

Pollution Characteristics and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils in Winter around Zhongyuan Oilfield, China

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The degree of contamination with polycyclic aromatic hydrocarbons (PAHs) in soil samples in winter was determined. The contents of PAHs in samples were analyzed with HPLC. The PAHs contents of soil samples in winter around three different oily sludges from high to low represented the Third Wenming Plant of the oily sludge (3W), the Third Mazhai plant of the oily sludge (3M), and the Fourth Wener Plant of the oily sludge (4W), respectively. PAHs with 2–4 rings were major pollutants in oily sludge. Based on Nemero index P, the classification evaluation showed that soils around oily sludge were heavily polluted in winter. The health risk assessment and ecological risk assessment in soil in winter around oily sludge in Zhongyuan Oil Field was also analyzed.

Keywords oily sludge, soil, polycyclic aromatic hydrocarbons, nemero index P

Introduction

Polycyclic aromatic hydrocarbons (PAHs), which are categorized as persistent organic pollutants (POPs), represent a significant threat to the ecosystem and especially to people due to their widespread distribution in the environment and potential toxicity to organisms. For example, many of the PAHs with four or more rings are carcinogenic and mutagenic because of their metabolic transformation capability. Consequently, PAHs are among the priority pollutant list of the Environmental Protection Agency (EPA). Many countries, including China, also place several of the PAHs into a black list or gray list of priority pollutants (Maria et al., 2006; Patryk and Stanislaw, 2005; Baran et al., 2004).

PAHs originate mainly from anthropogenic sources such as the combustion of fossil fuels and direct release of oil and its products. Due to rapid development of the demand in oil during the last two decades, air, water and soil have been significantly polluted (Jiang

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et al., 2005). Sources, environmental behaviors, ecological effect, and remediation of PAHs in air and water have been presented by many authors (Qiao et al., 2006; Ge et al., 2005; Doick et al., 2005; Hafner et al., 2005; Duan et al., 2005; Kannan et al., 2005; Li et al., 2004; Tao et al., 2004; Zhu et al., 2004; Tian et al., 2003; Jia, 1999). However, few of the researchers focused on PAHs from oily sludges (Ling et al., 2006; Zhan et al., 2006; Ling et al., 2005; Zhang et al., 2005; Ding et al., 2004; Tao et al., 2003; Zhan and Zhou, 2003; Liste and Alexander, 2000; Menzies et al., 1992). As PAHs could easily enter sediment, the determination of the degree of contamination with PAHs in soils around oilfield was therefore of particular significance.

In order to carry out the pollution treatment and reasonable distribution of the agricultural products in the region pertinently, this work attempts to analyze the distribution of PAHs controlled by EPA in the agricultural soil. The agricultural soil around Zhongyuan Oil Field was chosen as the research object. The main factors that influenced the distribution of PAHs were also discussed. By nemero index P, the pollution level of the soil adjacent to oily sludge was determined, which was used for oily sludge environmental health risk analysis. The results will provide the theoretical basis for the proper utilization and the scientific management of oily sludge in Zhongyuan Oil Field.

Samples and Experiments

Samples Collection

Oily sludge samples were collected from fresh oily sludge and air-dried oily sludge of the Third Wenming Plant of the oily sludge (3W), the Third Mazhai Plant of the oily sludge (3M), and the Fourth Wener Plant of the oily sludge (4W) in Zhongyuan Oil Field on December 4 and 8, 2006. According to the local monsoon feature, soil samples and corn samples were collected along with the leeway from the agricultural soil (topsoil 5–10 cm) distant from the oily sludge 10, 20, 50, 100, 200 and 500 m, respectively. There were no other factories and residents in the sampling areas. The details of sampling sites are listed in Table 1. The method of sampling was introduced through an example of 3W-1. We took a square in the place that was distant from the 3W oily sludge 10m, and the side length of square was 2m. We took a sample in the center of the square and four other samples in four corners of the square, then mixed the five samples as a sample of 3W-1. Samples of the other place can be taken according to the above sampling method. The tools of sampling

Table 1
Sampling sites

Sample	Sample	Sample	Type	Distance
3M-1	3W-1	4W-1	fresh oil sludge	—
3M-2	3W-2	4W-2	dried oil sludge	—
3M-3	3W-3	4W-3	soil	10 m
3M-4	3W-4	4W-4	soil	20 m
3M-5	3W-5	4W-5	soil	50 m
3M-6	3W-6	4W-6	soil	100 m
3M-7	3W-7	4W-7	soil	200 m
3M-8	3W-8	4W-8	soil	500 m

were a small soil spade, woven bag, or plastic bag. We put soil samples into a clean woven bag or plastic bag using a small soil spade, then labelled in and out of the bags to mark sampling sites and sample numbers.

Samples Treatment

We put fresh wet soil samples onto clean paper, crumbled them, and flattened samples to a lamella (about 2cm thick). Then, samples were air-dried among shade, and grinded homogeneously to the fullest extent possible with the order of the distance from farness to nearness, and sieved into particles with size of 60 meshes. They were placed in a polyvinyl chloride bag and stored at room temperature after sieving.

Instruments

High Performance Liquid Chromatography (HPLC, Shimadzu, Japan) with a fluorescence detector and VP-ODS column (Serial No. 9122504, 150L×4.6) was used for determination of PAHs. The ultrasonic washer (KQ5200, Kun Shan in China) was used for the extraction of PAHs. The rotary evaporator (Shen Sheng SENCO-R, China) and the thermostat water bath (Shen Sheng W201B, China) were used for the concentration of PAHs liquors. Low-speed tabletop centrifuge (TDL-40B, Shanghai) was used for separating PAHs samples. Water cycling multipurpose vacuum pump (SHB-III, Zheng Zhou in China) and quick mixer (Chang Zhou, China) were used in this study.

Reagents

Dichloromethane, cyclohexane, and methanol were analytically pure. Acetonitrile was of chromatographic pure. Silica-gel (dikma, the diameter was from 0.15 mm to 0.074 mm) were reactivated at 130°C for 16 h immediately prior to use. Anhydrous sodium sulphate were heated at 500°C in a furnace for 2 h prior to use and stored in the sealed desiccator. Sixteen PAHs standards were from Supelco Co.

Analytical Procedure

1) The extraction, concentration and purification of PAHs. 5.00 g of sample was put into the 100 mL centrifuge bottle. Then 20.00 mL of dichloromethane was added. The centrifuge bottle was kept in the ultrasonic washer of 40°C for 2 h and then transferred into the centrifugal vacuum pump of 2000 r/min for 5 min. 10.00 mL of supernatant was moved into the egg yard type bottle, and all the liquids were dried by rotary evaporator at 40°C. Afterwards, the resulting residue was dissolved in 2.00 mL of cyclohexane. 0.50 mL of the obtained solution was put on the mini silica column packed with 1.0 g of silica gel. The column was eluted with methylene chloride/hexane (v/v = 1:1), and the eluate was discarded with 1.00 mL. The second fraction containing PAHs was collected with 2.00 mL, and blown drying by nitrogen. The residue was redissolved in 1 mL of acetonitrile and stored at 4°C.

2) Determination of PAHs. HPLC equipped with fluorescence detector and VP-ODS column was used. The acetonitrile-water (90:10) solution was used as the mobile phase. The flow rate was 0.5 mL/min and the column temperature was at 30°C. Sample preconcentration liquid and mixed certificated liquid with same volume were extracted separately, and samples were determined by external standard method.

Table 2
Contents of PAHs of oily sludge samples and peripheral soil samples from 3M

Compound	3M-1	3M-2	3M-3	3M-4	3M-5	3M-6	3M-7	3M-8
NaP	886.6	461.4	612.9	600.1	602.4	485.4	360.1	275.4
Any	482.3	274.5	103.5	62.3	51.0	32.3	19.5	11.4
Ane	644.3	386.1	143.5	118.6	89.7	33.5	24.2	13.3
Flu	712.1	451.4	189.4	149.8	121.7	41.8	30.2	23.0
Phe	456.8	289.6	403.2	309.6	256.8	209.6	87.2	95.2
Ant	46.5	35.3	98.3	81.0	56.3	45.8	29.3	9.00
Fla	31.5	23.6	96.5	82.8	71.4	66.1	22.8	12.2
Pyr	77.3	66.8	175.5	140.3	86.3	35.3	9.75	9.75
BaAn	70.5	57.0	113.3	96.8	75.8	57.8	24.0	12.0
Chy	96.8	73.5	120.9	98.3	61.1	23.8	6.15	5.64
Bbf	29.9	26.0	31.4	13.5	14.3	14.3	12.7	11.9
Bkf	46.2	40.8	33.9	31.6	24.7	17.0	12.4	12.4
BaP	57.5	48.1	19.9	18.3	15.2	5.94	4.06	5.40
IIP	19.6	10.0	25.3	24.5	11.6	2.41	1.28	0.96
Daa	13.0	10.6	31.2	27.0	14.7	3.25	1.30	1.16
BgP	20.0	17.5	42.6	33.7	15.1	5.12	1.33	1.16
ΣPAHs	3690.9	2272.2	2241.3	1888.2	1568.1	1079.4	646.3	499.9

3) Quality control. The retention time of PAHs standard compound was used to analyze and compare in qualitative analyses and the determination of PAHs external standard method was used in quantitative analyses. The recovery of known samples was 47.5%–103.4%, and the relative standard deviation was 5.8%–9.7%. In addition, principal component analyses were conducted with SPSS1 1.0. Categories and contents of PAHs in samples were illustrated in Table 2.

Distribution Characteristics of PAHs in Soil Samples

As given in Tables 2–4, all sixteen PAHs in soil samples can be detected. Figure 1 shows the relations between the distances and contents of PAHs in soil samples. As seen, the

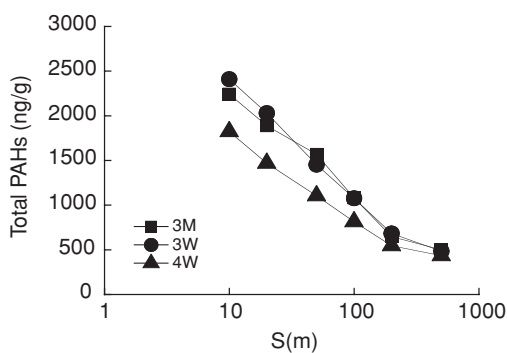


Figure 1. The relations between the distances and contents of PAHs in soil samples.

Table 3
Contents of PAHs of oily sludge samples and peripheral soil samples from 3W

Compound	3W-1	3W-2	3W-3	3W-4	3W-5	3W-6	3W-7	3W-8
NaP	1048.6	527.4	693.9	675.1	531.1	503.4	363.9	267.1
Any	546.0	318.0	117.0	65.3	48.8	31.5	21.0	10.4
Ane	678.5	391.6	160.7	130.3	85.0	32.8	23.4	12.5
Flu	812.9	504.7	228.2	180.7	91.4	53.3	33.1	20.9
Phe	527.2	328.8	445.6	324.0	243.2	183.2	105.6	89.6
Ant	58.5	39.0	102.8	84.8	53.3	44.3	31.5	8.25
Fla	38.8	25.1	108.7	93.5	69.2	65.4	24.3	12.9
Pyr	73.4	57.0	164.3	130.5	90.0	36.8	11.3	10.5
BaAn	68.3	58.5	110.3	98.3	81.0	54.8	25.5	12.8
Chy	90.3	65.4	101.9	91.7	63.2	21.6	7.03	7.03
Bbf	26.0	23.6	27.5	18.9	18.2	15.0	13.5	13.5
Bkf	47.8	40.1	34.7	33.1	22.4	15.4	13.9	10.0
BaP	53.6	44.2	21.5	19.1	12.8	8.92	5.55	4.30
IIP	17.2	6.66	29.3	27.7	13.2	1.44	1.04	0.96
Daa	11.4	8.77	28.7	26.2	11.4	2.92	1.28	1.19
BgP	13.5	10.3	33.7	30.5	17.5	4.55	1.16	1.08
ΣPAHs	4112.0	2449.1	2408.8	2029.7	1451.7	1075.3	683.1	483.0

Content Unit of PAHs in oily sludge: $\times 10^3$ ng/g; Content Unit of PAHs in soil: ng/g; PAHs: NaP: naphthalene, Any: acenaphthylene, Ane: acenaphthene, Flu: fluorine, Phe: phenanthrene, Ant: anthracene, Fla: fluoranthene, Pyr: pyrene, BaAn: benz(a)anthracene, Chy: chrysene, Bbf: benzo[b]fluoranthene, Bkf: benzo[k]fluorathene, BaP: benzo[a]pyrene, IIP: indeno(1, 2, 3-cd)pyre, Daa: dibenzo (a, h) anthrace, BgP: benzo(g,h,i)perylene.

Table 4
Contents of PAHs of oily sludge samples and peripheral soil samples from 4W

Compound	4W-1	4W-2	4W-3	4W-4	4W-5	4W-6	4W-7	4W-8
NaP	787.6	444.9	573.9	545.4	503.4	456.1	333.9	240.9
Any	506.3	279.8	99.8	56.3	46.5	30.0	17.3	12.0
Ane	612.3	356.5	156.8	122.5	75.7	29.6	20.3	14.0
Flu	643.7	419.8	195.1	143.3	84.2	43.9	26.6	18.7
Phe	308.0	191.2	340.8	233.6	172.0	121.6	69.6	71.2
Ant	36.8	27.0	60.8	50.3	36.0	24.0	9.48	6.03
Fla	22.8	16.7	62.3	60.0	41.0	23.6	12.2	13.7
Pyr	54.8	43.5	119.3	102.8	39.0	17.3	9.12	10.5
BaAn	43.5	36.8	49.5	32.3	26.3	18.0	11.3	12.0
Chy	60.3	46.5	65.4	49.4	33.3	18.0	6.30	4.26
Bbf	22.1	18.2	25.2	14.3	13.5	13.5	11.1	11.9
Bkf	24.7	18.5	23.1	17.7	12.4	11.6	10.0	11.6
BaP	40.3	37.1	15.2	12.8	7.90	2.18	3.83	4.06
IIP	6.66	4.09	11.6	10.0	6.90	1.12	0.96	1.12
Daa	5.97	5.47	14.7	13.9	3.09	1.36	1.28	1.36
BgP	7.70	6.73	8.51	4.07	2.70	1.16	1.08	1.16
ΣPAHs	3183.5	1953.8	1822.0	1468.7	1103.9	813.0	544.4	434.5

contents of PAHs in soil samples were dramatically decreased with the increase of the distance from oily sludge. The contents of PAHs in soil samples in 3M, 3W and 4W were 499.9–2241.3 ng/g, 578.1–2408.8 ng/g and 434.5–1822.0 ng/g, respectively (Kuang et al., 2008). The order of pollution degree in soil near the three plants was 3W > 3M > 4W, which was consistent with the order of the contents of PAHs of oily sludges in three plants. Tables 2–4 show that naphthalene, acenaphthene, fluorine, phenanthrene, and pyrene were characteristic factors of PAHs in soil samples of 3M and 3W, whereas, naphthalene, acenaphthene, fluorine, and phenanthrene were characteristic factors of PAHs in soil samples of 4W. Mass fractions of characteristic factors of PAHs in soil samples of 3M, 3W and 4W were 72.4%, 72.8% and 74.2%, respectively.

The Pollution Degree of PAHs and Ecological Risk Assessment in Soils Around Zhongyuan Oil Field

The Pollution Degree Evaluation of PAHs in Soils Around Zhongyuan Oil Field in Winter

Many researchers have shown that the total content of the environment priority control of 16 typical PAHs were usually chosen to evaluate their pollution level. West Europe proposed that the pollution degree of PAHs in soils were divided into four grade containing not contaminated, light contaminated, medium contaminated and heavily contaminated, based on the content determination range of PAHs in soils, the evaluation of exposure risk to human and the average absorption rate. Such pollution levels of PAHs in soils are given in Table 5. According to such standard, classification results of the PAHs pollution in soils of Zhongyuan oil field in winter investigated in this study are listed in Table 6. As seen, the pollution level of PAHs in soils around Zhongyuan Oil Field was correlative with the distance from oily sludge plants, which represented that the pollution level of PAHs in soils dramatically decreased with the increase of the distance from oily sludge plants. The soil samples of 3M-3, 3M-4, 3M-5, 3M-6, 3W-3, 3W-4, 3W-5, 3W-6, 4W-3, 4W-4 and 4W-5 were heavily contaminated, whereas the soil samples of 3M-7, 3W-7 and 4W-6 were medium contaminated. Moreover, the soil samples of 3M-8, 3W-8, 4W-7 and 4W-8 were light contaminated. In all soil samples of Zhongyuan oil field in winter, heavily contaminated samples, medium contaminated samples, and light contaminated samples accounted for 61.1%, 16.7% and 22.2%, respectively. The pollution degree around soils in 4W was lower than that of the soils in 3M and 3W, which was ascribed to the content of PAHs in 4W oil sludge was lower than that of 3M and 3W oil sludge.

Table 5
Pollution levels of PAHs in soils (ng/g)

Pollution levels of PAHs in soils (K)	not contaminated	light contaminated	medium contaminated	heavily contaminated
Concentration ranges of PAHs in soils	<200	200–600	600–1000	> 1000

Table 6
Evaluating results of the PAHs pollution in soils of Zhongyuan oil field in winter

Soils	K	soils	K	soils	K
3M-3	heavily contaminated	3W-3	heavily contaminated	4W-3	heavily contaminated
3M-4	heavily contaminated	3W-4	heavily contaminated	4W-4	heavily contaminated
3M-5	heavily contaminated	3W-5	heavily contaminated	4W-5	heavily contaminated
3M-6	heavily contaminated	3W-6	heavily contaminated	4W-6	medium contaminated
3M-7	medium contaminated	3W-7	medium contaminated	4W-7	light contaminated
3M-8	light contaminated	3W-8	light contaminated	4W-8	light contaminated

The Health Risk Assessment in Soils of Zhongyuan Oil Field in Winter

According to the health risk assessment, different PAHs have different toxicity. We can not only simply use the concentration of these compounds to evaluate human exposure dose. In fact, toxicity equivalent factors (TEF) of different composition should be combined to calculate equivalent concentration. Table 7 gave the TEF for 16 priority control PAHs given by Nisbet and LaGoy, which was calculated by the equivalent concentrations (BaP_{ep}) of the reference object (BaP). Based on such parameters, BaP equivalent concentrations of PAHs in soil samples in winter were given in Table 8.

Figure 2 shows that the distribution of BaP equivalent concentrations of PAHs in soil samples in winter were basically identical with the gross distribution of PAHs. Also it can reach maximum value near oil sludge sampling point, and reach minimum value in the farthest oil sludge sampling point, which mainly resulted from the fact that the distribution of PAHs in different samples was comparative close.

Contribution rates of different rings PAHs on BaP equivalent concentrations in soil samples in winter are given in Figure 3. The distribution of different rings PAHs on BaP equivalent concentrations and on PAHs measured total quantity had significant difference. This phenomenon was mainly caused by the differences between TEF. As TEF value was very low, contribution rates of 2–3 rings PAHs, which originally occupied a large proportion in the concentration of total PAHs on BaP equivalent concentrations, were very little. When TEF value was very high, contribution rates of 5 rings PAHs, which originally occupied

Table 7
The toxic equivalency factors (TEF) for 16 PAHs

PAHs	TEF	PAHs	TEF	PAHs	TEF	PAHs	TEF
NaP	0.001	Phe	0.001	BaAn	0.1	BaP	1
Any	0.001	Ant	0.01	Chy	0.01	IIP	0.1
Ane	0.001	Fla	0.001	Bbf	0.1	Daa	1
Flu	0.001	Pyr	0.001	Bkf	0.1	BgP	0.01

Table 8
BaP equivalent concentrations of PAHs in soil samples in winter (ng/g)

Components	3M-3	3M-4	3M-5	3M-6	3M-7	3M-8	3W-3	3W-4	3W-5	3W-6	3W-7	3W-8	4W-3	4W-4	4W-5	4W-6	4W-7	4W-8
NaP	0.6129	0.6001	0.6024	0.4854	0.3601	0.2754	0.6939	0.6751	0.5311	0.5034	0.3639	0.2671	0.5739	0.5454	0.5034	0.4561	0.3339	0.2409
Any	0.1035	0.0623	0.051	0.0323	0.0195	0.0114	0.117	0.0653	0.0488	0.0315	0.021	0.0104	0.0998	0.0563	0.0465	0.03	0.0173	0.012
Ane	0.1435	0.1186	0.0897	0.0335	0.0242	0.0133	0.1607	0.1303	0.085	0.0328	0.0234	0.0125	0.1568	0.1225	0.0757	0.0296	0.0203	0.014
Flu	0.1894	0.1498	0.1217	0.0418	0.0302	0.023	0.2282	0.1807	0.0914	0.0533	0.0331	0.0209	0.1951	0.1433	0.0842	0.0439	0.0266	0.0187
Phe	0.4032	0.3096	0.2568	0.2096	0.0872	0.0952	0.4456	0.324	0.2432	0.1832	0.1056	0.0896	0.3408	0.2336	0.172	0.1216	0.0696	0.0712
Ant	0.983	0.81	0.563	0.458	0.293	0.09	1.028	0.848	0.533	0.443	0.315	0.0825	0.608	0.503	0.36	0.24	0.0948	0.0603
Fla	0.0965	0.0828	0.0714	0.0661	0.0228	0.0122	0.1087	0.0935	0.0692	0.0654	0.0243	0.0129	0.0623	0.06	0.041	0.0236	0.0122	0.0137
Pyr	0.1755	0.1403	0.0863	0.0353	0.00975	0.00975	0.1643	0.1305	0.09	0.0368	0.0113	0.0105	0.1193	0.1028	0.039	0.0173	0.00912	0.0105
BaAn	11.33	9.68	7.58	5.78	2.4	1.2	11.03	9.83	8.1	5.48	2.55	1.28	4.95	3.23	2.63	1.8	1.13	1.2
Chy	1.209	0.983	0.611	0.238	0.0615	0.0564	1.019	0.917	0.632	0.216	0.0703	0.0703	0.654	0.494	0.333	0.18	0.063	0.0426
Bbf	3.14	1.35	1.43	1.43	1.27	1.19	2.75	1.89	1.82	1.5	1.35	1.35	2.52	1.43	1.35	1.35	1.11	1.19
Bkf	3.39	3.16	2.47	1.7	1.24	1.24	3.47	3.31	2.24	1.54	1.39	1	2.31	1.77	1.24	1.16	1	1.16
BaP	19.9	18.3	15.2	5.94	4.06	5.4	21.5	19.1	12.8	8.92	5.55	4.3	15.2	12.8	7.9	2.18	3.83	4.06
IlP	2.53	2.45	1.16	0.241	0.128	0.096	2.93	2.77	1.32	0.144	0.104	0.096	1.16	1	0.69	0.112	0.096	0.112
Daa	31.2	27	14.7	3.25	1.3	1.16	28.7	26.2	11.4	2.92	1.28	1.19	14.7	13.9	3.09	1.36	1.28	1.36
BgP	0.426	0.337	0.151	0.0512	0.0133	0.0116	0.337	0.305	0.175	0.0455	0.0116	0.0108	0.0851	0.0407	0.027	0.0116	0.0108	0.0116
ΣPAHs	75.8325	65.5335	45.1443	19.9922	11.3196	10.88425	74.6824	66.7694	40.1787	22.1149	13.2035	9.8035	43.7351	36.4316	18.5818	9.1157	9.10362	9.5775

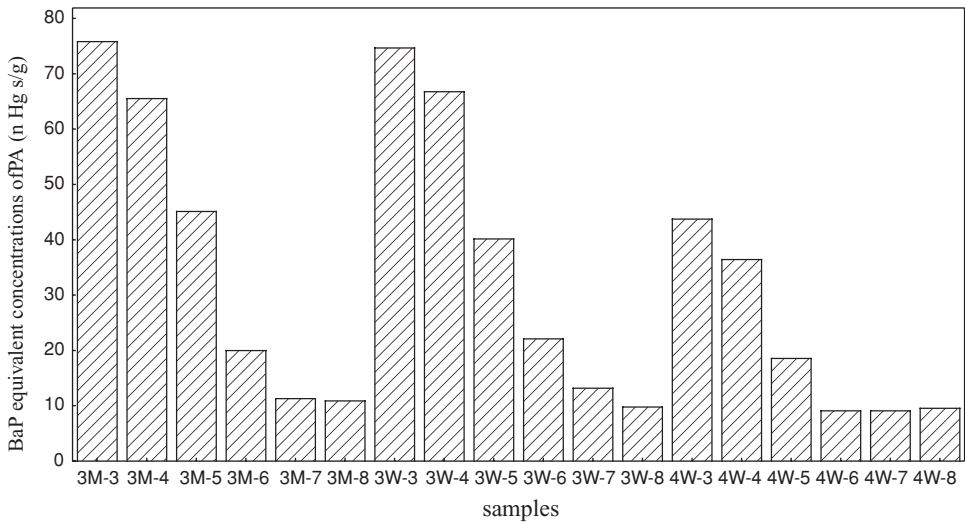


Figure 2. The distribution of BaP equivalent concentrations of PAHs in soil samples in winter.

a small proportion in the concentration of total PAHs on BaP equivalent concentrations, were very large.

Ecological Risk Assessment of PAHs in Soils Around Zhongyuan Oil Field in Winter

At present, the allowable PAHs residues in farmland soils of China had not been established. In this research, the standard of PAHs in farmland soils in Canada was borrowed. The regulation is that the prohibitive contents of naphthalene, phenanthrene, pyrene, Benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluorathene, dibenzo[a, h]anthrace and indeno[1, 2, 3-cd]pyre were 100 ng/g (Annokkee, 1990). The range of values of this classification (<0.7, 0.7–1, 1–2, 2–3, >3), for “not contaminated,” “warning,” “light contaminated,” “medium contaminated” and “heavily contaminated”

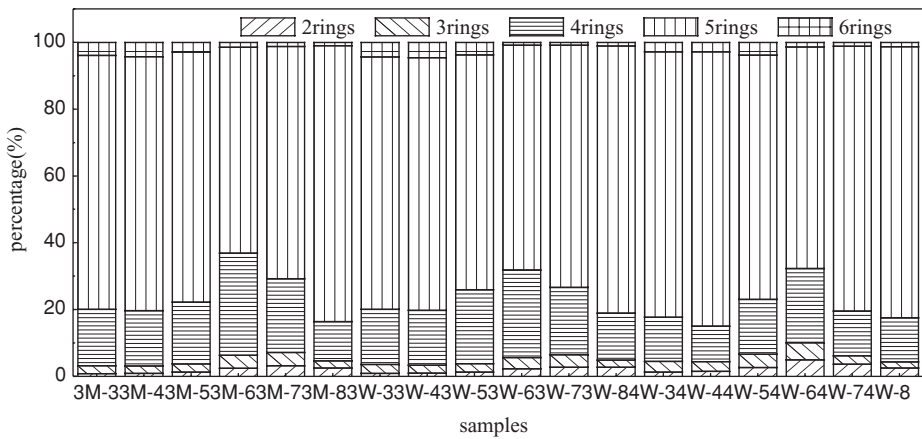


Figure 3. Contribution rates of different rings PAHs on BaP equivalent concentrations in winter.

Table 9
The marker of P in soil samples

No.	P	No.	P	No.	P
3M-3	4.49	3W-3	5.06	4W-3	4.16
3M-4	4.36	3W-4	4.90	4W-4	3.93
3M-5	4.35	3W-5	3.84	4W-5	3.61
3M-6	3.50	3W-6	3.62	4W-6	3.26
3M-7	2.58	3W-7	2.61	4W-7	2.39
3M-8	1.98	3W-8	1.92	4W-8	1.72

samples, respectively, were derived from nemero index P. Although the weather in the winter in Canada is cooler than that of China, and having influence on distribution, dispersion, volatilization, and degradation of PAHs, they cannot play decisive roles in a fundamental sense.

Nine PAHs residues in all eighteen sampling points were evaluated by nemero index P. Table 9 illustrated the marker of P in soil samples. Around 3M soil samples in winter, the range of nemero index P values was 1.98–4.49, and it was correlative with the distance from oily sludge plants. Such results represented that the nemero index P values increased with the increasing of the distance from oily sludge plants. The minimum value of 1.98 appeared at the 3M-8 sampling point and the maximum value of 4.49 appeared at the 3M-3 sampling point. The soil samples of 3M-3, 3M-4, 3M-5 and 3M-6 were heavily contaminated and the soil samples of 3M-7 were medium contaminated. The soil samples of 3M-8 were light contaminated. The range of nemero index P values was 1.92–5.06 around 3W soil samples and the variation characteristics of nemero index P values were consistent with P of 3M soils. The minimum value of 1.92 appeared at the 3W-8 sampling point and the maximum value of 5.06 appeared at 3W-3 sampling point. The soil samples of 3W-3, 3W-4, 3W-5 and 3W-6 were heavily contaminated and the soil samples of 3W-7 were medium contaminated. However, the soil samples of 3W-8 were light contaminated. The range of nemero index P values was 1.72–4.16 around 4W soil samples and the variation characteristics of nemero index P values were consistent with P of 3M and 4W soils. The minimum value of 1.72 appeared at the 4W-8 sampling point, and the maximum value of 4.16, appeared at 4W-3 sampling point. The soil samples of 4W-3, 4W-4, 4W-5 and 4W-6 were heavily contaminated and the soil samples of 4W-7 were medium contaminated. For comparison, the soil samples of 4W-8 were light contaminated.

The evaluation results of the marker of P showed that 66.7% of the samples obtained around Zhongyuan Oil Field in winter were as “heavily contaminated,” 16.7% as “medium contaminated,” and 16.6% as “light contaminated.” The result of classification evaluation presented that soils around oily sludge was seriously polluted.

Conclusion

According to the determination of contamination degree with polycyclic aromatic hydrocarbons (PAHs) in samples of soils in winter around three different oily sludges in Zhongyuan Oil Field, soils around oily sludge were heavily polluted. Although the pollution degree of PAHs in different plants (3M, 3W, 4W) was different, the detection rate has reached 100%.

1. The contents of PAHs in soil samples in 3M, 3W and 4W were 499.9–2241.3 ng/g, 578.1–2408.8 ng/g and 434.5–1822.0 ng/g, respectively. The order of pollution degree in soil near the three plants was 3W > 3M > 4W. Naphthalene, acenaphthene, fluorine, phenanthrene and pyrene were characteristic factors of PAHs in soil samples of 3M and 3W, whereas, naphthalene, acenaphthene, fluorine and phenanthrene were characteristic factors of PAHs in soil samples of 4W.
2. According to the total content of the PAHs in soil samples that can evaluate their pollution level, in the soil samples of Zhongyuan oil field in winter, heavily contaminated samples accounted for 61.1%; medium contaminated accounted for 16.7%, and light contaminated accounted for 22.2%. The evaluation results of the marker of P showed that 66.7% of the samples obtained around Zhongyuan Oil Field in winter were “heavily contaminated,” 16.7% as “medium contaminated,” and 16.6% as “light contaminated.” All the results of classification evaluation presented that soils around oily sludge were seriously polluted.

References

- Annoke, G. J. 1990. MT-TNO research into the biodegradation of soils and sediments contaminated with oils and PAHs. *J. Wolf K. Contaminated Soil*, Kluwer Academic Publishers, New York, 941–945.
- Baran, S., Bielinska, E. J., and Oleszczuk, P. 2004. Enzymatic activity in an airfield soil polluted with polycyclic aromatic hydrocarbons (PAHs). *J. Geoderma*, **118**, 221–232.
- Ding, K. Q., Luo, Y. M., Liu, S. L., Song, J., Wu, L. H., Xing, W. Q., Li, Z. G., and Tao, S. 2004. Dynamics in benzo [a] pyrene concentrations in soil as influenced by ryegrass plants. *J. Acta. Petrol Sin.*, **41**(3), 348–353.
- Doick, K. J., Klingelmann, E., Burauel, P., Jones, K. C., and Semple, K. T. 2005. Long-term fate of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in an agricultural soil. *J. Environ. Sci. Technol.*, **39**, 3663–3670.
- Duan, J. C., Bi, X. H., and Tan, J. H. 2005. The differences of the size distribution of polycyclic aromatic hydrocarbons (PAHs) between urban and rural sites of Guangzhou, China. *J. Atmos. Res.*, **78**, 190–203.
- Ge, C. J., An, Q., and Dong, Y. H. 2005. Residue and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils around a steel mill. *J. Rural Eco-Environ.*, **21**, 66–69.
- Hafner, W. D., Carlson, D. L., and Hites, R. A. 2005. Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. *J. Environ. Sci. Technol.*, **39**, 7374–7379.
- Jia, R. B. 1999. Studies on determination method of polycyclic aromatic hydrocarbons (PAHs) in water samples. *J. Environ. Monit. China*, **15**, 40–42.
- Jiang, Y., Zhao, C. C., and Zhao, D. F. 2005. Characteristic of oily sludge and several treatment methods. *J. Environ. Protect. Oily Gas Fields*, **15** (4), 38–41.
- Kannan, K., Johnson-Restrepo, B., Yohn, S. S., Giesy, J. P., and Long, D. T. 2005. Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from michigan inland lakes. *J. Environ. Sci. Technol.*, **39**(13), 4700–4706.
- Kuang, S. P., Sun, D. Y., and Sun, Y. H. 2008. Pollution characteristics of PAHs in oily sludge and around soils of Zhongyuan Oil Field. *J. Agro-Environ. Sci.*, **27**(3), 855–861.
- Li, J., Zhang, G., Qi, S. H., and Liu, G. Q. 2004. Source analysis and apportionment of particulate phase polycyclic aromatic hydrocarbons (PAHs) in Guangzhou City. *J. Acta. Sci. Circum.*, **24**, 661–666.
- Ling, W. T., Gao, Y. Z., Li, Q. L., Xie, Z. M., and Xiong, W. 2006. Uptake of phenanthrene and pyrene by ryegrass from water. *J. Acta. Ecologica. Sinica.*, **26**(10), 3332–3338.

- Ling, W. T., Zhu, L. Z., Gao, Y. Z., and Xing, W. 2005. Root uptake and its prediction model of PAHs from soils. *J. Acta. Ecol. Sin.*, **26**(9), 2320–2325.
- Liste, H. H., and Alexander, M. 2000. Plant-promoted pyrene degradation in soil. *J. Chemosphere*, **40**, 7–10.
- Maria, B., Celia, D., and Cristina, N. 2006. Use of lichens as pollution biomonitors in remote areas: comparison of PAHs extracted from lichens and atmospheric particles sampled in and around the somport tunnel (Pyrenees). *J. Environ. Sci. Technol.*, **40**, 6384–6391.
- Menzies, A., Potockib, B., and Santodonato, J. 1992. Exposure to carcinogenic PAHs in the environment. *J. Environ. Sci. Technol.*, **1**(26), 1278.
- Patryk, O., and Stanislaw, B. 2005. Polycyclic aromatic hydrocarbons content in shoots and leaves of willow (*salix viminalis*) cultivated on the sewage sludge-amended soil. *J. Water Air Soil Pollut.*, **168**, 91–111.
- Qiao, M., Wang, C. X., and Huang, S. B. 2006. Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake. *J. China. Environ. Int.*, **32**, 28–33.
- Tao, S., Cui, Y. H., Xu, F. L., Li, B. G., Cao, J., Liu, W. X., Schmitt, G., Wang, X. J., Shen, W. R., Qing, B. P., and Sun, R. 2004. Polycyclic aromatic hydrocarbons (PAHs) in agricultural soil and vegetables from Tianjin. *J. Sci. Total Environ.*, **320**, 11–24.
- Tao, X. Q., Dang, Z., Lu, G. N., and Yi, X. Y. 2003. Biodegradation mechanism of polycyclic aromatic hydrocarbons (PAHs) in soil: a review. *J. B Miner Petrol Geochem*, (10), 356–360.
- Tian, Y., Zheng, T. L., Wang, X. H., and Luo, Y. R. 2003. Contamination characteristics of polycyclic aromatic hydrocarbons and bioremediation strategy in sediments of Western Xiamen Harbor and its adjacent sea area. *J. Oceanogr Taiwan Strait*, **22**, 192–200.
- Zhan, X. H., and Zhou, L. X. 2003. Environmental behavior of PAHs in soil-plant system. *J. Ecol. Environ.*, **12**(4), 487–492.
- Zhan, X. H., Zhou, L. X., and Wan, Y. J. 2006. Impact of dissolved organic matter on plant uptake of phenanthrene and its mechanisms. *J. Environ Sci*, **27**(9), 1884–1889.
- Zhang, H. B., Luo, Y. M., Huang, M. H., Zhang, G. L., and Zhao, Q. G. 2005. Hong Kong soil researches III. PAHs contents in soils and their origins. *J. Acta. Petrol. Sin.*, **42**(6), 936–941.
- Zhu, L. Z., Chen, B. L., Wang, J., and Shen, H. 2004. Pollution survey of polycyclic aromatic hydrocarbons in surface water of Hangzhou, China. *J. Chemosphere*, **56**(11), 1085–1095.