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Accumulation and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils around oil sludge in Zhongyuan oil field, China

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Abstract In this paper, the contents of polycyclic aromatic hydrocarbons (PAHs) in soil samples around three different oily sludge plants in winter were analyzed by high performance liquid chromatography (HPLC) and the pollution degree with PAHs in soil samples was determined. Soil samples were collected from the agricultural soil around three different oily sludge plants (the Third Wenming Plant, the Third Mazhai Plant, and the Fourth Wener Plant) along with the leeway in Zhongyuan oil field. The distances from collected sample sites to oily sludge plants are 10, 20, 50, 100, 200, and 500 m, respectively. The results show that the contents of PAHs in soil samples decrease dramatically with the increase of the distance from the oily sludge, and that the PAHs with 2–4 rings are major pollutants in the oily sludge and soil samples. The main factors, which influenced the distribution of PAHs are discussed. Based on Nemero Index P, the classification evaluation shows that the soils around the oily sludge are heavily polluted in winter. The health risk assessment and ecological risk assessment of the soils around the oily sludge in Zhongyuan oil field in winter are analyzed.

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Introduction

In recent years, concern about persistent organic pollutants (POPs) has considerably increased (Nadal et al. 2004). One of the most common representatives of POPs in nature environment are polycyclic aromatic hydrocarbons (PAHs), which represent 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, USA). Many countries including China also place several of PAHs into black list or gray list of priority pollutants (Maria et al. 2006; Patryk and Stanislaw 2005; Baran et al. 2004).

Polycyclic aromatic hydrocarbons originate mainly from anthropogenic sources such as combustion of fossil fuels and direct release of oil and its products (http://www.chem.unep.ch/gmn/default.htm). Owing to the rapid demand for oil during the last two decades, air, water, and soil have been significantly polluted (Jiang 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, there are few reports about the degree of pollution involving PAHs in agricultural soil around oil fields (Ling et al. 2005, 2006;

Zhan et al. 2006; Zhang et al. 2005; Ding et al. 2004; Tao et al. 2003; Zhan and Zhou 2003; Liste and Alexander 2000; Menzies et al. 1992). It is of particular significance to determine the degree of contamination involving PAHs in soils around oil fields as PAHs can easily enter the sediment.

In this paper, the distribution of PAHs in agricultural soil around the Zhongyuan oil field was analyzed to carry out the pollution treatment and reasonable distribution of the agricultural products in this region pertinently. The main factors, which influenced the distribution of PAHs were also discussed. Nemero Index P determined the pollution level in the soil adjacent to the oily sludge that was used for environmental health risk analysis. The results will provide theoretical basis for proper utilization and scientific management of oily sludge in Zhongyuan oil field.

Samples and experiments

Samples collection

The oily sludge samples were collected from fresh oily sludge and air-dried oily sludge of the Third Wenming Plant of oily sludge (3W), the Third Mazhai Plant of oily sludge (3M) and the Fourth Wener Plant of oily sludge (4W) in Zhongyuan oil field on December 4 and 8, 2008, respectively. According to the local monsoon feature, the soil samples were collected from the agricultural soil (topsoil 5–10 cm) along with the leeway, which are distant from the oily sludge 10, 20, 50, 100, 200, and 500 m, respectively. There were no factories or residents in the sampling areas. The details of sampling sites are listed in Table 1.

Samples treatment

The collected samples were air-dried in the shade; the samples were ground according to the order of distance from farthest to nearest, and sieved into 60-mesh size

Table 1 Sampling sites

Sample	Sample	Sample	Type	Distance (m)
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
3M-4	3W-4	4W-4	Soil	20
3M-5	3W-5	4W-5	Soil	50
3M-6	3W-6	4W-6	Soil	100
3M-7	3W-7	4W-7	Soil	200
3M-8	3W-8	4W-8	Soil	500

particles. 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 PAH liquors. Low-speed tabletop centrifuge (TDL-40B, Shanghai) was used for separating PAH samples. A water-cycling, multipurpose vacuum pump (SHB-III, Zheng Zhou in China) and a quick mixer (Chang Zhou, China) were used in this study.

Reagents

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

Analytical procedure

The extraction, concentration, and purification of PAHs

A 5.00 g sample was put into a 100 mL centrifuge bottle. Then 20.00 mL of dichloromethane was added. The centrifuge bottle was kept in the ultrasonic washer at 40°C for 2 h and then transferred into a centrifugal vacuum pump of 2,000 r/min for 5 min. 10.00 mL of supernatant was moved into an egg yard type bottle, and all the solvent was evaporated 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 in the mini silica column packed with 1.00 g of silica gel. The column was eluted with methylene chloride/hexane (1:1, v/v), 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 1.00 mL of acetonitrile and stored at 4°C.

Determination of PAHs

HPLC equipped with fluorescence detector and VP-ODS column was used. The acetonitrile–water (90:10, v/v)

solution was used as the mobile phase. The flow rate was 0.50 mL/min and the column temperature was at 30°C. A sample preconcentration liquid and a mixed certificate liquid of the same volume were extracted separately, and the samples were determined by the external standard method.

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 $(87.74 \pm 8.05)\%$. In addition, principal component analyses were conducted with SPSS 11.0 software. Categories and contents of PAHs in samples are illustrated in Tables 2, 3, 4.

Distribution characteristics of PAHs in soil samples

As given in Tables 2, 3, 4, all 16 PAHs from the soil samples were detected. Figure 1 shows the relations between the distances and the contents of PAHs in the soil samples. As seen, the contents of PAHs in soil samples dramatically decreased as the distance from the oily sludge increased. The contents of PAHs in soil samples in 3M, 3W

and 4W were 499.9–2,241.3, 483.0–2,408.8 and 434.5–1,822.0 ng/g, respectively (Kuang et al. 2008). According to the PAHs' content in soil, the order of pollution degree in soil near the three plants was 3W > 3M > 4W, which was consistent with the order of the PAHs contents in oily sludge from the three plants. Tables 2, 3, 4 show that naphthalene, acenaphthene, fluorene, phenanthrene and pyrene were characteristic PAH factors in the soil samples of 3M and 3W, whereas, naphthalene, acenaphthene, fluorene and phenanthrene were characteristic PAH factors in the soil samples of 4W. In the soil samples of 3M, 3W and 4W, mass fractions of the characteristic factors of PAHs were 72.4, 72.8 and 74.2%, respectively.

Concentrations ranges of individual PAHs compounds in the tested soils in winter are listed in Table 5. From Table 5, it can be seen that the concentrations ratios (C_{max}/C_{min}) of 16 PAHs in the 18 soil samples range from 2.83 to 39.4. The ratio order is: Bgp > I1P > Chy > Daa > Pyr > Ant > Ane > Flu > Any > BaAn > BaP > Fla > Phe > Bkf > Nap > Bbf. This result indicates that the pollution degree is significantly different between individual soil samples. As the distance to oily sludge increases, content of each PAHs component decreases. The farther the distance from the oily sludge, the lighter the pollution level.

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
I1P	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	3,690.9	2,272.2	2,241.3	1,888.2	1,568.1	1,079.4	646.3	499.9
Fla/Pyr	0.408	0.353	0.550	0.590	0.827	1.87	2.34	1.25

Content Unit of PAHs in oily sludge: $*10^3$ ng/g; Content Unit of PAHs in soil: ng/g

PAHs: *NaP* naphthalene, *Any* acenaphthylene, *Ane* acenaphthene, *Flu* fluorene, *Phe* phenanthrene, *Ant* anthracene, *Fla* fluoranthene, *Pyr* pyrene, *BaAn* benzo(a)anthracene, *Chy* chrysene, *Bbf* benzo[b]fluoranthene, *Bkf* benzo[k]fluoranthene, *BaP* benzo[a]pyrene, *I1P* indeno(1, 2, 3-cd)pyrene, *Daa* dibenzo (a, h) anthracene, *BgP* benzo(g,h,i)perylene

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	1,048.6	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
I1P	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	4,112.0	2,449.1	2,408.8	2,029.7	1,451.7	1,075.3	683.1	483.0
Fla/Pyr	0.529	0.440	0.662	0.716	0.769	1.78	2.15	1.23

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
I1P	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	3,183.5	1,953.8	1,822.0	1,468.7	1,103.9	813.0	544.4	434.5
Fla/Pyr	0.416	0.384	0.522	0.584	1.05	1.36	1.34	1.30

Now, many researchers have made use of the concentration ratios of Fla/Pyr as a standard to determine the sources of PAHs. Sicre et al. (1987) have indicated that PAHs are mainly from fossil fuel combustion when Fla/Pyr ratio is >1, and PAHs are mainly from oil products when Fla/Pyr ratio is <1. From Tables 2, 3, 4, it can be found that the Fla/Pyr ratios in the 18 soil samples increase with the distance to oily sludge increasing. These phenomena show that the influence of oil source diminishes as the distance to oily sludge increases. The Fla/Pyr ratios became >1 at distance up to 100 m from oily sludge for soil samples of 3M and 3W, while the distance was 50 m for soil sample of 4W. The results indicate that combustion sources become major sources of PAHs in soil when the distance from the
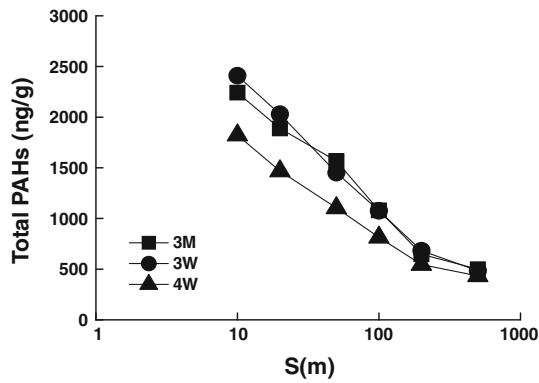
Fig. 1 The relations between the distances and contents of PAHs in soil samples

oily sludge is up to a certain value. Through analyzing distribution characteristics of PAHs and Fla/Pyr ratios in soil samples, oil sources are major sources of PAHs in soil close to oily sludge. With the distance to oily sludge increasing, the influence of oil sources decreases gradually, while the influence of combustion sources increases gradually. Oil sources and combustion sources become the corporate sources of PAHs in soil when the distance from oily sludge is up to a certain value.

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 researches have shown that the total content of the environment priority control of 16 typical PAHs were usually chosen to evaluate their pollution level. Maliszewska (1996) proposed that the pollution degree of PAHs in soils could be divided into four grades, viz., 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. This standard has been used to evaluate pollution levels in west Europe. Such pollution levels of PAHs in soils are given in Table 6. According to such standard, classification results of the PAHs pollution in soils of Zhongyuan oil field in winter are listed in Table 7. As seen, the pollution level of PAHs in soils around Zhongyuan oil field was correlative with the distance from oily sludge plants, which indicated 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 showed heavy contamination, whereas the soil samples of 3M-7, 3W-7, and 4W-6 showed medium contamination. Moreover, the soil samples of 3M-8, 3W-8, 4W-7, and 4W-8 showed light contamination. In all the soil samples from Zhongyuan oil field in winter, heavily contaminated samples, medium-contaminated samples, and lightly contaminated samples accounted for 61.1, 16.7 and 22.2%, respectively. The pollution degree of soils in 4W was lower than that of soils in 3M and 3W, which was ascribed to the content of PAHs in 4W oil sludge lower than that of 3M and 3W oil sludge.

The health risk assessment in soils of Zhongyuan oil field in winter

According to the health risk assessment, different PAHs have different toxicities. It is unreasonable to evaluate human exposure dose by simply adding the concentration of these compounds. In fact, toxicity equivalent factors (TEF) of different composition should be combined to calculate equivalent concentration. Table 8 shows the TEF for 16 priority control PAHs given by Nisbet and LaGoy (1992), which was calculated by the equivalent concentrations (BaP$_{ep}$) of the reference object (BaP). Based on such parameters, BaP equivalent concentrations of PAHs in the soil samples in winter are given in Table 9.

Figure 2 shows that the distribution of BaP equivalent concentrations of PAHs in the soil samples in winter are basically identical with the gross distribution of PAHs. In

Table 5 Concentration of individual PAHs compounds in the tested soils (ng/g) in winter

Compounds	Concentration range	C_{max}/C_{min}	Compounds	Concentration range	C_{max}/C_{min}
NaP	240.9–693.9	2.88	BaAn	11.3–113.3	10.0
Any	10.4–117	11.3	Chy	4.26–120.9	28.4
Ane	12.5–160.7	12.9	Bbf	11.1–31.4	2.83
Flu	18.7–228.2	12.2	Bkf	10.0–34.7	3.47
Phe	71.2–445.6	6.26	BaP	2.18–21.5	9.86
Ant	6.03–102.8	17.0	I1P	0.96–29.3	30.5
Fla	12.2–108.7	8.91	Daa	1.16–31.2	26.9
Pyr	9.12–175.5	19.2	BgP	1.08–42.6	39.4

Table 6 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	600–1,000	>1,000

Table 7 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

Table 8 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	I1P	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

addition, it can reach a maximum value near the oil-sludge-sampling site, and a minimum value in the farthest oil-sludge-sampling site, which mainly results from the fact that the distribution of PAHs in different samples was comparatively close.

Contribution rates of different rings PAHs on BaP equivalent concentrations in the soil samples in winter are given in Fig. 3. The contribution of different rings PAHs on BaP equivalent concentrations and on PAHs measured total quantity was significantly different. 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-ring PAHs, which originally occupied 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

In this paper, the standard of PAHs in farmland soils in Canada is used to assess ecological risk since the allowable PAHs residues in farmland soils of China have not been established. Although the weather in winter of Canada is cooler than that of China, and therefore has influence on

distribution, dispersion, volatilization, and degradation of PAHs, they cannot play decisive roles in a fundamental sense. According to the standard of PAHs in farmland soils in Canada, the prohibitive contents of naphthalene, phenanthrene, pyrene, Benz[a]anthracene, benzo[a]pyrene, benzo [b]fluoranthene, benzo[k]fluorathene, dibenzo[a, h]anthracene and indeno[1, 2, 3-cd]pyre were 100 ng/g (Annokkee 1990). The ranges of this classification values (<0.7, 0.7–1, 1–2, 2–3, >3) for 'not contaminated', 'warning', 'light contaminated', 'medium contaminated' and 'heavily contaminated' samples, respectively, were derived from Nemero Index P.

Nemero Index P evaluated 9 PAH residues from all 18 sampling points. Table 10 illustrates 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, which was correlative with the distance from oily sludge plants. Such result suggested 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 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 variation characteristics of Nemero Index P values around 3W and 4W soil samples were consistent with P of 3M soils. The range of Nemero Index P values was 1.92–5.06 and 1.72–4.16 around 3W and 4W soil samples, respectively. For 3W soil samples, the minimum P value of 1.92 appeared at the 3W-8 sampling site and the maximum p value of 5.06 appeared at 3W-3 sampling site. For 4W soil samples, the minimum value of 1.72 appeared at the 4W-8 sampling site and the maximum value of 4.16 appeared at 4W-3 sampling site. The soil samples of 3W-3, 3W-4, 3W-5, 3W-6, 4W-3, 4W-4, 4W-5 and 4W-6 were heavily contaminated. The soil samples of 3W-7 and 4W-7

Table 9 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
IIP	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

Fig. 2 The distribution of BaP equivalent concentrations of PAHs in soil samples in winter
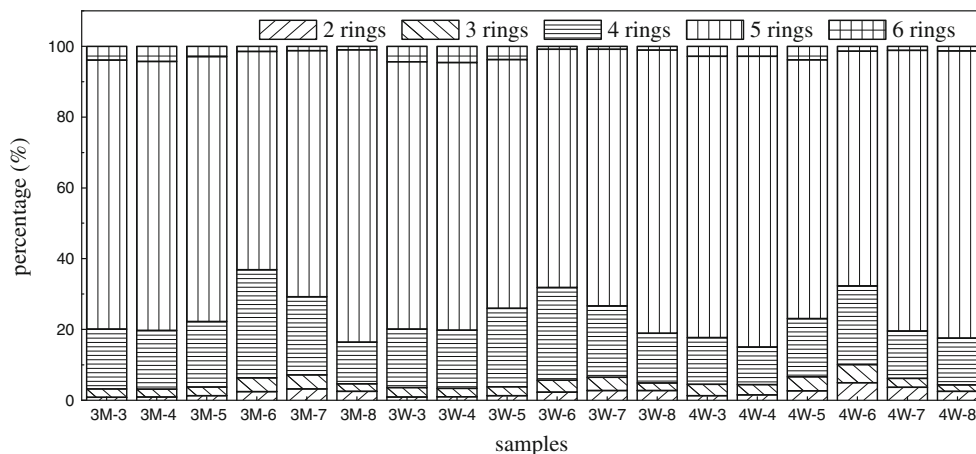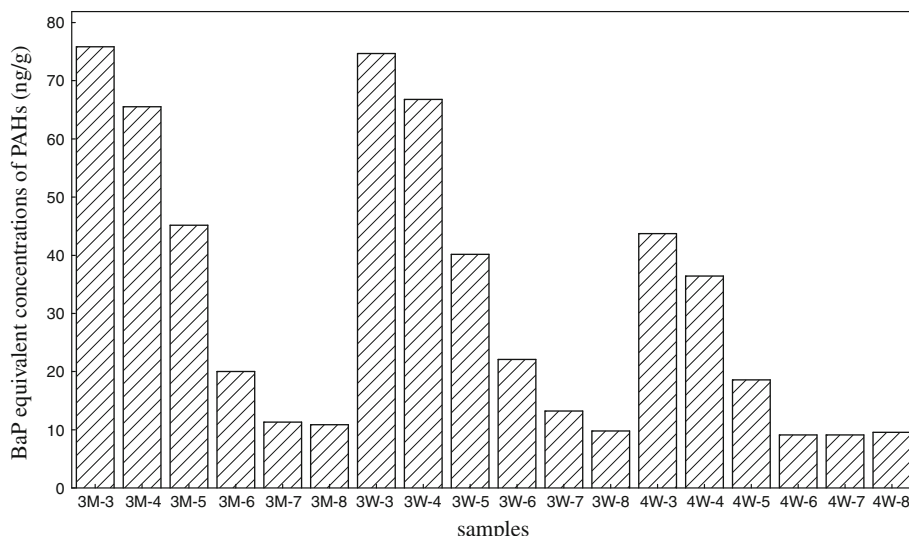
Fig. 3 Contribution rates of different rings PAHs on BaP equivalent concentrations in winter

Table 10 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

were medium contaminated. For comparison, the soil samples of 3W-8 and 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'. Result of classification evaluation presented that the soils around oily sludge was seriously polluted.

Conclusion

According to the contamination degree of PAHs in soil samples in winter, soils around three different oily sludges in Zhongyuan oil field were heavily polluted. Although the pollution degree of PAHs in different plants (3M, 3W, 4W) is different, the contamination rate has reached 100%.

1. The contents of PAHs in soil samples in 3M, 3W and 4W were 499.9–2,241.3, 483.0–2,408.8 and 434.5–1,822.0 ng/g, respectively. The order of pollution degree in soil near the three plants was 3W > 3M > 4W. Naphthalene, acenaphthene, fluorene, phenanthrene and pyrene were characteristic factors of PAHs in soil samples of 3M and 3W, whereas, naphthalene, acenaphthene, fluorene and phenanthrene were characteristic factors of PAHs in soil samples of 4W.

2. According to the total content of PAHs in the soil samples, heavily contaminated samples accounted for 61.1%; medium contaminated samples accounted for 16.7% and light contaminated samples accounted for 22.2% in the soil samples of Zhongyuan oil field in winter. 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'. All the results of classification evaluation presented that soils around oily sludge were seriously polluted.

Due to ubiquity and persistence of PAHs, the PAHs contents are excessive in most soils of petrochemical area, which has done harm to the health of oil workers and ambient residents. Much attention ought to be given to pollution from oily sludge.

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