

Investigations of Flare Gas Emissions in Taq Taq Oil Field on the Surrounding Land

Jafar A. Ali and Loghman A. Khodakarami

Department of Petroleum Engineering, Faculty of Engineering, Koya University
University Park, Danielle Mitterrand Boulevard, Koya KOY45, Kurdistan Region - F.R. Iraq

Abstract—Environmental pollution caused by oil takes many different forms; one of the most damaging sources is simply the combustion of oil products, such as a well flare burn-off. This paper presents the results of a survey of the agriculture lands around the Taq Taq Oil Production Company. The aim of the survey was to determine the potential contamination caused by the gas emissions from the well flares. Taq Taq field is located in the Kurdistan Region of Iraq, 60 km north of the giant Kirkuk oil field, 85 km south-east of Erbil and 120 km north-west of Suleimani. Samples of soil were collected from several locations around the site and analyzed to determine the content of Polycyclic Aromatic Hydrocarbons PAH present. A gas chromatography linked to a mass spectrometry (GCMS) machine was used for these measurements. The PAH contamination at each location of soil was determined and the 16-PAHs, as listed in the US Environmental Protection Agency (EPA) documentation were investigated. The average content of total PAH in all samples of the agricultural soil was $0.654 \text{ mg}\cdot\text{kg}^{-1}$ with the concentrations ranging from 0.310 to $0.869 \text{ mg}\cdot\text{kg}^{-1}$. It was found that the PAH concentrations decreased with increasing distance from the TTOPCO oil field, indicating that pollution was evident, the area close to the field being more affected by the gas pollution.

Index Terms—Flare, geographic information system, pollution, polycyclic aromatic hydrocarbon, TTOPCO.

I. INTRODUCTION

The concern for oil field emissions of pollutants and their effect on the Kurdistan environment has been increasing since 2004 and in Koya city since 2005 when Taq Taq field started to expand by Addax Petroleum world Class Company. Excessive discharge of hydrocarbons to flare is resulting in

flooding of black smoke (plume) which is caused a disaster to the environment.

Soil is the primary environmental reservoir for persistent organic pollutants (POPs) in the terrestrial environment. Once deposited, POPs may reside in the soil for many years. However, soil may not be a permanent sink for these compounds; they tend to recycle continuously between the atmosphere and the terrestrial environment over long periods of time. The soil therefore can either be a sink for POPs or become a source of POPs back into the atmosphere (Mackay, 2001; Cousins, Beck and Jones, 1999). Among the persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are very important. Polycyclic aromatic hydrocarbons (PAHs) contain complex chemicals which include carbon and hydrogen with a fused ring structure, containing at least two benzene rings (Sexton, et al., 2011). PAHs are generally produced by the incomplete combustion of organic material, for example, fossil fuels. Burning carboniferous materials release copious amounts of smoke containing polynuclear aromatic hydrocarbons (PAHs). Via atmospheric deposition PAHs also reach soil and sediments in areas remote from industry, airports and highways. In addition, oil spills due to accidents or careless oil handling are polluting factors. More than 100 PAHs have been characterized in nature, sixteen of which were classified as priority pollutants according to US Environment Protection Agency (Bishnoi, et al., 2005). PAHs that have accumulated in soils may directly or indirectly pose a risk to human and ecosystem health (Jones, 1991).

Polynuclear aromatic hydrocarbons have been documented to cause several health problems (Hati, et al., 2009). Some PAHs and their derivations are highly toxic. Their mutagenic or carcinogenic properties are the main risk to human health (Prycek, Ciganek and Srinek, 2007). Risk assessment and source apportionment of PAH-contaminated soils require accurate analysis of the concentration of each PAH component in the soil. At present the analytical equipment used for the measurement of PAHs in soils mainly comprises gas chromatography (GC) (Kuosmanen, et al., 2003; Zuazagoitia, Millán, and Garcia-Arrona, 2009), gas chromatography–mass spectrometry (GC–MS) (Ene, et al., 2012) and high performance liquid chromatography (HPLC) (Yang, et al., 2011). In this study all samples were analyzed by gas chromatography–mass spectrometry. Soil contamination by

refining oil products has been studied widely by the researchers across the world. Since the beginning of the last century the oil industries are running in Iraq, whilst in Kurdistan Region the oil industries started after Kurdish uprising in 1991. Although the large number of oil fields across the country, the researchers have not studied fairly their effects on the environment.

The objective of this paper is to investigate the occurrence of PAHs in agricultural soils that are directly impacted by Taq Taq oil field in topsoil in the vicinity of a TTOPCO (5000-meter buffer) in the Kurdistan region, This information on PAH distribution can be used for health risk assessment and future urban development.

II. METHODS AND MATERIALS

A. Study Site

The area of the study site is about 2827.4 Hectares (ha) and located between 453636 and 459635 longitudes and 3981823 and 3987823 latitudes. The Taq Taq is one of the largest oil fields in Kurdistan Region, it is located near the town of Koya in the heart of the region; 60 km north of the giant Kirkuk oil field, 85 km south-east of Erbil and 120 km north-west of Suleimani, Fig. 1. Addax Petroleum was the first international oil company participated to develop Taq Taq field in 2005 (Sinopic, 2013). Taq Taq is currently producing 40000 bpd of oil and burning the waste gases via two flares, one of them is not burning the gases properly so it is discharging wastes more than the other. The predominant land use of these catchment areas are: agriculture with predominant crops of wheat, barley, alfalfa and potato, garden and orchard. The minimum and maximum height of study area from sea surface is 449 m and 639 m respectively.

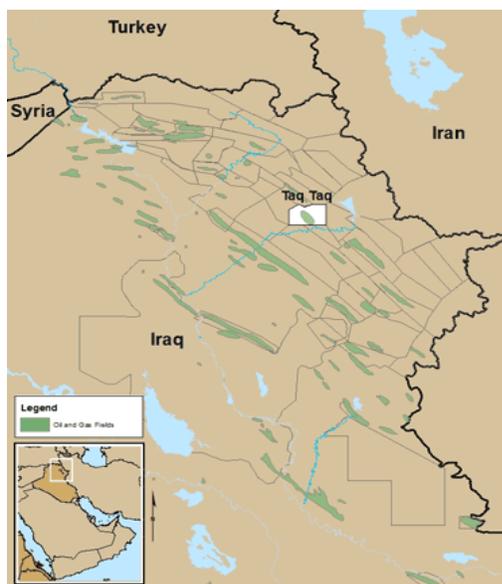


Fig. 1. The field location, from Addax Petroleum Website.

B. Sampling of Soils and Analytical Methods

Soil Sampling and Preparations

Twelve composite soil samples were collected from 0-10 cm depth by dividing the affected area into a grid of 500 m \times 500 m using random systematic method, Fig. 2. The area at each sampling point was about 20 m \times 20 m grid and soil samples were taken from each corners and center of each grid. The sampling sites were selected in order to reflect the diverse exposure of soils to the pollution sources and dominant wind directions. The sampling sites are shown in Fig. 2 and described in Table 1. The samples were collected from the surface layer (from 0-10 cm depth), after removing grass in agricultural soil.

Approximately 500 g of material were collected from a square area of 20 \times 20 m in each sampling site. All samples were put into envelope of sealed aluminums foil containers with a minimum headspace of air, and immediately transported to the laboratory. The envelopes of the samples were kept with ice through the survey and during the transportations to avoid the escaping of hydrocarbons, in laboratory they are kept in refrigerator. The containers were used only once with clean equipment for each sample.

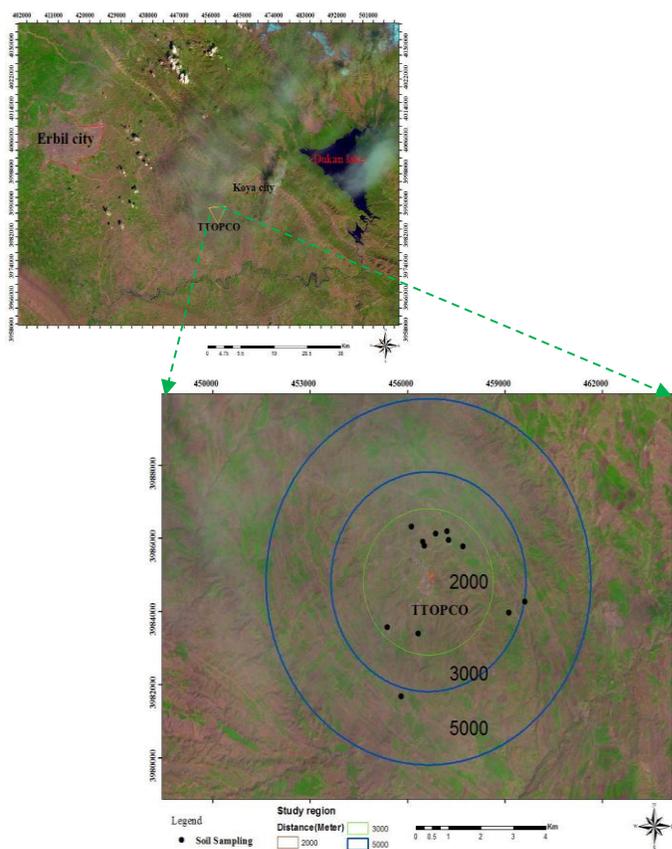


Fig. 2. The status of study region and samples stations.

TABLE I
PAH CONCENTRATIONS IN THE SOIL SAMPLES AT TTOPCO (5000-METER BUFFER), (mg·kg⁻¹)

Station	NAP	ANY	FLU	PHEN	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IPY	DBA	BgP	ACP	tPAHs
1	0.060	ND	0.053	0.060	0.061	0.070	0.052	ND	0.080	0.060	0.059	0.056	ND	ND	0.060	ND	0.671
2	0.070	0.052	0.060	0.069	0.058	0.067	0.08	0.056	0.082	0.063	0.090	0.051	ND	ND	0.055	ND	0.853
3	0.065	ND	0.055	0.058	0.070	0.077	0.075	0.064	0.076	0.070	0.089	0.053	0.060	ND	0.057	ND	0.869
4	0.055	0.051	0.051	0.067	0.087	0.058	0.069	ND	0.077	0.075	0.078	0.065	0.064	ND	ND	ND	0.797
5	0.075	ND	ND	0.059	0.076	0.053	0.070	0.076	0.065	0.066	0.092	ND	ND	ND	ND	ND	0.632
6	0.080	ND	ND	0.073	0.069	0.087	0.078	0.063	ND	ND	0.078	ND	0.070	ND	0.059	ND	0.657
7	0.081	ND	ND	0.090	0.083	0.065	ND	ND	ND	0.077	0.087	0.065	ND	ND	ND	ND	0.548
8	0.056	0.054	ND	0.088	0.055	ND	ND	0.051	0.078	0.065	0.065	ND	ND	ND	ND	ND	0.512
9	0.057	ND	ND	ND	0.058	ND	ND	0.053	0.077	ND	0.065	ND	ND	ND	ND	ND	0.310
10	0.052	ND	0.053	ND	0.051	0.051	0.054	ND	ND	0.067	0.073	0.065	ND	ND	ND	ND	0.466
11	0.055	ND	ND	0.087	0.052	ND	0.056	0.063	0.090	0.077	0.079	0.073	0.080	ND	0.060	ND	0.772
12	0.063	0.053	0.053	0.098	0.074	0.090	ND	0.055	0.079	ND	0.080	ND	0.063	ND	0.055	ND	0.763

ND = Not Detected, tPAHs = Total PAHs

Extraction and Analysis of PAHs

Initially, all samples were thoroughly homogenized by a sieve shaker on a 2 mm metal sieve. The water content (10-14% w) was determined on portions of homogenized samples after 24h drying at 105 °C. Different drying procedures, including thermal and chemical drying, were applied. Thermal drying was performed at 40 °C for five days and at 105 °C for 24h. The soil samples were subsequently extracted using the Ultrasonic Extraction method. Four gram from each soil samples were subjected to ultrasonic extraction according to the analytical scheme described by Berset, et al. (1999). Briefly, the samples were put into glass conic bottles with 25ml of a solvent mixture (hexane/acetone 85/15 v/v) and were left in the ultrasonic bath (300 W) for 30 min. The extracts were filtered twice through Whatman paper No 42 (2.5 µm pore size) and stored in the refrigerator in dark amber glass flasks, closed with teflon screw caps for subsequent analysis. A known amount of internal standard (hexamethylbenzene) was added to all extracts prior to PAHs analysis. These PAHs were quantitatively analyzed by GCMS (GC17AAF) using a 30 m × 0.25 mm fused silica capillary column (SUPELCO PTE) with helium as the carrier gas at flow rate of 1.2 ml·min⁻¹. 1 µL of aliquot from a known volume of analytic solution was injected manually. Verification of peaks was carried out based on key fragment ions, retention times compared to those of external PAHs standards, and/or mass spectra. Only those peaks located within the proper range (2%) of retention time were integrated for qualification and quantification. Quantitation were performed using external standards of a mixture of PAHs.

The GC temperature program was as follows: initially at 80 °C for 5 min, increased to 290 °C at 3 °C/min, and held for 30 min. A 1 µL sample was injected into the split/split less injector with a 5 min solvent delay.

All solvents used in this study were of analytical grade from Merck. A standard mixture of the 16 EPA priority PAHs, 2000 µg/ml each from Supelco was used for the GC-MS calibration and n-dodecane (99%) from Aldrich as internal standard. Aluminum oxide (90 active neutral), 70-230 mesh from Merck and Silica gel, 100-200 mesh from Aldrich, were also used. In this study, 16 priority pollutant PAHs identified by the US Environmental Protection Agency (EPA) were analyzed.

Sixteen USEPA (United State Environmental Protection Agency) priority PAHs were selected and they are abbreviated as Naphthalene (NAP), Acenaphthylene (ANY), Acenaphthene (ACP), Fluorine (FLU), Phenanthrene (PHEN), Anthracene (ANT), Fluoranthene (FLT), Pyrene (PYR), Benz(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IPY), Dibenz(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BgP).

C. GIS Mapping

A geographic information system (GIS) was used to create a survey map of PAH. A GPS receiver of type (GPS Garmin 62s, USA) was used to record the position of sample locations. From the Global Positioning Satellite (GPS) receiver, the WG84 coordination system was transformed to the TM coordination system to fit the actual map. For the distribution map, GIS software, Arc GIS (ver. 10.1, ESRI, USA), was used, and the concentration of PAH was displayed as distribution map on the GIS map.

III. RESULTS AND DISCUSSION

Most PAHs reach the soil via deposition from the atmosphere, and PAH concentrations in the soils tend to increase with the increasing impact of industry, traffic, and domestic heating (Jones, et al. 1989). It is known that low molecular weight PAHs are relatively more volatile and could likely be evaporated by the high temperature and solar radiation of tropical soils.

The measured data for every individual and total PAHs are presented in Table 1, there are PAHs have not been detected at some locations, but Acenaphthene and Dibenz(a,h)anthracene were totally not detected in all samples. The range and arithmetic mean and median of PAH concentrations in soil samples are presented in Table 2. Total PAH concentrations ranged from 0.310 to 0.869 mg·kg⁻¹ dry weight, with an average value of 0.654 mg·kg⁻¹. It is clear from the presented tables that the measured detected values of PAHs are close to zero or they are the minimum. Whilst the black plume that is released from Taq Taq field indicate to more than these values of PAHs could be found in the surrounding lands. The reason of that is due to lack of facilities that were between hands during this research work.

TABLE II
MEAN, MEDIAN AND RANGE OF PAH IN COLLECTED SOIL SAMPLES (mg·kg⁻¹)

	Mean	Median	Range
Naphthalene	0.064	0.0615	0.052 - 0.081
Acenaphthylene	0.042	0.0520	0.000 - 0.054
Fluorine	0.054	0.0530	0.051 - 0.060
Phenanthrene	0.075	0.0710	0.058 - 0.098
Anthracene	0.066	0.0650	0.051 - 0.087
Fluoranthene	0.069	0.0670	0.051 - 0.090
Pyrene	0.067	0.0695	0.052 - 0.080
Benz(a)anthracene	0.053	0.0560	0.000 - 0.076
Chrysene	0.078	0.0780	0.065 - 0.090
Benzo(b)fluoranthene	0.069	0.0670	0.063 - 0.077
Benzo(k)fluoranthene	0.078	0.0785	0.059 - 0.092
Benzo(a)pyrene	0.061	0.0650	0.051 - 0.073
Indeno(1,2,3-cd)pyrene	0.056	0.0635	0.000 - 0.080
Dibenz(a,h)anthracene	0.000	0.0000	ND
Benzo(g,h,i)perylene	0.058	0.0580	0.055 - 0.060
Acenaphthene	0.000	0.0000	ND
tPAHs	0.654	0.6640	0.310 - 0.869

Fig. 3 presents the total PAHs profile at all locations, at location 3 the total PAH was detected as maximum, whilst the minimum value was detected at location 9. In Fig. 4, the two dimensional map of PAH distribution around the survey area is presented, the red color indicates to highest polluted area and the blue color is the area that is less affected.

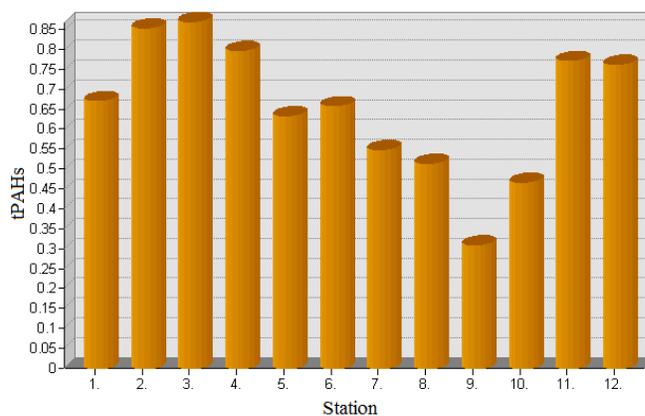


Fig. 3. Total PAH profile at all stations.

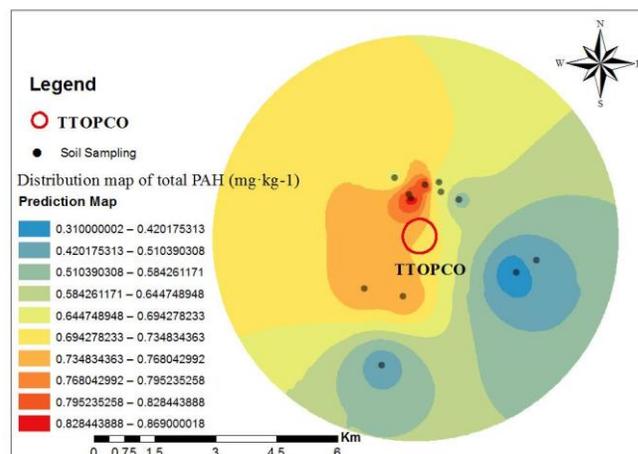


Fig. 4. Total PAH distribution for the surveyed area.

IV. CONCLUSION

The highest concentration of total identified PAHs was obtained at station 3 with the concentration of 0.869 mg·kg⁻¹ and the lowest were detected at stations 9 and 10 with values of 0.310 and 0.466 mg·kg⁻¹ respectively. Evaluation of several diagnostic ratios suggests that these PAHs were mainly derived from combustion of the flare rather than petro-genic. Stations that have more PAHs detected are located to the north west of the field where the direction of the wind most of times. The detected PAHs in this study are less than that is expected; this is because of lack of facilities. It is necessary to obtain correct and adequate emission inventory to minimize the impact of pollutants discharged from flare. Therefore, in future this work should be repeated using closer laboratories for testing the samples to avoid the possibility of hydrocarbons escape and achieving better results.

REFERENCES

Bishnoi, N.R., Mehta, U., Sain, U. and Pandit, G., 2005. Quantification of polycyclic aromatic hydrocarbons in tea and coffee samples of Mumbai city using high performance liquid chromatography. *Environ. Monit. Assess.*, 107(1-3), pp.399-406.

- Berset, J.D., Ejem, M., Holzer, R. and Lischer, P., 1999. Comparison of different drying, extraction and detection techniques for the determination of priority polycyclic aromatic hydrocarbons in background contaminated soil samples. *Anal. Chim. Acta*, 383(3), pp.263-275.
- Cousins, I.T., Beck, A.J. and Jones, K.C., 1999. A review of the process involved in the exchange of semi-volatile organic compounds (SVOC) across the air-soil interface. *Science of the Total Environment*, 228(1), pp.5- 24.
- Ene, A., Bogdevich, O., Sion, A. and Spanos, T., 2012. Determination of polycyclic aromatic hydrocarbons by gas chromatography–mass spectrometry in soils from southeastern Romania. *Microchem. J.* 100(1), pp.36–41.
- Hati, S.S., Dinar, G.A., Egbu, G.O. and Ogunbajana, V.O., 2009. Polycyclic Aromatic Hydrocarbons (PAHs) contamination of synthetic industrial essentials utilized in the Northern Nigeria. *African Journal of Pure and Applied Chemistry*, 3(5), pp. 86 – 91.
- Jones, K.C., Stratford, J.A., Waterhouse, K.S. and Vogt, N.B., 1989. Organic contaminants in Welsh soils: Polycyclic aromatic hydrocarbons. *Environmental Science and Technology*, 23, pp.540–550.
- Jones, K.C., 1991. Contaminant trends in soils and crops. *Environ. Pollut.* 69(4), pp.311-325.
- Kuosmanen, K., Hyötyläinen, T., Hartonen, K. and Riekkola, M.L., 2003. Analysis of polycyclic aromatic hydrocarbons in soil and sediment with on-line coupled pressurised hot water extraction, hollow fibre microporous membrane liquid– liquid extraction and gas chromatography. *Analyst*, 128(5), pp.434–439.
- Mackay, D., 2001. *Multimedia Environmental Models: the Fugacity Approach*, 2nd ed. Lewis/CRC, Boca Raton FL.
- Prycek J., Ciganek, M. and Srinek, Z., 2007. Clean up of extracts for nitrated derivatives of polycyclic aromatic hydrocarbons analysis prior their gas chromatography determination. *Journal of the Brazilian Chemical Society*, 18(6), doi:10.1590/S0103-50532007000600004.
- Sexton, K., Sahmas, J.J., MacDonald, T.J., Gowen, R.M.Z., Miller R.P., McCormick, J.B. and Fisher-Hosh, S.P., 2011. PAHs in Maternal Umbilical cord blood from pregnant Hispanic women living in Brownsville, Texas. *International Journal Environmental Research and Public Health*, 8(8), pp.3365 – 3379.
- Sinopec – Addax Petroleum Foundation – Middle East, 2013. [Online] Available at <https://www.addaxpetroleum.com/operations/middle-east>. [Accessed 25 July 2013].
- Yang, F., Long, Y.M., Shen, R., Chen, C.Y., Pan, D., Zhang, Q.L., Cai, Q.Y. and Yao, S.Z., 2011. Ultrasonication extraction coupled with magnetic solid-phase clean-up for the determination of polycyclic aromatic hydrocarbons in soils by high-performance liquid chromatography. *J. Sep. Sci.* 34(6), pp.716–723.
- Zuazagoitia, D., Millán, E. and Garcia-Arrona, R., 2009. Comparison of two extraction methods for the determination of polycyclic aromatic hydrocarbons in surface soils using headspace SPME with GC–FID. *J. Chromatogr. Sci.*, 47(2), pp.97–102.