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Distribution of Polycyclic Aromatic Hydrocarbons in a Municipal Solid Waste Landfill and Underlying Soil

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The most important emission route of various contaminants from unprotected landfills is the infiltration of landfill leachates through the vadose soil layers into the aquifer (Christensen and Kjeldsen 1989). The composition of contaminants in landfill leachates is rather complex and includes numerous organic compounds of both biogenic and xenobiotic origins (Christensen 1992). One of the most common classes of organic pollutants detected in landfills and in the adjacent aquifers are polycyclic aromatic hydrocarbons (PAHs) (Gade et al. 1996; Kerndorff 1995). They are introduced into the landfills along with petroleum hydrocarbon residues (Loehr et al. 1993) and by deposition from the atmosphere (Wild and Jones 1995) but they can also be formed on the spot in municipal landfill fires (Ruokojarvi et al. 1995). Moreover, municipal solid waste landfills are operated as reactor landfills, where significant percentage of biological waste is transformed under highly anaerobic (methanogenic) conditions. In analogy with the transformation pattern of organic matter in reducing lake sediments (Barnes and Barnes 1983), an intensive production of biogenic (diagenetic) PAHs in landfills is very likely. PAHs formed by pyrolytic processes are complex mixtures of non-substituted compounds, which exhibit a considerable ecotoxicity. In contrast, biogenic PAHs are usually alkyl-substituted species and are considered ecotoxicologically harmless. PAH assemblages found in environmental samples are rather variable and cover a wide range of physico-chemical properties such as volatility and aqueous solubility. During infiltration of the leachate PAH mixtures undergo a significant geochemical fractionation, which can result in rather different distribution patterns for individual PAH compounds. The aim of this paper was to determine the distribution of PAHs, ranging from 2 to 5 condensed rings, in the solid waste, soil and aquifer sediments below a municipal solid waste landfill with a special emphasis on the differentiation between pyrolytic and biogenic PAHs.

MATERIALS AND METHODS

The main landfill of the city of Zagreb, Croatia, covers a large area of 800,000 m^2 and contains about 5 million tons of solid waste. The waste is composed mostly of domestic refuse, however, the presence of commercial and industrial waste was also detected (Ahel et al. 1998). The landfill is actually an open dump without

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liner and/or leachate collection system, while underlying soil is composed of highly permeable alluvial sediments. The permanently saturated zone of the aquifer is located about 4 m below the bottom of the landfill. The landfill is situated only 2-3 km upstream from the main groundwater resources in the area and there has been a growing concern about possible infiltration of contaminants into underlying soils and further into the groundwater. The present study was focused on the south-eastern part of the landfill, which covers an area of about 80,000 m^2. The height of waste filling reaches up to 12 m. Earlier studies carried out in the aquifer near this part of the landfill revealed that emissions of various organic pollutants from the landfill can exert a major impact on groundwater quality (Ahel 1991).

Samples of solid waste and soil were obtained from 10 randomly distributed boreholes, ranging from 10 to 25 m in depth. The soil samples from boreholes no. 2 and no. 3 are not considered in this report since the soil at these microlocations was not covered with a layer of solid waste. Drilling was performed in such a manner that the vertical structure of the cores remained undisturbed. The analyses of solid waste were performed on composite samples, which were obtained by mixing of sub-samples taken from different layers of the drilled core. Each soil sample, including aquifer sediments from the saturated zone, represented a distinct layer with a thickness of 1 meter. All analyses were performed on size-fractions <2 mm, which were obtained by sieving from air-dried original samples.

Thirteen non-substituted PAHs (ns-PAH), including compounds with 2 to 5 aromatic rings (naphthalene, biphenyl, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene and perylene), as well as 1-methyl-7- (1-methylethyl)phenathrene (retene) were determined simultaneously using high-resolution gas chromatography/mass spectrometry (GC/MS). Qualitative identifications, using authentic standards, were performed in the full scan mode by scanning the masses in the range from 40-450 daltons, while all quantitative determinations were carried out using single ion monitoring technique and deuterated PAHs as internal standards. Before GC/MS analyses, the samples (15 g of solid waste or 30 g of soil) were extracted with 50 ml of dichloromethane using an ultra-sonic bath and the extraction was subsequently repeated with 50 ml of methanol. The combined extracts were evaporated to dryness, transferred into n-hexane and purified using a silica gel column. The final fractions containing PAHs were analysed on a Hewlett Packard instrument (GC 5890 Series II, MSD 5971A), equipped with a 22 m x 0.2 mm i.d. fused silica capillary column coated with 0.25 µm thick film of HP-5. The reproducibility of the applied analytical procedure for individual PAHs, expressed as the relative standard deviation of 4 independent determinations of the same soil sample, was in the range of 5-17 %. The detection limit based on a 30 g-sample was 1 ng/g.

RESULTS AND DISCUSSION

The total concentration of PAHs in solid waste and soil layer immediately below the landfill bottom varied in wide ranges of 394-3879 ng/g and 108-1182 ng/g, respectively. Such a strong heterogeneity of the spatial distribution is the reflection of conspicuous variability in the organic composition of the disposed waste (Ahel et al. 1998). However, the relationship between non-substituted PAHs and the main biogenic PAH in the landfill, retene, showed an interesting regularity (Fig. 1). The contribution of non-substituted PAHs was highly predominant in solid waste (67.0-98.6 %), while retene was more abundant (66-90.4 %) in all examined soil samples. Since the physico-chemical partitioning of retene is expected to be very similar to that for 4- to 5-ring PAHs, such a marked reversal of the ns-PAH/retene ratio can be explained only by differences in their biotransformation behaviour during the leachate infiltration. According to literature reports ns-PAH can be degraded efficiently in soils by various microbial

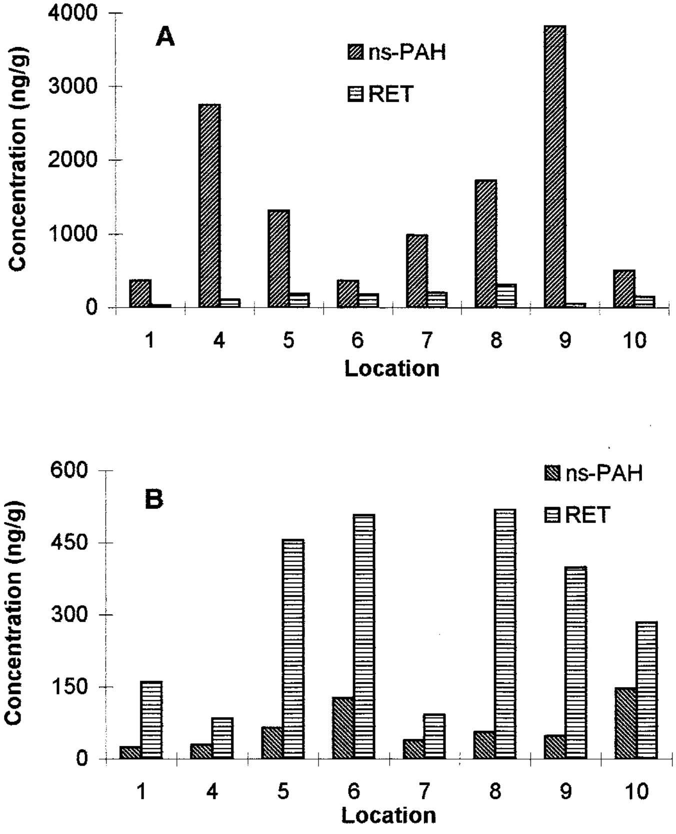

Figure 1. Spatial distribution of the total non-substituted polycyclic aromatic hydrocarbons (ns-PAH) and retene (RET) in (A) solid waste and (B) underlying soil (0-1 m below the landfill bottom) at the landfill of the city of Zagreb.

consortia (Guerin 1999) and consequently the pronounced elimination during the passage through the microbially highly active sequence of redox environments of the landfill is very likely. The overall elimination efficiency of ns-PAH was 95.5 %. By contrast, the concentration of retene in the soil layer below the landfill was higher than in the solid waste, which revealed its intensive formation in the lower parts of the landfill. The presence in the same samples of abietic acid derivatives (Ahel et al. 1998), which are well-known precursors of retene (Barnes and Barnes), strongly supported this assumption. Moreover, all relevant parameters determined in the deeper zones of the landfill and underlying soils indicated that the redox conditions in the unsaturated zone were methanogenic (Ahel et al. 1998).

A relatively non-specific impact of physico-chemical processes on the transport from solid waste to the underlying soil layer is also indicated by a rather uniform elimination efficiency of all ns-PAHs (93.0-97.6 %). As illustrated in Fig. 2, there

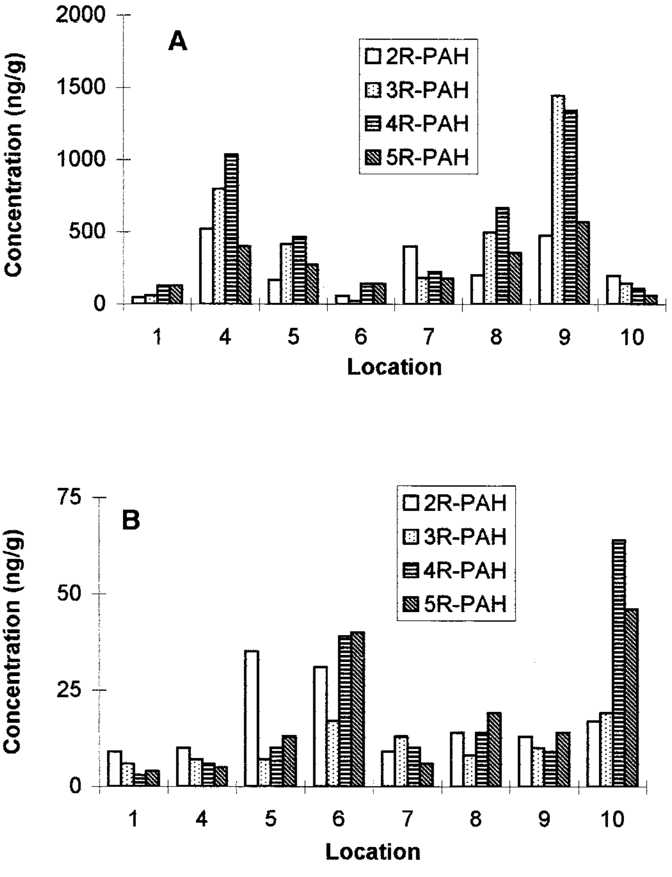

Figure 2. Spatial distribution of 2-ring to 5-ring PAHs in (A) solid waste and (B) underlying soil layer (0-1 m) at the landfill of the city of Zagreb.

is no indication of any regular changes in the composition of 2-ring to 5-ring ns-PAH as going from solid waste to underlying soil, which could be related to differences in their hydrophobicity. The prevalent PAHs in solid waste were those having 3 and 4 condensed rings, while in most of the soil samples slight predominance of 4- and 5-ring PAHs was observed. Due to the higher hydrophobicity, the higher congeners are less mobile and should be better retained in the landfill. Therefore, the increase of the relative percentage of higher congeners in the soils below the landfill reflects very probably their comparatively higher persistence towards microbial transformation (Guerin 1999).

However, further infiltration through the soil layer, down to the permanently saturated zone of the aquifer, revealed the expected chromatographic behaviour. Detailed vertical profiles of individual ns-PAH are shown for the borehole no. 8 (Fig. 3).

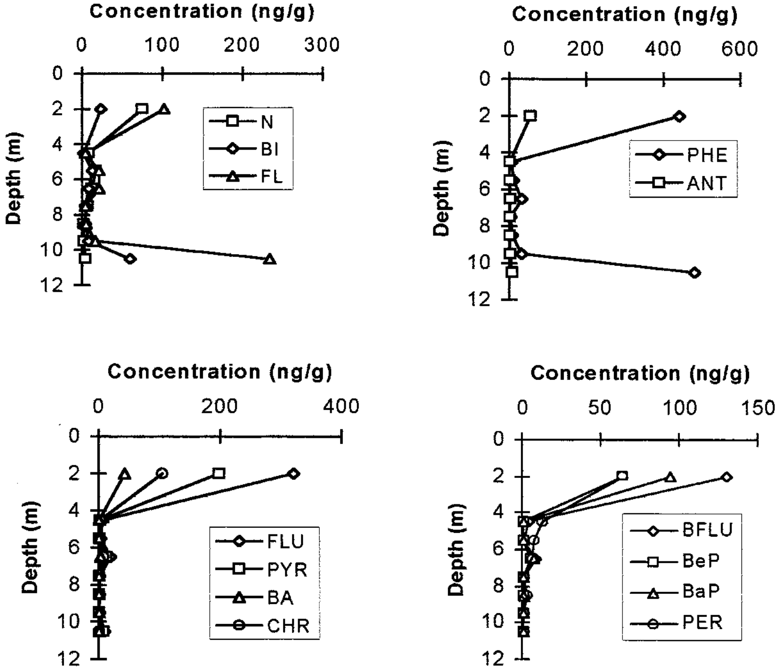

Figure 3. Vertical distribution of the individual non-substituted PAH in the borehole no. 8 at the landfill of the city of Zagreb (N=naphthalene, BI= biphenyl, FL=fluorene, PHE=phenanthrene, ANT=anthracene, FLU=fluoranthene, PYR= pyrene, BA=benzo(a)anthracene, CHR=chrysene, BFLU=benzo(k)fluoranthene, BaP=benzo(a)pyrene, BeP=benzo(e)pyrene, PER=perylene).

The height of the waste filling at this location was 4 m, while the permanently saturated zone was situated in the depth of 8 meter. As can be seen, after a sharp reduction of all ns-PAH going from solid waste (point at 2 m) to the first meter of the soil layer (4-5 m), there is only a small peak of ns-PAH in the vadose zone (6-7 m). This maximum can be explained as a consequence of association of ns-PAH with organic matter, which also showed a pronounced maximum in the same layer (Ahel et al. 1998). However, in the permanently saturated aquifer sediments there was a significant difference between the distributions of lower (2- and 3-ring PAHs) and the higher ones. The 2-ring PAHs as well as phenantherene showed a marked increase of their concentration in the lowest layer, while the levels of all higher PAHs remained low. A plausible explanation of such a difference lays in lower solubilities, i.e. lower mobilities of higher PAHs (Reemtsma and Mehrtens 1997). Along these lines, there is also a possibility that more water-soluble PAH reached deeper aquifer sediments at the location no. 8 by horizontal transport from other more polluted microlocations. Earlier analyses of groundwater samples from the same part of the landfill confirmed a strong predominance of naphthalene and phenanthene over higher PAHs (Ahel 1991).

The comparison of detailed vertical profiles of the total ns-PAH and retene (Fig. 4) confirms the reversal of their ratio in the section between the solid waste and unsaturated saturated zone of soil. As expected, the maximum of retene was associated with organic-rich zone at the depth of 6-7 m, which clearly supported the assumption about its microbial formation in the highly reduced leachate. In the saturated zone of the aquifer the distribution curve of retene was very similar to that of higher PAHs, which indicated the prevalence of physico-chemical partitioning over biological processes in that zone.

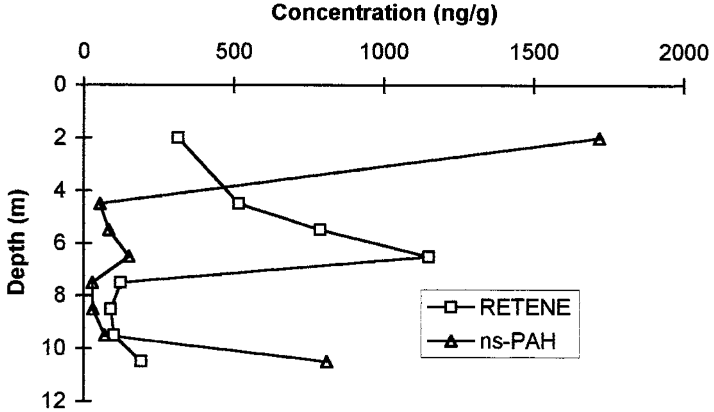

Figure 4. Vertical distribution of the total non-substituted polycyclic aromatic hydrocarbons (ns-PAH) and retene at the landfill of the city of Zagreb.

The results presented above suggest that, despite their high concentration in solid waste, higher PAHs (>4-ring) usually do not pose a major risk to groundwater due to the very efficient biological elimination in the landfills as well as an efficient sorption on the organic rich soils immediately below the landfill. This is in a good agreement with our earlier observations in the aquifer near the landfill of the city of Zagreb. The concentration of the most abundant 4-ring PAH, fluoranthene, in the adjacent groundwater never exeeded 100 ng/L, while all 5-ring PAHs were never detected at the levels that exceed 10 ng/L (Ahel 1991). On the other hand, an important part of the total PAH concentration, sometimes even the largest percentage, can derive from biogenic PAH such as retene, which precludes reliable estimation of the total anthropogenic PAHs and petroleum hydrocarbons by simple fluorimetric methods.

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