene; BaA, Benzo[a]anthracene; BbF, Benzo[b]fluoranthene; BkF, Benzo[k]fluorathene; BaP, Benzo[a]pyrene; DBA, Dibenzo[a,h]anthracene; BghiP, Benzo[ghi]perylene; IDP, Indeno[1,2,3-cd]pyrene

tration and toxic equivalent factor (TEF) (EPA USA, 2006; Nisbet and Lagoy, 1992). Expressed as a simple formula, the cancer risk = $0.24 \times 10^{-6} \times$ average concentration (ng/L) × TEF. Estimates of the cancer risk in household drinking water from the three metropolitan areas are shown in Table 3. The risk of cancer mortality for Kaoshiung residents can be estimated from their consumption of PAHs as approximately 4.4×10^{-4}. The risk was significantly higher than USEPA's acceptable risk (10^{-6}), approximately 44.8 times higher. The risk of cancer mortality from drinking water was significantly higher in Kaoshiung ($p < 0.05$) than in Taipei (1.2×10^{-6}) or Taichung (0.8×10^{-6}), suggesting that PAHs were being introduced into drinking water via petrochemical industrial effluents. Differences in risk levels between Taipei and Taichung were not statistically significant ($p > 0.05$). In Taipei and Taichung, the risks were similar to USEPA's acceptable risk (10^{-6}). Nevertheless, monitoring drinking water concentrations of these PAHs should continue in these areas.

The present study shows that household drinking water in Kaoshiung is highly contaminated with PAHs and poses a high risk to the aquatic life. PAHs concentrations exceeded the EU recommended permissible level and, consequently, the cancer risk was significant higher than USEPA's acceptable risk. The findings support that the PAHs present in Kaoshiung drinking water originate from the petrochemical industry effluents. This is the first study that monitors PAH distribution and PAH-associated risk in Taiwanese household drinking water. Permissible levels of PAHs in Taiwanese drinking water have not been established. However, the government can use these results as a reference for regulation purposes, and to help develop a drinking water management strategy for protecting public health. To minimize health risks, long-term exposure to elevated levels of PAHs present in household drinking water should be measured and further study is warranted.

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