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Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals (HMs) as well as their genotoxicity in soil after long-term wastewater irrigation

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Abstract

A study was carried out on the residue level of major concern pollutants (PAHs, PCBs and HMs) and the assessment of their genotoxicity in soils obtained from Shenyang, northeast of China which had been subjected to wastewater irrigation for more than 40 years. Topsoils (0–20 cm) in paddy fields were sampled along the upper, middle and lower reaches of the wastewater disposal channel. Sixteen USEPA PAHs were determined by High Performance Liquid Chromatography (HPLC) with fluorescence detector, eight PCBs were detected by Gas Chromatography (GC) with electron capture detector, and six heavy metals (Cd, Cu, Pb, Zn, Ni, and Cr) were measured by Atomic Absorption Spectrophotometer (AAS). The genotoxicity effect of soils was examined by *Vicia faba* micronucleus (MN) test. Archived soils that had undergone a similar history of wastewater irrigation provided by Technical University of Berlin, Germany were subjected to analysis of the above pollutants and *Vicia faba*/MN test for comparison.

Results indicated elevated residues of the studied pollutants (PAHs, especially benzo (a) pyrene, the eight PCB congeners and heavy metals) in both tested and archived soils. The MN frequencies were 2.2–48.4 times higher compared with the control. However, there was no correlation between the MN frequencies and the concentration of pollutants detected. This investigation suggested a potential ecological risk even with a lower level of residual pollutants in soil matrix after long-term wastewater irrigation.

Keywords: Soils; Persistent organic pollutants; Heavy metals; Wastewater irrigation; Genotoxicity

1. Introduction

Land application of wastewater has been a worldwide agricultural practice in many countries for several decades (Baveye et al., 1999; Anikwe and Nwobodo, 2002; Bhogal et al., 2003). In China, urban wastewater has been considered as an important resource and has been used for agricultural irrigation since the 1950s (Tao et al., 2002, 2004; Wang et al., 2003). Since then, wastewater irrigation, as a means of waste treatment and also of recycling the valuable water and nutrient resource into the soil-plant ecosystem, prevailed in the suburbs around the industrial cities in the northern China (e.g., Bejing, Tianjin, Xian, Shenyang, Jinan, etc.), due to the serious problems of water pollution and shortage in these areas (Song et al., 1995; Duan et al., 1997; Wang and Xi, 1997). However, long-term irrigation with industrial effluent mixed with the municipal wastewater has resulted in the excessive accumulation of toxicants in agricultural soils and has brought a potential risk to human health due to the accumulation of toxicants through the food-chain (Wang and Wu, 1997; Graaff et al., 2002).

Hunpu irrigation area, with an area of about 30 670 ha, is located in western Shenyang, Liaoning Province, a heavy

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industry city of northeastern China. It has an irrigation history of more than 40 years. The wastewater used for irrigation consisted of 30% of municipal sewage and 70% of industrial effluent containing hundreds of organic chemicals and heavy metals due to the discharge of waste fluids from dielectrics, coatings, and sealants, etc., used in the industries.

Amongst the numerous contaminants in the effluent, polycyclic aromatic hydrocarbons (PAHs), polychylorinated biphenyls (PCBs) and heavy metals (HMs) are of particular interest for several reasons as follows. Firstly, the PAHs and PCBs are persistent pollutants in the environment. They have the lower metabolism and degradability by most living organisms, and are easily sorbed. HMs are also easily absorbed and tend to accumulate onto soil particles, so that the soil can be a source of all of these compounds as well as the final sink (Baveye et al., 1999; Stefanutti et al., 2002; Nicholson et al., 2003; Wang et al., 2003; Warman and Termeer, 2005). Secondly, these pollutants are powerful toxicants. For instance, some of the PAHs are powerful carcinogens (Song et al., 1995; Yunker et al., 2002; Tao et al., 2004), PCB mixtures can also elicit various toxicities, such as dermal lesions, body weight loss, hepatotoxicity, immunosuppression, reproductive and developmental toxicity, endocrine disruption, neurotoxicity, and carcinogenicity, despite the cessation of PCB exposure (Covaci et al., 2001; Negoita et al., 2003; Schuhmacher et al., 2004; Zhang et al., 2004; Borghini et al., 2005). Thirdly, the physiochemical and biological reactions of organic and inorganic pollutants with naturally occurring inorganic compounds in soil might lead to the formation of by-products which are mutagenic or carcinogenic.

These pollutants remain a widely distributed health, ecological and environmental concern, which makes it necessary to know both their residue levels and their toxicity in the soil ecosystem. Investigations of the long-term effects of municipal sewage on the accumulation of selected pollutants (PAHs, PCBs, or HMs) in soils have been reported by many authors (Anikwe and Nwobodo, 2002; Bhogal et al., 2003; Udom et al., 2004). However, few studies have been conducted on the evaluation of potential risks of wastewater application in soil which combines analysis of the residue levels of the (mainly) priority pollutants and genotoxicity assessment (Kong and Ma, 1999).

In the present research, concentrations of PAHs and PCBs and HMs in soils were determined, and their genetoxicity potential was assessed by mean of *Vicia faba*/MN test (Ma et al., 1995). This study aimed to investigate the residues of persistent potentially toxic compounds (namely PAHs, PCBs and HMs) in soils and their genotoxicity potential after long-term wastewater irrigation.

2. Materials and methods

2.1. Soil collection and preparation

Six sites were selected in the Hunpu wastewater irrigation area, Shenyang, Liaoning Province, Northeastern China. These sites covered the distance from the upper reach (site 1), to the lower reach (site 6) over a distance of 30 km (5 km between each site), and were considered as the representative paddy areas. At each site, five soil sub samples (0–20 cm) were collected from a 10×10 m segment of the paddy field and mixed thoroughly on site to create a single sample for that site. The samples were stored in polyethylene bags after being screened through a 2-mm or 5-mm sieve in the field and kept at -20 °C until use. Four soil samples (0–20 cm), which had undergone the similar history of wastewater irrigation to those of Shenyang, and had been taken from wastewater irrigation areas in the former Eastern Berlin were provided for comparison by Technical University of Berlin, Germany. Standard LUFA soil was used as a control in the MN assay. Selected physico-chemical properties of the tested soils are listed in Table 1.

2.2. Extraction and determination of PAHs and PCBs

2.2.1. Extraction of PAHs and PCBs

Extraction of PAHs and PCBs was performed according to the Verband Deutscher Landwirtschaftlicher, Untersuchungs-und Forschungsanstalten (VDLUFA) method (Offenbächer et al., 1996). Dried soil (10 g) was weighed into a 500 ml brown bottle prior to the addition of 50 ml of double distilled water, 15 g of NaCl, 100 ml of acetone and 75 ml of dichloromethane (CH_2Cl_2), and was extracted at 125 rpm for 16 h on a mechanical shaker. The supernatant was collected, and reduced to dryness in a rotary evaporator and made up to 10 ml with acetone for analysis of PAHs and PCBs (5.0 ml of supernatant for each) (Offenbächer et al., 1996). All extractions were carried out in triplicate.

2.2.2. PAH determination

A 20 μl aliquot of extract was injected onto a 125 mm × 2.0 mm I.D. 5 μm RP-CB_{18} octadecylsilane column and separated using an acetonitrile/water eluent at a flow rate of 1.0 ml min^{-1} with a gradient running at 50:50 water:acetonitrile to 100 acetonitrile over 30 min.

Table 1
Some physical and chemical properties of the tested soils

Samples	pH	Content%			
		Organic matter	Clay	Silt	Sand
S1	5.7	1.74	17.71	47.22	35.07
S2	5.47	3.14	17.38	47.4	35.22
S3	5.69	1.77	14.88	29.87	55.25
S4	5.66	1.95	17.08	23.53	59.39
S5	6.43	1.23	29.49	30.21	40.3
S6	5.26	1.57	19.55	32.79	47.66
G1	3.4 ($CaCl_2$)	0.2[a]	91.2	7.8	1
G2	7 ($CaCl_2$)	0.84	46.5	49	4.5
G3	6.6 ($CaCl_2$)	2.5	5.3	24	70.7
G4	6.1 ($CaCl_2$)	17.5	16.4	71.9	11.6
LUFA	5.62 ($CaCl_2$)	2.5	7	16.0	77.0

[a] Organic carbon.