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Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Runoff Sediments (Case Study: Tehran City)

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) are of special importance because of their toxicity, stability, lipophilicity, bioaccumulation, carcinogenesis and mutagenic impacts on living organisms and human. Urban runoff contains significant amounts of PAH compounds, which result in transfer them to receiving environments and have significant environmental and health risks. Because of the hydrophobicity characteristic, transport of these compounds in aquatic environment, mainly coupled to suspended particles and sediments. Hence, evaluation of sediments is considered as one of the environments that affect the fate and transport of these compounds. Present study was performed to evaluating the concentrations and sources of PAH compounds in sediments of Tehran urban runoff network. The sediment samples were taken from the three main sub catchments of Tehran city in April 2017 and the concentration of 16 priority PAH compounds and organic carbon was measured and finally their probable emission sources were determined using five indexes of diagnostic ratios. The total PAHs concentration in three sub-catchments ranged from 57 to 978.2 ng / g dry weight. Also, distribution of concentrations in sub- catchment 2(57-976.6 ng/g) was higher than the sub-catchment 1(84.4-773.2 ng/g) and Sub-catchment 3(76.3–978.2 ng/g) due to the locating in center of the city and the diversity of pollutant sources. Moreover, the survey of the relationship between total organic carbon and PAHs showed a significant and strong correlation between these two variables, but its coefficient varied in each sub-catchments. At all stations except the station C1S27, 3 and 4 rings compounds in comparison with the other compounds had significant dominance. Four indexes showed the origin of compounds at all stations are pyrogenic and The LMW/HMW index showed that the source of contamination in 30% of the stations is petrogenic. Generally, the results showed that the portion of pyrogenic sources is significantly higher due to high population density, traffic and human activities.

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1. INTRODUCTION

Polycyclic Aromatic hydrocarbons(PAHs) are a group hydrophobic organic compounds with a widespread occurrence in the environment due to its sustainability, hydrophobicity, and high emission and transportation potential are considered as one of the most important environmental concerns[1]. Growing urbanization along with the increase of anthropic activities in the last few decades have turned urban runoff into a major problem both from the point of view of the flow quantities and its quality. In urban storm water discharge PAHs are likely to be the main group of organic contaminants with the greatest potential toxicity[2]. These compounds in aquatic environments are both soluble and coupled to particulate matter and sediment. But due to the hydrophobicity and low vapor pressure, the concentrations reported in the sediments are significantly higher than the concentration in soluble. Therefore transport of these compounds in aquatic environment, mainly coupled to suspended particles and sediments. Hence, evaluation of sediments is considered as one of the environments that affect the fate and transport of these compounds[3]. Due to abundance of PAHs in urban runoff and their environmental and health importance, recognize of the concentration and behavior of these pollutants in sediments in order to evaluation, management and control them is necessary. Therefore, the purpose of this study was to investigate the concentration and source of PAHs and TOC as one of the effective parameters on distribution of these compounds in the insoluble phase in the three main sub basins of Tehran runoff network.

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2. MATERIAL AND METHODS

Thirty separate sediment samples were collected from

the three main sub catchments of Tehran urban runoff network during may 15th-18th 2008 in three stages, 24 hours after rainfall with a one-month dry period. Each sample were placed in aluminum cover and kept at the temperature of 4◦C, then transferred to the laboratory and placed in oven at about 70◦C for 4h to remove moisture. The Soxhlet extraction method was used to extract PAHs compounds from sediment samples[4]. Sediment sample (10 g) previously sieved through mesh no. 230 was weighed and spiked with 100µL Surrogate. the sample was transferred to the Soxhlet system and extracted with 250 ml (1:1 v/v) of n-hexane and Methylene Chloride solvent for 8h. Using a rotary evaporator, the extract was concentrated to a total volume of 5 ml. Then, it was fractionated in a clean-up column containing silica gel, sodium sulfate, and glass wool that had been initially washed with 30 ml of n-hexane and Methylene Chloride (9:1 v/v), and the extracts were concentrated to 1ml using mild Flow of Nitrogen Gas for injection. The Agilent 7890A GC-FID along with the split-less injector was used to determine the concentration of PAHs. The separation was performed on a fused silica capillary column (HP-5, 30 m, 0.25 mm I.D., and 0.25 µm film thickness). High-purity (99.999 %) Helium was used as the carrier gas at a flow rate of 1 ml min−1, and the temperature program was 80 °C to 290°C (held 10 min) at a rate of 7 °C min−1. Also, total organic Carbon of sediment was determined by the Loss on Ignition standard method. After removing the mineral carbon content, the sample (2g) was weighed and placed in an electric furnace at 450°C for six hours. Finally, the TOC value was determined in mg/kg by difference of dry weight before and after the furnace.

3. RESULT AND DISCUSSION

The total PAHs concentration in three sub-catchments ranged from 57 to 978.2 ng / g dry weight (mean: 368.7, median: 301.7). This range of These concentrations were lower compared to other similar studies such as in urban river sediments in Germany (112-22,900 ng/g)[5], in South Africa (270 to 5400 ng / g)[6], in Kansas City States (290 to 82150 ng/g)[7], as well as to the measured concentration in the road dust of Isfahan city (184.6 to 3221.7 ng/g)[8] Which could be due to differences in the type and concentration of human activities and emission sources, land use type, characteristics of catchments and emission standards. generally, distribution of concentrations in sub- catchment 2(57-976.6 ng/g) was higher than the sub-catchment 1(84.4 -773.2 ng/g) and Sub-catchment 3(76.3 – 978.2) due to the locating in center of Tehran , high population density and a significant level of human activities, the diversity of pollution sources is high, and also concentrations are more dispersed than the other two sub-catchments. Among the 16 PAHs, compounds with 3 and 4 ring especially Chrysene, Fluoranthene and Pyrene due to the high contribution of the emission sources these compounds (incomplete combustion)were dominant at all stations, except for the station C1S27. The results of some similar studies have shown the dominance of compounds with 4, 3[9], and 4 rings[10] in urban runoff. The major results of 4 diagnostic indexes includes ∑16PAH , Phe/Ant, Flu/Pyr, Flu/Pyr+flu and Ant/Ant+Ph showed pyrogenic emission sources are predominant in Tehran city. However, the range of LMW / HMW index in the whole catchment were 0.16 to 7.9. According to this index, the petrogeneic sources were dominant in comparison to the pyrogenic sources in 30% of the stations (C2S5, C2S12, C3S15, C1S28, C2S18, C3S29, C3S30 and C2S14). Based on the results, TOC concentrations in the whole catchment ranged from 5.94 to 21.02(mean: 47.71 mg/g). In this study, the relationship between the two variables of TOC concentration and PAH concentration in sediments was determined by Pearson correlation test. Results showed that there is a positive and significant correlation between these two variables in all three sub-catchments. Results showed that in sub-catchments 1, 2 and 3 the correlation coefficient between two variables is 0.83, 0.74 and 0.76 respectively (P value is 0/004, 045/0 and 0/01 respectively), which shows the amount TOC can play an important role in maintaining PAHs on suspended particles and sediments.

4. CONCLUSION

The results showed that more than 80 percent of PAHs comprise 3 and 4 ring compounds, including Acenaphthene, Acenaphthylene, Florene, Phenantrene, Anthracene, Fluoranthene , pyrene and chrysene. Among these compounds, Chrysene, Fluoranthene and Pyrene had a higher abundance than other compounds in most of the samples. On the other hand, high molecular weight compounds include benzo(a) anthracene,benzo(b)fluoroantene,benzo(k) fluoranthene, benzo (a) pyrene, dibenzo (a, h) anthracene, benzo (g, h, i) perylene and indeno (1,2,3-c, d) pyrene was lower than the device's detection limit in all stations. According to the results of the diagnostic ratio indexes, sediments contamination of Tehran runoff network has a pyrogenic and petrogeneic sources, but the contribution of pyrogenic sources is predominant in comparison with petrogenetic sources. But The LMW/HMW index showed petrogenic sources were dominant in 30% of stations and pyrogenic sources were dominant in the rest. are Incomplete combustion, Small and large industrial units, household activities and atmospheric deposition are the most probable pyrogenic sources in this city are considered. Also leakage or the loss of oil and fossil fuels were the most probable petrogenic sources of PAHs compounds in Tehran runoff. Therefore, at stations where petrogenic compounds had a significant concentration, the runoff was affected by washing the surfaces of fuel stations, repair shops, and etc. Moreover, the survey of the relationship between total organic carbon and PAHs showed a significant and strong correlation between these two variables, but its coefficient varied in each sub-catchments. Finally, considering the bioavailability and potential risks of PAHs contain less than 4 rings and their significant concentration in runoff sediment of Tehran city, controlling and monitoring of runoff and sediment yields in this city is necessary.

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