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Investigation on the rate of horizontal spread of anthracene in a sandy clay soil

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Extent of horizontal spread of anthracene in soil is examined in a 180 days experiment under natural environment during winter and spring seasons. Here the rate of spread is calculated from a point source in 1 m radius plot. Prior to placement of known quantity of anthracene from outside at the center of the spot, a few physico-chemical parameters of the soil were examined. It has been found from HPLC analysis that a maximum of 12020 ppm of anthracene moves a distance of 0.50 m in 60 days and a maximum of 8473 ppm moves a distance of 0.75 m in 180 days from the point source. A part of the applied PAH has undergone oxidation producing oxygenated derivatives as evidenced from the lowering of pH and increase of EC against time. It has been found that in a soil of 56% porosity, anthracene moves a maximum distance of 8.33×10^{-3} m per day where the concentration of the point source is 5 g. With the increase of time, the concentration of PAH in the point source decreases due to spreading and degradation of the PAH and by180 days of the experiment maximum speed has been found to be 4.17×10^{-3} m per day.

Keywords: Horizontal spread rate, anthracene, sandy clay, porosity, HPLC.

Introduction

Conservation of soil brings a worldwide concern currently. It is due to some factors such as increasing population, urbanization and industrialization over the last few decades. These have boosted the discharge of toxic organic pollutants viz. polycyclic aromatic hydrocarbons (PAH) into the environment because of various anthropogenic activities such as fuel burning, industrial emissions, etc. Due to their toxicity, exposure to such pollutants in environment is harmful to human health and consequently has developed the focus of much attention[1]. The key involvement of these organic pollutants into the soil surface is via air-to-surface precipitation that persists in the top layer of the soil.

The United States Environmental Protection Agency (USEPA) has designated 16 PAH as the most vital ones to be investigated in a number of environmental matrices because of their toxicity[2]. PAH have stable chemical structure that favor adsorption onto soil particles. This let the PAH to fix in soil matrix for longer time[3]. The growth of plants in soils is adversely affected by the petroleum hydrocarbons[4]. The PAHs are prevalent in the atmosphere and are enduring organic pollutants. These are known to be potential carcinogens implicating significant public health hazards[5]. Volatile organic compounds perform a significant role in modifying oxidizing capability of the atmosphere as well as in the physico-chemical method of the troposphere because of their large input to the formation of ozone along with other photochemical oxidants[6,7]. Volatile organic compounds penetrate into the environment in the course of various oil production practices, also through the leaks from transport pipelines, storage tanks and waste areas[8].

PAH are ubiquitously spread in the environment, such as soil, sediments, air, water, plants, animals and human bodies. Recognising the processes which control the behaviour of these chemical contaminants is essential if their effects on soil, water and biota are to be instituted[9]. PAH are lipophilic compounds having very low water solubility and consequently, they exist in low concentration in water[10,11]. Bioaccumulation of PAH in plants and animals body causes a risk to public health[12]. Oral intake can also be regarded as the main path of exposure to PAH, beyond the share other paths like inhalation and skin contact. Mutagenicity and carcinogenicity of PAH are not only because of their detrimental effects, but also due to their affinity to accumulate in the food chain[13–15].

Experimental

Standard procedures for soil analysis are adopted for the entire experiment[16,17]. A circular plot of 3.14 m^2 area are cleared nicely by removing all the grasses and stones and made it homogeneous and planer. 5 g of anthracene (ANT) is then placed at the center of the plot and allowed to stay under protection. Samples from the demarcation lines of 0.25, 0.50, 0.75 and 1.0 m radius circumferences were drawn at definite intervals for analysis. Quantity of drawn soil is reduced through quartering process. A few important physico-chemical parameters such as Texture, Bulk Density, Particle Density, pH, Electrical Conductivity (EC), Soil Organic Carbon (SOC) etc. of the soil, drawn before hydrocarbon addition, are determined to asses the quality of the experimental soil.

The hydrocarbon present in soil is extracted through Soxhlet Extraction method[18]. 5 g of the soil is Soxhlet extracted for 16 h using dichloromethane (DCM) solvent and two cycles per hour. The extract so obtained is concentrated and partitioned into cyclohexane. This extract is them passed through a silica gel column eluted by DCM. The column was pre-eluted by pentane. The collected fraction was concentrated and exchanged with methanol and used for concentration determination along with standard solutions with serial dilution of the anthracene sample in the same solvent. HPLC is done with following specifications: Sample amount 1, Multiplier 1, DAD: Signal A, 254 nm, Bw 4 nm.

Results and discussion

Physico-chemical parameters of the soil sample are summarized in Table 1. Texture of the sample is almost moderate – sandy loam, suitable for agricultural purposes. The bulk density value is 1.0212 which is closer to 1.13, the expected value of a good soil. Contrary to it, the particle density is slightly higher than expected double of the bulk density. It results in higher value of porosity, which is found to be 56%, slightly higher than that of expected 50% of a good soil. In such a porous soil; the vertical and horizontal movement of the experimental hydrocarbon is likely to be more. pH is slightly alkaline. EC, SOC are in the normal range. During the period of the experiment the average of maximum and minimum daily temperatures was moderate and rainfall was negligible. Overall impression is that the soil is suitable for horizontal movement as well as biodegradation of the applied PAH[19].

On increase of time of placement of PAH, pH of the sample gradually decreases. This indicates formation of acidic substances as a result of oxidation of PAH in soil. In informs that during the period of the experiment, a part of the applied PAH has undergone bioremediation or photocatalytic oxidation. Also, increase of EC with time indicates the formation of polar substances from non-polar hydrocarbons (Table 2).

The concentrations of anthracene reported at distances of 0.25, 0.50 and 0.75 m from the point source (point of placement) after 60 days are given in Table 3. The concerned chromatogram is at Fig. 1. Here, the minimum of the concentrations i.e. 0.034% has been considered as the quantity of anthracene, the soil originally contains. Therefore, a large number of the anthracene molecules move a distance of 0.50 m in 60 days. Hence, horizontal rate of spread of anthracene in this soil is 8.34×10^{-3} m per day. Since equal amount of soil from each of the lines were extracted for analysis, and the three lines are the three circumferences of the same circle, they have lengths in the ratio of 1:2:3; therefore concentrations can be reported as shown in Table 4. It has been seen that 12020 ppm, the highest concentration moves 0.50 m in 60 days, the most probable speed seems to be 8.34×10^{-3} m per day.

Similarly, for samples drawn after 6 months, the concentration of anthracene obtained at different distances from the point source has been found as shown in Table 5. The concerned chromatogram is at Fig. 2. Here, the minimum of the concentrations i.e. 0.02301% has been considered as the

Table 1. Physico-chemical parameters of the soils

Parameters	Texture	Bulk density	Particle density	Porosity	pH	EC	SOC	SOM
Units	–	(g cm^{-3})	(g cm^{-3})	(%)	–	(at 25°C)	(%)	(%)
Results	Sandy loam	1.0212	2.345	56	7.15	0.785	1.75	3.017

Table 2. Changes in pH and EC of the soil samples

Parameter	Parent soil	Polluted soil at			
		20 d	40 d	60 d	80 d
pH	7.15	7.21	6.85	6.67	6.37
EC	0.785	0.748	0.913	0.919	1.112

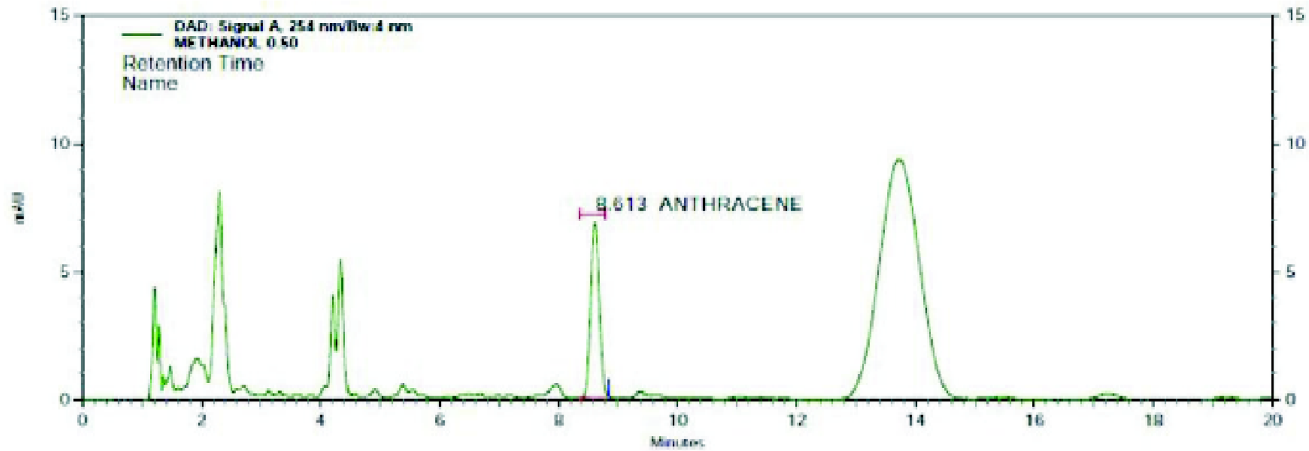

Fig. 1. HPLC chromatogram of the sample at 0.50 m on 60 days.

Table 3. Concentration of anthracene at different distances on 60 days

Distance (m)	Concentration [a] (%)	Minimum concentration of anthracene treated as existing in soil [b] (%)	Amount moved horizontally from point source [a–b] (%)	Amount moved horizontally from point source [a–b] (ppm)	Speed (m per day)
0.25	0.404	0.034	0.370	3700	4.17×10^{-3}
0.50	0.601	0.034	0.567	5670	8.34×10^{-3}
0.75	0.034	0.034	0.0	0	0

Table 4. Rate of distribution of anthracene molecules on 60 days

Distance (m)	Concentration [a] (%)	Ratio of path length [b]	Amount moved horizontally from point source [a×b] (%)	Amount moved horizontally from point source [a×b] (ppm)	Speed (m per day)
0.25	0.404	1	0.404	4040	4.17×10^{-3}
0.50	0.601	2	1.202	12020	8.34×10^{-3}
0.75	0.034	3	0.102	1020	12.51×10^{-3}

Table 5. Concentration of anthracene at different distances on 180 days

Distance (m)	Concentration [a] (%)	Minimum concentration of fluorine treated as existing in soil [b] (%)	Horizontal movement from point source [a–b] (%)	Horizontal movement from point source [a–b] (ppm)	Speed (m per day)
0.25	0.09865	0.02301	0.07564	756	1.39×10^{-3}
0.50	0.03310	0.02301	0.01009	101	2.78×10^{-3}
0.75	0.28243	0.02301	0.25942	2594	4.17×10^{-3}
1.00	0.02301	0.02301	0.0	0	0

quantity of anthracene, the soil naturally contains. A large number of the anthracene molecules move a distance of 0.75 m in 180 days. Hence, horizontal rate of spread of anthracene in this soil is 4.17×10^{-3} m per day. Since equal amount of soil from each of the lines were extracted for analysis, and the four lines are the four circumferences of the same circle, they have lengths in the ratio of 1:2:3:4; therefore, concentrations can be reported as shown in Table 6. Since, 8473 ppm, the highest concentration moves 0.75 m in 180 days, the most probable speed seems to be 4.17×10^{-3} m per day.

Table 6. Rate of distribution of anthracene molecules on 60 days

Distance (m)	Concentration [a] (%)	Ratio of path length [b]	Amount moved horizontally from point source [a×b] (%)	Amount moved horizontally from point source [a×b] (ppm)	Speed (m per day)
0.25	0.09865	1	0.09865	986	1.39×10^{-3}
0.50	0.03310	2	0.06620	662	2.78×10^{-3}
0.75	0.28243	3	0.84729	8473	4.17×10^{-3}
1.00	0.02301	4	0. 09204	920	5.56×10^{-3}

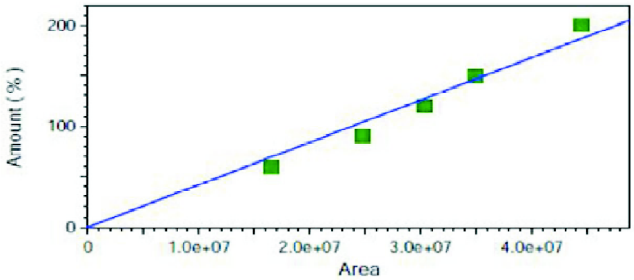

Fig. 2. Calibration curve for HPLC chromatogram of the sample at 60 days.

Conclusion

From a comparison of the data at 60 and 180 days, it seems that the speed of the PAH has decreased on increase of time. This might be due to decrease of concentration on increase of distance and also due to loss of the anthracene molecules due to degradation. PAH are generated from natural and anthropogenic causes. Existence of some of them in the environment has been found to be detrimental to the living kingdom because they become bioavailable. The process of biodegradation, photolytic activities etc. are some of the processes of nature for a cleaner environment. In an open system, along with their bioremediation, horizontal spread also plays an important role. It has been found that in a soil of 56% porosity, anthracene moves a maximum distance of 8.34×10^{-3} m per day where the concentration of the point source is 5 g. With the increase of time, the concentration of PAH in the point source decreases due to spreading and degradation of the PAH and at 180 days of the experiment maximum speed has been found to be 4.17×10^{-3} m per day.

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References

1. Momita Das, Devendra Kumar Patel, Arup Kumar Sarma, Binode Kumar Baruah, Sofia Banu and Jibon Kotoky, *Current Science*, 2016, **110(12)**, 2285.
2. P. D. Sharma, "Nutrition and health among the tribes of India", in: 'Tribal Health and Medicines', eds. A. K. Kalla and P. C. Joshi, Concept Publishing Company, New Delhi, 2004, pp. 73-84.
3. Karishma Hussain and Raza Rafiqul Hoque, *Chemosphere*, 2015, **119**, 794.
4. I. L. R. Oyem, I. L. Oyem *et al.*, *Int. J. Mod. Engineering Res.*, 2013, **3(6)**, 3336.
5. X. Tian, J. Liu, G. Zhou, P. Peng, X. Wang, C. Wang *et al.*, *Environmental Pollution*, 2008, **156**, 306.
6. C. Sarkar, A. Chatterjee, D. Majumdar, S. K. Ghosh, A. Srivastava, S. Raha *et al.*, *Atmospheric Chemistry and Physics Discussion*, 2014, **14**, 32133.
7. Gitumani Devi, Arundhuti Devi and K. G. Bhattacharyya, *Environ. Monit. Assess.*, 2017, 189:62.
8. P. Baltrenas, E. Baltrenaite, V. Sereviciene, P. Pereira *et al.*, *Environ. Monit. Assess.*, 2011, **182**, 115.
9. D. J. Shilla, *Chemistry and Ecology*, 2016, **32(5)**, 472.
10. I. N. Nasr, M. H. Arief, A. H. Abdel-Aleem and F. M. Malhat, *J. Applied Science Res.*, 2010, **6(1)**, 13.
11. Nursiah La Nafie, Asmawati, Musa Ramang and Adiba Arief, *International Journal of Applied Chemistry*, 2016, **12(4)**, 675.
12. M. Gavrilescu, *Environmental Engineering and Management Journal*, 2009, **8(6)**, 1517.
13. E. Yoon, K. Park, H. Lee, J. H. Yang and C. Lee, *Human & Ecological Risk Assessment*, 2007, **13(3)**, 669.
14. S. C. Chen and C. M. Liao, *Science of the Total Environment*, 2006, **366(1)**, 112.
15. M. Nicoleta, M. Edward and M. D. Marcel, *Pro. Environment*, 2015, **8**, 285.
16. D. Singh, R. K. Chhonkar and R. N. Pandey, "Soil Plant Water Analysis–A Method Manual", Indian Council of Agricultural Research, New Delhi, 2000, **1**, 2-35.
17. P. K. Gupta, "Methods in Environmental Analysis Water, Soil and Air, Agrobios (India), Jodhpur, India", 2011, pp. 208-286.
18. APHA, "Standard methods for the Examination of Water and Waste water", 17th ed., Washington DC, 1989.
19. Z. Khan and Y. Anjaneyulu, *Res. J. Chem. Environ.*, 2005, **9(2)**, 75.