Polycyclic aromatic hydrocarbons in highway plants and soils. Evidence for a local distillation effect

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Poa trivialis grasses and soils from the side slope of a high-traffic highway were analysed for their PAH content by gas chromatography coupled to mass spectrometry. The ratios of volatile, low-molecular weight PAHs *versus* high-molecular weight PAHs increase with side slope height. For instance, naphthalene/pyrene values increase from 0.3 to 3.4 in plants. Acenaphthene/fluoranthene values increases from 0.017 to 0.123 in soils. Moreover, soil PAHs can be classified into two categories according to variations of absolute concentrations with height: low-molecular weight PAHs showing an increase and high-molecular weight PAHs showing a decrease. These results demonstrate the occurrence of an atmospheric distillation effect which favour the concentration of high-molecular weight PAHs near the PAH source. Environmental implications of such a phenomenon are discussed.

Introduction

Trace levels of polycyclic aromatic hydrocarbons (PAHs) are widely occurring in modern ecosystems [1-4]. Since some PAH members are mutagenic, their presence in plant [1,5-7] is of increasing concern because PAHs may ultimately be transferred to food. Moreover, the presence of PAHs in soils has been correlated with highway traffic and cancer incidence [8]. Nonetheless, despite several reports suggesting that airborne PAHs should be transferred over great distances [9-10], the mechanisms ruling atmospheric transfer are still poorly known. A recent investigation [6] suggests that PAHs should be partitioned between air and plant as a function of ambient temperature. Such an atmospheric distillation process has also been evidenced for organochlorine compounds in snow sampled at increasing height in the mountains of western Canada [11]. Here, we show that a similar process is operating on the side slope of a high-traffic French highway (39 000 vehicles per day).

Experimental

Soils and *Poa trivialis* grasses were sampled in march 1998 at heights of 2 m, 4 m and 6 m above road level on the eastern side slope of the A31 highway 30 km north of Nancy, France (Fig. 1). At each height, three 1 kg soil samples were taken 1 m apart at 0-10 cm depth, dried at 20 °C, sieved to 2 mm then mixed. A 100 g sub-sample was finely ground then sonicated 15 min with 150 ml distilled CH_2Cl_2 in 600 ml pyrex beakers (3 times). The CH_2Cl_2 extracts were mixed, filtered over CH_2Cl_2-prewashed paper filter, concentrated under reduced pressure to about 1 ml, transferred into a 2 ml glass vial then allowed to concentrate to dryness under a ventilated hood. A similar procedure was followed for plant sampling (50 g). Plant samples were mixed, dried at 40 °C and finely crushed. A 150 mg sub-sample was then extracted with CH_2Cl_2 using the pipette Pasteur method [12]. Extracts (5 mg) were fractionated over a Pasteur pipette loaded with 600 mg of CH_2Cl_2-prewashed silica-gel then with 150 mg of CH_2Cl_2-prewashed Florisil (TLC, Merck). Alkane fractions were eluted with 3×500 µl of *n*-pentane in pre-weighted 2 ml screw-top Varian glass vial. Aromatic fractions were then eluted with 3×500 µl of *n*-pentane-CH_2Cl_2 (65/35 v/v).

Aromatic fractions were analysed with a Varian Star 3400 gas chromatograph coupled to a Saturn 2000 ion trap mass spectrometer. Conditions: helium pressure 8 psi; autosampler; on column injector; 28 m × 0.25 mm i.d. fused silica gel column coated with 5 % phenyl-, 95 % methylpolysiloxane phase (0.25 µm thickness); oven temperature: 30 °C isothermal 1 min, 35-110 °C at 25°/min, 110-300 °C at 3°/min then 310 °C isothermal 10 min; EI 70 eV, scan 100-300 amu. Calibration was performed on reconstructed
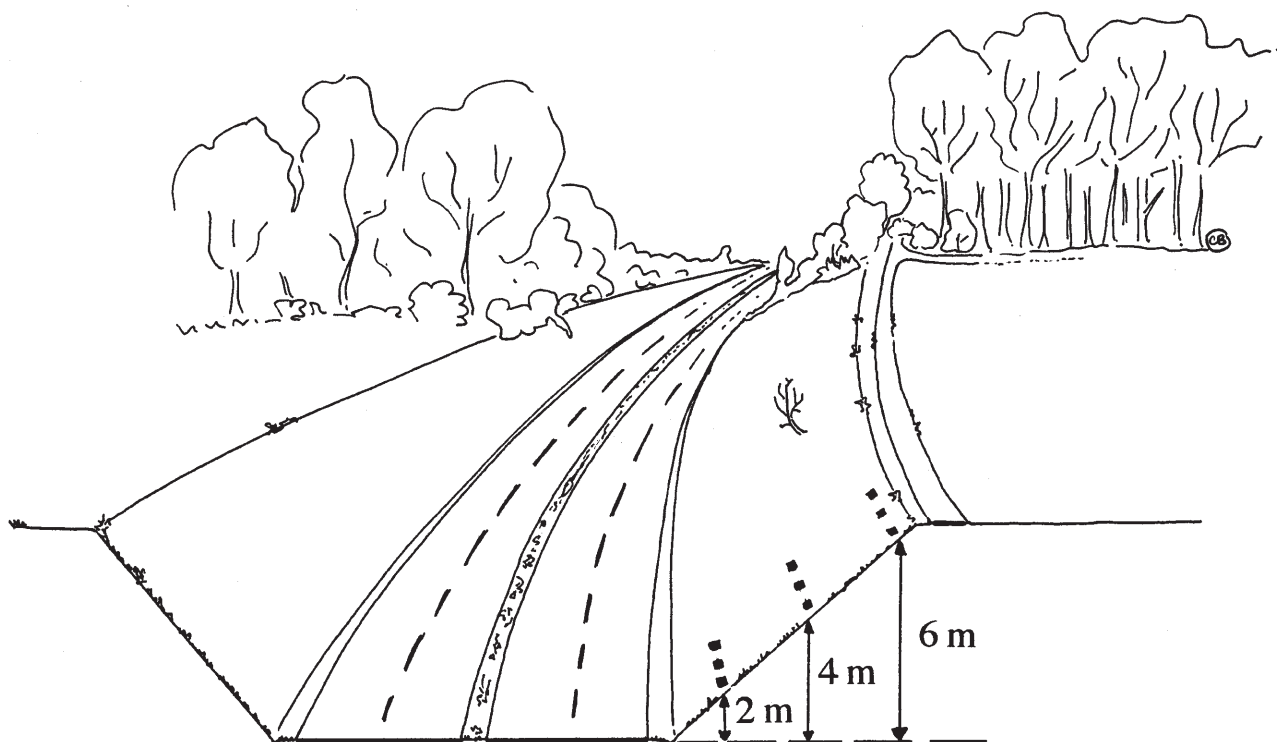

Figure 1. Plant and soil were sampled at increasing height (2 m, 4 m and 6 m) on the side-slope of a major French highway.
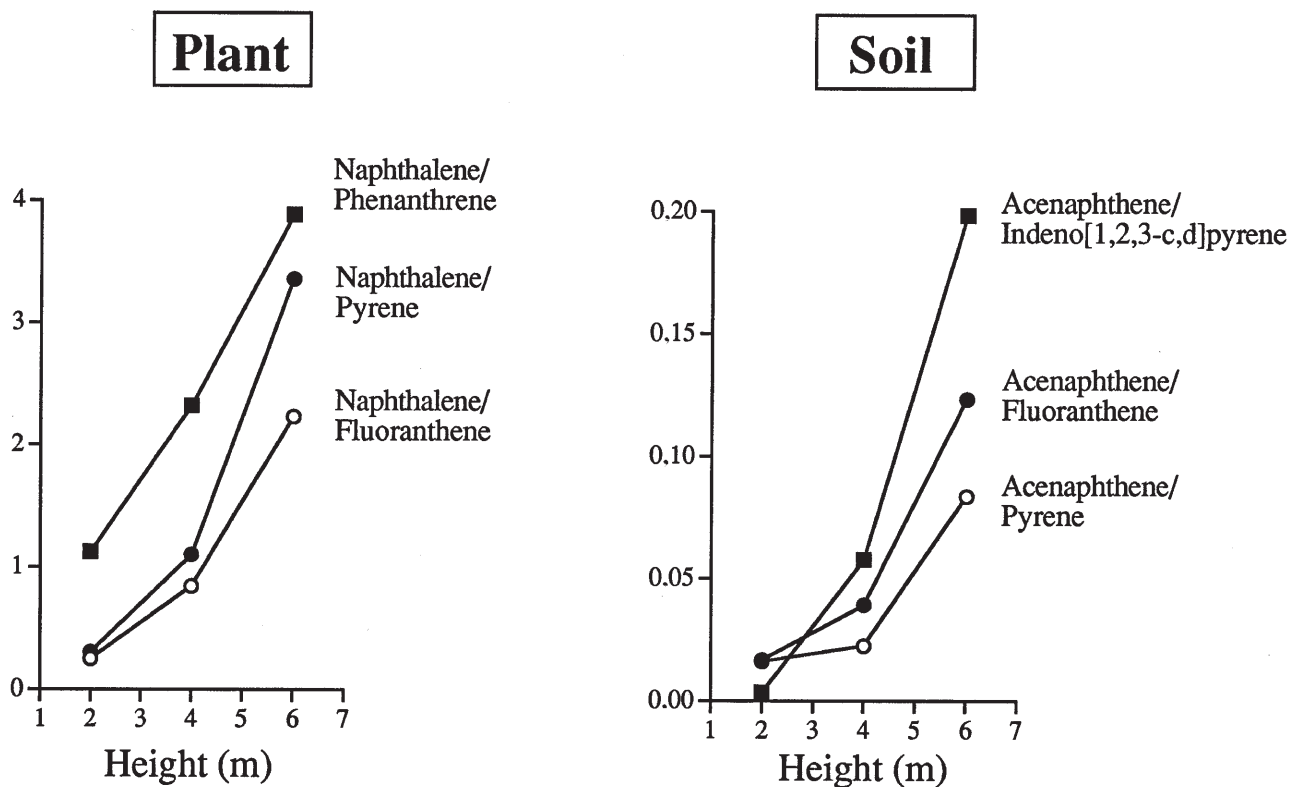
Figure 2. Ratios of low- versus high-molecular PAHs of plant and soil sampled at increasing heights on the side slope of the highway.

Table I. Concentrations of PAHs in ng/g dry weight of plants and soils sampled at increasing height. (+) and (–) refers respectively to increases and decreases of concentrations of 6m- *versus* 2m-samples. nd: not detected.

Height	PLANT			SOIL		
	2 m	*4 m*	*6 m*	*2 m*	*4 m*	*6 m*
Naphthalene	25	65	598 (+)	3	3	9 (+)
Acenaphthylene	nd	nd	nd	75	29	82 (+)
Acenaphthene	nd	nd	105	149	237	848 (+)
Fluorene	nd	nd	nd	949	775	980 (+)
Phenanthrene	24	28	154 (+)	2390	3075	3476 (+)
Anthracene	nd	nd	nd	809	1428	1582 (+)
Fluoranthene	107	77	268 (+)	8851	6045	6872 (–)
Pyrene	88	59	178 (+)	9159	10464	10143 (+)
Benz[a]anthracene + chrysene	50	100	158 (+)	40371	10384	18897 (–)
Benzo[b]- + benzo[k]-fluoranthene	nd	nd	nd	18288	3967	5770 (–)
Benzo[a]pyrene	nd	nd	nd	33924	6188	12421 (–)
Indeno[1,2,3-c,d]pyrene	nd	nd	nd	41811	4114	4275 (–)
Benzo[g,h,i]perylene	nd	nd	nd	36674	4414	4780 (–)
Dibenz[a,h]enthracene	nd	nd	nd	8126	359	nd (–)

ion current with standard PAH mixtures of naphthalene (m/z 128), acenaphthene (154), acenaphthylene (152), fluorene (166), phenanthrene (178), anthracene (178), fluoranthene (202), pyrene (202), benzo[a]anthracene (228), chrysene (228), benzo[b]- and benzo[k]fluoranthene (252), benzo[a]pyrene (252), indeno[1,2,3-c,d]pyrene (276), benzo[g,h,i]perylene (276) and dibenz[a,h]anthracene (278).

Results and discussion

Plant PAHs

Soil and plant were sampled at increasing height on the side slope of a high traffic highway (Fig. 1). PAH concentrations are reported in table I. In *Poa trivialis*, the relative concentrations of naphthalene versus phenanthrene, fluoranthene and pyrene increase with height (Fig. 2). Since naphthalene is the most volatile compound, this result suggests that PAHs from exhausts are partitioned in the atmosphere above the highway before adsorption on plant waxes. This phenomenon is analogous to the frationation of volatile compounds in a distillation column. Indeed, the partitioning of PAHs should be due to temperature variations [6] from hot engine exhausts to colder air. This distillation effect is confirmed by analysis of soil PAHs as described below.

Soil PAHs

The 16 EPA PAHs found in soils can be classified into two categories according to their changes of absolute concentrations with height. First, low-molecular weight PAHs such as naphthalene, fluorene and anthracene show a concentration increase from 2 to 6 m (Tab. I). Second, high-molecular weight PAHs such as benzo[a]pyrene and benzo[g,h,i]perylene show a concentration decrease from 2 to 6 m. These results strengthen the hypothesis of a local distillation effect. Furthermore, the relative concentrations of low- *versus* high-molecular weight PAHs increase sharply with height, as shown for acenaphthene versus fluoranthene, pyrene and indeno[1,2,3-c.d]pyrene (Fig. 2). A such finding thus confirms the occurrence of a distillation effect around the highway. It is in full agreement with previous studies on vegetation-atmosphere partitioning of PAHs [6].

Environmental implications

The non-homogeneous transfer of PAHs along highways has several environmental implications. First, the most mutagenic PAHs, *e.g.* benz[a]pyrene, should be concentrated near the highway. As a consequence, breathing highway atmosphere will increase the health hazards of vehicle drivers. Second, the most carcinogenic PAHs will also concentrate into the rain washings of road surface. We therefore advice to collect these waters in closed systems in order to avoid further contamination of groundwaters. Third, the distillation effect should favour the medium-range transfer of the less mutagenic and most biodegradable PAHs towards plant crops.

Conclusion

Analysis of PAHs in plants and soils from the side slope of a major highway gives evidence for a local distillation effect. Further studies are in progress to assess the precise origin of PAHs in agronomic plants.

Acknowledgements

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