Determination of Chrysene by Gas Chromatography in Selected Soils from Al-Diwaniya Province, Iraq

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Determination of polycyclic aromatic hydrocarbons compounds in the soil samples is of interest due to their carcinogenic and mutagenic activity in biological systems. The present study focused on the determination concentrations of chrysene in selected soils from Al-Diwaniya province, Iraq. Four sampling sites have been selected of pollution locate on study area. For every sampling site, four sub samples of soils were chooses included: industrial soil, urban soil, cereal grown soil and rural soil, the comparison among these soils were achieved during this study. Soxhlet extraction method was applied to extract the chrysene of soil samples. Under the optimized conditions, low limits of detection and good linearity were obtained. Soil samples were then analyzed by gas chromatography. The analysis of chrysene in real soil samples gave percentage recoveries ranged from 72.23 to 96.11 % with relative standard deviations (RSD) ranged from 1.65 to 4.87 %.

Keywords: Chrysene, Pollution of soil, Al-Diwaniya pollution, Extraction of chrysene.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are considering an important contaminant source for the soil[1]. Polynuclear aromatic hydrocarbons defined as compounds that consist of two or more fused aromatic rings, containing only hydrogen and carbon atoms[2,3]. Polycyclic aromatic hydrocarbons are ubiquitous products of the incomplete burning of organic compounds[4-6] produced from combustion of fossil fuels, wood processing, domestic heating waste incineration and vehicular emission and other industrial factories sources[7,8]. Polynuclear aromatic hydrocarbons are a category of contaminants of significant environmental concern due to their stability to the degradation[9] and tendency to accumulate in food chains favored by their affinity for fatty tissues.

Most polycyclic aromatic hydrocarbons are suspected carcinogens and mutagens they are widespread in the soil, air and water[10]. Polycyclic aromatic hydrocarbons containing two fused aromatic rings or more are usually possess high stability in the environmental owing to the high hydrophobicity and stable chemical structure. They are not very soluble and can be adsorbed onto soil particles, especially on soil organic materials[11]. Polycyclic aromatic hydrocarbons can be dispersed in soil by surface runoff and dust production, soil therefore is considered as one of the contamination sources for polycyclic aromatic hydrocarbons pollution in the sediments and air[12]. Type of soils and properties like organic compounds contents play as the most important role in the adsorption of polycyclic aromatic hydrocarbons in soils[13].

The Soxhlet extraction has been frequently used as a benchmark technique for extraction of polycyclic aromatic hydrocarbons from sediments and soils. Basically, in this technique, the sample of sediments or soils is placed into an extraction thimble which is then extracted using a suitable solvent *via* the reflux cycle. Once the solvent is boiled by heating source, the vapor then passes through a bypass arm into the condenser. As the solvent reaches to the top of the siphon arm, the solvent and extract are siphoned back onto the lower flask whereby the solvent re evaporate and the cycle is repeated until all the sample is completely extracted into the lower flask. Nonetheless, this technique is still the preferred method owing to its comparative extraction events despite of the nature of mixture sample[14].

The kinetic model of polycyclic aromatic hydrocarbons desorption from soil is described as first-order mass transfer with single equilibrium desorption. Desorption of polycyclic aromatic hydrocarbons can be fitted to a first-order mass transfer coefficient model[15].

$$C_w = C_e [1\text{-}exp^{(-kt)}]$$

where: C_w is the liquid-phase concentration at any time; K is the lumped mass transfer coefficient; C_e is the equilibrium liquid-phase concentration; t is the contact time with the extraction solvent.

The most frequent analysis techniques for quantification polycyclic aromatic hydrocarbons compounds in an environment are gas chromatography-mass spectroscopy[16,17], gas chromatography[18,19] and high performance liquid chromato-

graphy[20-22] has also often been applied to measure polycyclic aromatic hydrocarbons. The main objective of this study was to determine the contamination of soils from different locations in Al-Diwaniya province, Iraq.

EXPERIMENTAL

Study area: Soil samples used in this study were collected from four zones located in Al-Diwaniya province there are (Al-Diwaniya city center, Afak, Al-Shamiya and Al-Hamza). At each site, four sub sites were chosen. Sub sites are represented (industrial soil, urban soil, cereal grown soil and rural soil), from every sub site six samples (at the depth 0-19 cm) were collected randomly and were bulked together to form one composite sample. All samples were collected and then treated with air-dried at room temperature after transported to the lab within 3 h. Air-dried soil samples were cashed to pass through sieve and homogenized, then kept in refrigerator until analysis.

All sample containers and glasswares were thoroughly washed with hot detergent solution followed by rinsing with purified water and acetone (analytical grade), respectively. These were finally kept in the oven at 120 °C overnight. To avoid contaminations of samples, different syringes and glassware were used for standard and for solutions extracted from samples.

The standard solution of chrysene was purchased from Supelco. This standard was stored at 4 °C, protected from light. Solvents such as dichloromethane, acetone, hexane and acetonitrile were purchased from Sigma Aldrich. All chemicals were used without further purification.

Validation of extraction: Several parameters for optimization the extraction technique were studied to select the optimum conditions for extraction of polycyclic aromatic hydrocarbons from the selected soils, these parameters are: type of the mixture of solvents for extraction, effect of time of extraction on the recovery percentage and effect of the mixture of solvents percentage (dichloromethane/acetone). Table-1 illustrate the mentioned parameters for extraction of chrysene from the soils.

Extraction procedure: 10 g of the soil samples was weighed precisely and mixed well with 2 g of anhydrous sodium sulfate. Extraction of chrysene had been achieved by Soxhlet for 24 h with 160 mL of dichloromethane/acetone solvent (7:9 v/v). Rotary evaporator was used to remove the solvents and to reduce the volume to 1 mL. The extract was then cleaned using a glass column packed with silica adsorption chromatography capped with anhydrous sodium sulfate and eluted with mixture of hexane and pentane.

Analysis conditions: The final concentrated extracts were analyzed using gas chromatography Shimadzu/2010 equipped with a split less injector, HP-5 capillary column: Hp5 (30 m × internal diameter 0.28 mm × Film thickness 0.25 μm) and FID detector. The carrier gas was nitrogen at flow rate 1 mL/min, while oven temperature was programmed to increase from 50 °C (2 min) to 200 °C (2 min) at a speed of 20 °C/min, to 240 °C (2 min) at 5 °C/min and to 290 °C at 3 °C/min and then held for 15 min. The injector and detector temperatures were 275 and 300 °C, respectively. Soil organic carbon (SOC) content was determined in triplicate using described method by Nelson and Sommers[21].

RESULTS AND DISCUSSION

A wide range of soil polycyclic aromatic hydrocarbons concentrations was regarded from 219 to 27,825 ppb (dry weight), which contained those polycyclic aromatic hydrocarbons considered as carcinogenic by Unites State Environmental Protection Agency. The summation concentrations of chrysene in Al-Diwaniya city center from four sub soils samples was 57.9 ppb as shown in Table-2. This level may be attributed to the crowded traffic for this city compared with other study sites. While the concentrations of chrysene was 37 ppb in soils samples from Al-Shamiya site, which may attributed to the Al-Kufa cement factory, this factory is locate about twenty kilometers from the sampling site. The sum concentrations of chrysene in Al-Hamza site was 29.3 ppb, less than both Al-Diwaniya and Al-Shamiya in spite of this site is located near the Al-Muthna cement factory in distance about fifty kilometers from sampling site. The lowest concentration was 16.5 ppb in Afak city. In literature, there are four classes of soil pollution with polycyclic aromatic hydrocarbons were proposed: not polluted soil when the sum of concentration for polycyclic aromatic hydrocarbons is lower of two hundred μg/kg; weakly polluted soil when sum of polycyclic aromatic hydrocarbons in the range 200-600 μg/kg; polluted soil when the sum of polycyclic aromatic hydrocarbons is in the range 600-1000 μg/kg; heavily polluted if the sum of polycyclic aromatic hydrocarbons is higher than 1000 μg/kg. The previous values which were expressed as the absolute sum of the content of 16 polycyclic aromatic hydrocarbons compounds in soil sample[23,24].

Several studies have shown that polycyclic aromatic hydrocarbons are strongly retained by the soil matrix. The partitioning concept of soil sorption of organic pollutants implies that the sorption of hydrophobic organic content of the sorbant.

The pH value and soil organic carbon is reported for the soil type of sampling site in Table-3. The organic species content considers very important parameter related to polycyclic aromatic hydrocarbons contamination of soil[25]. Soil organic

TABLE-1
EFFECT OF EXTRACTION CONDITIONS ON THE RECOVERY PERCENTAGE FOR EXTRACTED CHRYSENE FROM SOIL

	Recovery (%)		
Type of mixture of solvents	Dichloromethane/acetone	Benzene/acetonitrile	Benzene/acetone
	90 ± 4	84 ± 3	79 ± 4
Effect of extraction time	24 h	36 h	48 h
	91 ± 2	83 ± 5	57 ± 3
Effect of mixture of solvents percentage (mL)	7/9	7/7	7/11
dichloromethane/acetone)	93 ± 3	91 ± 4	89 ± 4

TABLE-2
CONCENTRATION OF CHRYSENE (ppb) IN DISTRIBUTED IN ALL SAMPLING SITES

Site name	Industrial soil	Urban soil	Cereal grown soil	Rural soil	Σ Chrysene
Al-Diwaniya city center	26.0	19.5	5.2	7.2	57.9
Afak	5.8	3.8	3.7	3.2	16.5
Al-Shamiya	13.4	8.5	5.6	11.5	37.0
Al-Hamza	9.1	6.1	4.9	10.2	29.3

carbon in this study varied between soils samples ranging from (1.0 %) found in cereal grown soil from Afak soils to (4.5 %) in Industrial soil from Al-Diwaniya soils Table-3. The correlation between the concentrations of chrysene and the percentage of soil organic compounds is clear in Fig. 2. The experimental shows direct proportional relationship between both variables. Fig. 2 illustrate that higher amount of chrysene mainly occur in soil with higher soil organic carbon content, this relation can be described by the following equation:

$$\text{Chrysene} = 3.6916 \text{ SOC } 1.1534, \ r^2 = 0.9254$$

TABLE-3
SOIL ORGANIC CARBON (SOC) PERCENTAGE
AND pH VALUE FOR STUDIED SOILS

| Site name	Soil type	pH	SOC (%)
Al-Diwaniya city center	Industrial soil	6.4	4.5
	Urban soil	6.6	3.6
	Cereal grown soil	6.9	1.1
	Rural soil	6.7	2.1
Afak	Industrial soil	6.5	1.4
	Urban soil	6.7	1.0
	Cereal grown soil	7.0	1.1
	Rural soil	6.8	1.0
Al-Shamiya	Industrial soil	6.5	3.0
	Urban soil	6.6	2.3
	Cereal grown soil	6.8	1.7
	Rural soil	6.7	2.8
Al-Hamza	Industrial soil	6.6	2.3
	Urban soil	6.7	1.9
	Cereal grown soil	6.9	1.0
	Rural soil	6.9	2.5
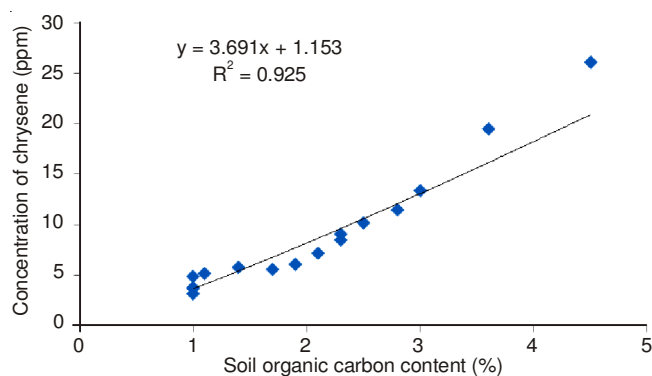
Fig. 2.   Relationship between soil organic carbon and concentration of chrysene in soil samples at several sampling sites in Al-Diwaniya city

Conclusion

In present study, the chrysene compound was determined in selected soils from Al-Diwaniya province. These cities are locate in Al-Diwaniya city center, Afak, Al-Shamiya and Al-Hamza. The highest sum concentration of chrysene was (57.9) ppb in Al-Diwaniya city center, while the lowest sum concentration of chrysene was (16.5) ppb in Afak city. Soil organic carbon content was measured for every sampling site of soil. The results showed the positive relationship between SOC with the concentration of chrysene in soils.

REFERENCES

1. A. Ene, O. Bogdevich, A. Sion and T. Spanos, *Microchem. J.*, **100**, 36 (2012).
2. L. Yan, X. Li, J. Chen, X. Wang, J. Du and L. Ma, *J. Environ. Sci. (China)*, **24**, 116 (2012).
3. Y. Chen, K.F. Ho, S.S.H. Ho, W.K. Ho, S.C. Lee, J.Z. Yu and E.H.L. Sit, *J. Environ. Monit.*, **9**, 1402 (2007).
4. B. Aichner, B. Glaser and W. Zech, *Org. Geochem.*, **38**, 700 (2007).
5. K. Srogi, *Environ. Chem. Lett.*, **5**, 169 (2007).
6. N. Rajput and A. Lakhani, *Environ. Monit. Assess.*, **150**, 273 (2009).
7. G. Liu, Z. Niu, D. Van Niekerk, J. Xue, L. Zheng, *Rev. Environ. Contam. Toxicol.*, **192** (2008).
8. S.K. Sahu, R.C. Bhangare, P.Y. Ajmal, S. Sharma, G.G. Pandit and V.D. Puranik, *Microchem. J.*, **92**, 92 (2009).
9. M. Malawska and B. Wio³komirski, *Water Air Soil Pollut.*, **127**, 339 (2001).
10. Y.G. Ma, J.P. Cheng, F. Jiao, K.X. Duo, Z. Rong, M. Li and W. Wang, *Environ. Monit. Assess.*, **146**, 127 (2008).
11. J.C. Means, S.G. Wood, J.J. Hassett and W.L. Banwart, *Environ. Sci. Technol.*, **14**, 1524 (1980).
12. B. Mai, S. Qi, E.Y. Zeng, Q. Yang, G. Zhang, J. Fu, Sheng, Peng and Wang, *Environ. Sci. Technol.*, **37**, 4855 (2003).
13. M.T.O. Jonker and F. Smedes, *Environ. Sci. Technol.*, **34**, 1620 (2000).
14. E.V. Lau, S. Gan and H.K. Ng, *Int. J. Anal. Chem.*, Article ID 398381 (2010).
15. P.J. Woolgar and K.C. Jones, *Environ. Sci. Technol.*, **33**, 2118 (1999).
16. C. Peng, Z. Ouyang, M. Wang, W. Chen and W. Jiao, *Environ. Pollut.*, **161**, 36 (2012).
17. D.H. Mebarka, S. Taleb, A. Benghalem, P. Tundo, M.T. Ahmed and M. Arabi, *Energy Procedia*, **18**, 1125 (2012).
18. R. García, M. Díaz-Somoano, M. Calvo, M.A. López-Antón, S. Suárez, I. Suárez Ruiz and M.R. Martínez-Tarazona, *Fuel Process. Technol.*, **104**, 245 (2012).
19. F.F. Karam, F.H. Hussein, S.J. Baqir, A.F. Halbus, R. Dillert and D. Bahnemann, *Int. J. Photoenergy*, Article ID 503825 (2014).
20. S. Baran, P. Oleszczuk, A. Lesiuk and E. Baranowska, *Pol. J. Environ. Stud.*, **11**, 299 (2002).
21. F.F. Karam, F.H. Hussein, S.J. Baqir and F.M. Abid, *Asian J. Chem.*, **24**, 5589 (2012).
22. F.H. Hussein, F.F. Karam and S.J. Baqir, *Asian J. Chem.*, **26**, 2768 (2014).
23. S. Orecchio, *J. Hazard. Mater.*, **173**, 358 (2010).
24. J.J. Nam, G.O. Thomas, F. Jaward, E. Steinnes, O. Gustafsson and K.C. Jones, *Chemosphere*, **70**, 1596 (2008).
25. P.D. Boehm, W.A. Burns, D.S. Page, A.E. Bence, P.J. Mankiewicz and J.S. Brown, *Environ. Forensics,* **3**, 243 (2002).