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Polycyclic Aromatic Hydrocarbons in Soils and Crops After Irrigation of Wastewater Discharged from Domestic Sewage Treatment Plants

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Abstract The effects of domestic wastewater application on the translocation and accumulation of polycyclic aromatic hydrocarbons (PAHs) in soil and crops (rice, lettuce, and barley) were investigated by Wagner's pot experiment. In the soils and crops after domestic wastewater irrigation, high-molecular weight PAHs (5 to 6 ring) were not detected, but low-molecular weight PAHs (3 to 4 ring) were only detected at trace levels.

Keywords Polycyclic aromatic hydrocarbons · PAHs · Domestic wastewater

Farmland application of wastewater discharged from domestic sewage treatment plants has greatly increased in a number of countries over the last three decades (Anikwe and Nwobodo 2002; Bhogal et al. 2003; Chen et al. 2005; Song et al. 2006). In the Republic of Korea, domestic wastewater has been considered as an important alternative resource that has been used locally as agricultural irrigation water.

Domestic wastewater contains persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals, and pathogenic microorganisms. Furthermore, long-term application of domestic wastewater may increase the excessive accumulation of hazardous materials in agricultural ecosystems, which may cause a potential risk to human health if these pollutants enter the food chain (Lee et al. 2005; Song et al. 2006).

Among the numerous POPs, some of the PAHs are powerful carcinogens that can also cause various toxicities such as dermal lesions, hepatotoxicity, and endocrine disruption (Tao et al. 2004). In addition, the PAHs are partly converted to oxygenated derivatives that are known to be even more toxic to humans (Harms 1996). Investigations of the long-term effects of domestic wastewater on the accumulation of POPs in soils have been reported by some authors (Anikwe and Nwobodo 2002; Bhogal et al. 2003; Song et al. 2006). However, few studies have been conducted on the behaviors of POPs in crops and soils after long-term irrigation with domestic wastewater.

In the present research, accumulations of PAHs in soils and crops (rice, lettuce, and barley) were determined after long-term irrigation of the domestic wastewater.

Materials and Methods

This study was conducted in a plastic film house in order to evaluate the behaviors of PAHs in soils and crops after long-term irrigation with domestic wastewater into Wagner's pots (25 cm diameter and 30 cm height). Experiments were conducted for three crop-years (April 1, 2004 to October 30,

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2006) with rice, barley, and lettuce crops. All treatments were replicated five times with a total of 15 plots. Domestic wastewater was used for irrigation to grow the crops. For each crop, 0.5–2 L of irrigation water was used, with the volume of irrigation water over 1 year being 50 L for rice, 30 L for barley, and 30 L for lettuce. The total amount of irrigation water was 90–150 L during the study period (three crop-years).

There was no serious incidence of nutrient deficiencies observed during the study period. Crops were kept healthy by applications of insecticides and fungicides as necessary. The Wagner's pots were kept weed-free by hand weeding conducted at 2-week intervals. The experimental soil belonged to the Gocheon series, and was composed of a coarse loamy over a sandy skeletal, mixed, mesic family of Fluvaquentic Dystrochrepts. Equal amounts of soils were packed into the Wagner's pots, at a depth of up to 25 cm. The experimental soil was a loam (sand: 37.0%, silt: 48.8%, clay: 14.2%) with a soil organic matter content of 3.19%, a pH of 6.30 (1:5 H_2O), CEC of 8.09 $cmol_c$/kg, T-N of 1002.2 mg/kg, and Avail.-P of 212.2 mg/kg.

Soil samples were collected before planting and after harvesting. An aliquot (1 kg) of the collected soil samples from each plot was immediately put into a polyethylene bag and stored at −20°C. One week later, frozen aliquots of samples were air-dried for 3–4 days. The dried aliquots were ground with a mortar and pestle, and were then passed through a 0.2 mm sieve. The crop samples were collected during the harvesting periods, washed with deionized water, and oven-dried for dry matter content at 60°C for 72 h. The dried plant samples were ground using a grinding mill. The domestic wastewater samples were collected in 1 L amber glass bottles, kept at 4°C, and transported to the laboratory, where they were analyzed within 1 week. All of the samples were stored in foil-wrapped vials at 4°C until extraction. More details concerning the analytical procedure, extraction, separation, cleanup, and analysis of PAHs in the samples were previously provided by Cho et al. (2003) and EPA method 3540 (1992).

Gas chromatography–mass spectrometry (GC–MS) analyses were conducted on an HP 5890 series II gas chromatograph (Hewlett-Packard, USA) equipped with a DB 5 capillary column. The injector was maintained at a temperature of 270°C. The oven temperature program was as follows: 50°C (2 min) to 290°C (20 min) at 5°C/min. Helium was used as a carrier gas at a constant flow rate of 1 mL/min. The gas chromatograph was coupled with an HP 5972 mass selective detector (electronic impact mode: 70 eV). The interface temperature was set at 290°C. The detection limits of this method for 14 individual PAHs ranged between 0.26 and 2.57 ng/g. The mean recoveries (%) for surrogates in the samples were 86.5–98.9% (average: 93.2%). The average recoveries of the 14 PAHs varied from 69.9% (naphthalene) and 99.1% (benzo [g,h,i] perylene) (average: 91.3%).

Results and Discussion

In the domestic wastewater used in this study, low-molecular weight (2 to 4 ring) PAHs were detected at trace levels, while high-molecular weight (5 to 6 ring) PAHs were either detected at trace levels or were not detected. The $\sum$PAH concentrations in the domestic wastewater ranged from 1.69 to 2.22 μg/L (mean: 1.90) (Table 1). This concentration range is rather low compared to the values reported in the literature for the domestic wastewater (Lee et al. 2005). There are numerous ways in which PAHs are introduced into the environment. It is generally accepted that industrial activities are the main sources of PAHs, but it is difficult to identify which PAHs have been introduced from pyrolytic or petrogenic origins (Cho et al. 2003). The anthropogenic release of the PAHs can be attributed to petrogenic and pyrogenic origins. For petrogenic origins, PAHs are derived from petroleum spill maturation characterized by the predomination of 2- or 3-ring PAHs. For pyrogenic origins, PAHs originate from the incomplete combustion of organic materials with high occupation of PAHs with more than four rings, such as fossil fuels, exhaust emissions, coal/coke combustion, crankcase oil, household heating stoves, etc. (Benner et al. 1990; cited in Chen et al. 2005). Consequently, it is believed that the sources of PAHs are of petrogenic origin, likely due to resulting from petroleum spill maturation.

Following irrigation of the domestic wastewater, POPs may remain sorbed to soil particles. Subsequent desorption of sorbed residues into the bulk soil solution enables losses by various processes, including leaching, volatilization, plant uptake, photochemical transformation, and biodegradation. These processes have been shown to be dependent on the physicochemical characteristics of the soil, environmental conditions, and the properties of the chemicals themselves (Beck et al. 1996). Table 1 shows the individual PAH concentrations in the soils irrigated with domestic wastewater. The most abundant individual PAHs investigated were NAP, FLU, PHE, and B[a]A. The $\sum$PAH concentrations ranged from 5.84 to 6.60 μg/kg (mean: 6.19) for rice cultivation soil, from 5.98 to 6.45 μg/kg (mean: 6.24) for barley cultivation soil, and from 3.48 to 4.39 μg/kg (mean: 3.99) for lettuce cultivation soil. High-molecular weight PAHs were not detected, but low-molecular weight PAHs were only detected at trace levels. $\sum$PAH concentrations were found to be similar for rice and barley cultivation soil, but were slightly lower for lettuce cultivation soil. This is probably related to the amount of irrigation water used for treatment during the cropping period of each

Table 1 Concentrations of individual PAH and ∑PAH (sum of 14 PAHs) in the experimental soil after wastewater irrigation

Components	Soil samples															
	Wastewater[a]				Rice				Barley				Lettuce			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min.	Max	Mean	SD	Min	Max
NAP	0.23	0.05	0.15	0.34	1.11	0.19	0.80	1.32	1.10	0.05	1.04	1.16	0.90	0.11	0.80	1.09
ACE	0.14	0.03	0.11	0.24	0.67	0.06	0.61	0.73	0.53	0.03	0.50	0.56	0.24	0.02	0.21	0.28
FLU	0.15	0.03	0.11	0.21	0.76	0.07	0.69	0.87	0.47	0.11	0.36	0.65	0.23	0.06	0.16	0.30
PHE	0.27	0.04	0.18	0.33	0.97	0.13	0.82	1.16	0.81	0.11	0.73	1.01	0.52	0.15	0.37	0.69
ANT	0.27	0.05	0.18	0.33	0.46	0.08	0.37	0.58	0.26	0.08	0.16	0.37	0.08	0.04	0.05	0.14
FLA	0.34	0.10	0.18	0.56	1.18	0.25	0.82	1.47	0.68	0.11	0.49	0.74	0.41	0.03	0.38	0.44
PYR	0.19	0.06	0.11	0.30	0.18	0.02	0.17	0.21	0.62	0.07	0.54	0.70	0.34	0.10	0.24	0.49
B(a)A	0.12	0.05	0.03	0.22	0.12	0.01	0.11	0.12	1.19	0.09	1.04	1.29	0.92	0.14	0.76	1.14
CHR	0.03	0.02	0.01	0.07	0.04	0.02	0.02	0.07	0.11	0.05	0.07	0.19	0.06	0.02	0.03	0.09
B(b)F	0.01	0.01	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0
B(k)F	0.01	0.01	0	0.03	0	0	0	0	0	0	0	0	0	0	0	0
B(a)P	0	0	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0
DB(ah)A	0	0	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0
B(ghi)P	0.01	0.01	0	0.02	0	0	0	0	0	0	0	0	0	0	0	0
∑PAH	1.90	0.17	1.69	2.22	6.19	0.29	5.84	6.60	6.24	0.20	5.98	6.45	3.99	0.36	3.48	4.39

The 14 PAH compounds used in this study were naphthalene [NAP], acenaphthene [ACE], fluorene [FLU], phenanthrene [PHE], anthracene [ANT], fluoranthene [FLU], pyrene [PYR], benzo[a]anthracene [B(a)A], chrysene [CHR], benzo[b]fluoranthene [B(b)F], benzo[k]fluoranthene [B(k)F], benzo[a]pyrene [B(a)P], dibenzo[ah]anthracene [DB(ah)A], benzo[ghi]perylene [B(ghi)P]

SD: standard deviation; unit: μg/L for wastewater and μg/kg for soil

[a] Wastewater used for irrigation water in this study

crop. Chen et al. (2003) reported that the ∑PAH concentrations ranged from 3,000 to 5,000 μg/kg in the agricultural soil within the wastewater irrigation region in Tianjin, China. Similarly, Song et al. (2006) indicated that the ∑PAH concentrations were between 950 and 2,790 μg/kg in soil after wastewater irrigation. The ∑PAH concentrations in the current study were much lower than those reported by Chen et al. (2003) and Song et al. (2006). This experiment was conducted for three crop-years. For this reason, it might be hard to compare the results of this study with those of previous reports. However, this investigation suggested a potential ecological risk even with a lower level of residual pollutants in soils after long-term wastewater irrigation (Song et al. 2006).

Figure 1 shows the ∑PAH concentrations in the crops (brown rice, barley corn, and lettuce foliage) irrigated with domestic wastewater. The data show the mean results for three crop-years. The ∑PAH concentrations ranged from 0.0050 to 0.0065 μg/kg (mean: 0.0055) for brown rice, from 0.0024 to 0.0032 μg/kg (mean: 0.0028) for barley corn, and from 0.0060 to 0.0083 μg/kg (mean: 0.0069) for lettuce foliage. The mean concentrations of the ∑PAHs were 72 ng/g in a less contaminated area compared to 210 ng/g in root crops grown at two contaminated sites in Tianjin, China (Tao et al. 2004). In addition, the ∑PAH concentrations of several vegetables in industrialized regions of

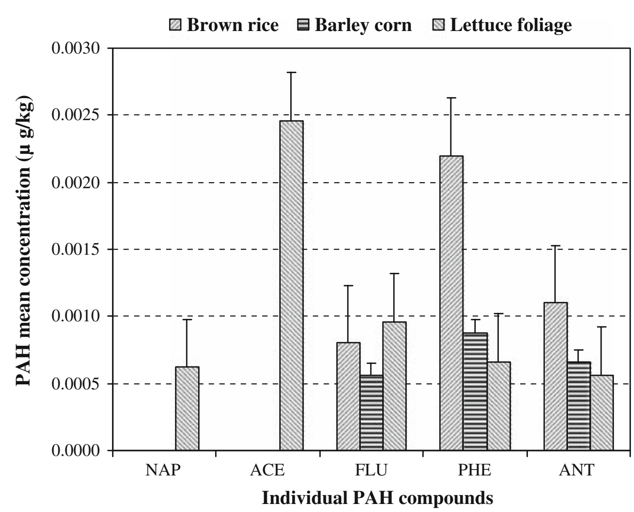

Fig. 1 The mean concentration of individual PAHs detected in crops

Greece ranged from 0.025 to 0.29 μg/g dry weight (Vousta and Samara 1998). The ∑PAH concentrations in the crops used in the current study were much lower than those reported by the researchers cited above. The individual PAHs detected in crops were NAP, ACE, FLU, PHE, and ANT. High-molecular weight PAHs were not detected; only low-molecular weight PAHs were detected. The results of this study were found to be similar to those reported by Tao et al. (2004). The low-molecular weight compounds dominated in all vegetables, with NAP, PHE, ANT, FLU, and FLA consistently being the most abundantly detected compounds, whereas the 5- and 6-ring PAHs were present at very low concentrations (Tao et al. 2004). The low-molecular weight PAHs in plants may be present due to their greater bioavailabilities. By contrast, the high-molecular weight PAHs were mainly associated with the soil particles and airborne particulates preventing root or foliar uptake (Edward 1987; cited in Tao et al. 2004). In this study, neither NAP nor ACE was detected in brown rice or barley corn, while FLU, PHE, and ANT were detected at trace levels. However, all of the five PAHs were detected in lettuce foliage. Hydrophobic PAHs are not drawn into the inner root because the epidermis of the root acts as the water system (Simonich and Hites 1995). In wastewater irrigation for agricultural purposes, the translocation of POPs into the crops does not occur through the roots, as in a normal mechanism, but instead occurs through external contamination of shoots by retention in the cuticle or penetration (Topp et al. 1986; Ryan et al. 1988).

Finally, this study suggested a potential ecological risk even with a lower level of POPs in soils and crops after long-term domestic wastewater irrigation. To minimize health risks, with the development of various treatment technologies for POPs found in domestic wastewater, it is necessary to study food safety in relation to various food crops. Furthermore, long-term exposure to elevated levels of PAHs present in domestic wastewater discharged from domestic sewage treatment plants should be measured, and further investigation is warranted (Chen 2007).

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