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Gas chromatography-mass spectrometry study of polycyclic aromatic hydrocarbons in grass and milk from urban and rural farms

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Abstract

PAH levels were studied in grass and milk sampled at two farms, one located in a non-contaminated, rural area, and another located in a urban area close to PAH sources such as highways, high-traffic roads, fuel-powered trains and a steel plant. PAH concentration were measured by gas chromatography coupled to mass spectrometry (GC-MS) using internal deuteriated standards. In grasses, unexpectedly, although the sum of PAH concentrations was only slightly higher at the urban farm (83.1 ± 16.1 ng/g) versus rural farm (51.8 ± 10.6 ng/g), this difference was not observed for all PAH members. This absence of striking difference of PAH levels between urban and rural grasses suggests that atmospheric PAH sources, e.g. vehicle exhausts and chimney fumes, could be rapidly diluted by winds. In milk, PAH concentrations were not significantly different at urban and rural farms.

1. Introduction

Polycyclic aromatic hydrocarbons are potentially mutagenic compounds widely occurring in natural media such as soils, atmosphere, sediments and plants (Edwards, 1983, Sims and Overcash, 1983, Baek et al., 1991, Wilson and Jones, 1993, Richnow et al., 1995, Wild and Jones, 1995, Henner et al., 1997, McRae et al., 1999, Lichtfouse et al. 1999, Wilcke, 2000, Bryselbout et al., 2000). There are natural as well as anthropogenic sources of PAHs such as vegetation fires, petroleum seepage and vehicle exhausts. The main known processes of PAH formation are 1) incomplete combustion of organic matter, e.g. fuel and wood burning (Freeman and Cattell, 1990) 2) the slow maturation of sedimentary organic matter to yield fossil fuels, e.g. coal and petroleum (Tissot et al., 1971), and 3) the rapid aromatisation of organic substances in modern sediments (Trendel et al., 1989). Noteworthy, a recent study of termite nests and wood points to a possible - modern - biological origin of PAHs (Wilcke et al., 2000).

While the sources of PAHs in heavily-contaminated environmental samples, e.g. coke-plant soils or highway plants, are rather easy to pinpoint, the precise origin of PAH occurring at trace levels is poorly known due to our lack of knowledge of transfer pathways (Simonich and Hites, 1994, Lichtfouse et al., 1997). More specifically, there is a strong need to study the relationships between plant contamination and food contamination (Eisele, 1985, Travis and Arms, 1988). Here we wish to report a comparison of PAH levels in grasses and milk from rural and urban farms.

2. Experimental

2.1 Grass and milk samples

Milk and grass samples were collected in July 2000 at two farms in Lorraine, France. One farm is located in a very remote, rural area, far away from major sources of PAHs such as highways and industrial activities. The other farm is located in a high-traffic zone of the suburbs of a major town in Lorraine, at 700 m from a steel factory, 500 m from fuel-powered railway trains, and 4 kms from two major highways. All sampling ware was pre-washed successively with distilled water, acetone, and then hexane. At each farm, five grass samples were collected in dairy cattle-meadows. This grass was the sole food source of the cows (in summer). Each grass sample of about 1 kg is the sum of 8 sub-samples collected on a circle of 10-m radius. The five grass samples were dried at room temperature, finely ground then mixed together. Five 10g sub-samples were analysed. Five milk samples of 500 ml were collected at the cooled tank (4°C) of the farm, then stored at -20°C.

2.2 PAH analysis

Detailed extraction procedures are described in the NF ISO 15302 method, and were conducted by Micropolluant Technologie Ltd. PAH were quantified by gas chromatography coupled to mass spectrometry (HP) in the single ion monitoring mode, using internal deuterated standards : naphthalene- d_8 (m/z 136) for naphthalene; acenaphthene- d_{10} (m/z 164) for acenaphthene, acenaphthylene, and fluorene; phenanthrene- d_{10} (m/z 188) for phenanthrene, anthracene, fluoranthene and pyrene; chrysene- d_{12} (m/z 240) for chrysene and benzo[a]anthracene, and perylene- d_{12} (m/z 264) for perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene. Analytical detection levels : 0.50 ng PAH/g grass, 0.25 ng PAH/g milk fat. Results were statistically analysed with the SAS system software using the GLM procedure (SAS, 1996).

3. Results and discussion

3.1 PAHs in grasses

The concentration of PAHs in grasses from rural and urban farms is reported on Table 1 and Figure 1. PAH concentrations were measured by GC-MS in the single ion monitoring mode using internal deuterated standards : naphthalene- d_8 (m/z 136), phenanthrene- d_{10} (m/z 188), chrysene- d_{12} (m/z 240), perylene- d_{12} (m/z 264). A such procedure allows to quantify trace levels of PAHs in biological samples (Baumard et al., 1997). The sum of PAH concentrations is slightly higher in urban meadow grass (83.1 ± 16.1 ng/g) versus rural grass (51.8 ± 10.6 ng/g). Nonetheless, PAH concentrations are statistically different only for three members: phenanthrene ($P < 0.01$), anthracene ($P < 0.001$), and fluoranthene ($P < 0.001$). These results are rather unexpected because the urban farm is located in a high-traffic area, near a steel plant, two major highways, and a fuel-powered train. Indeed, phenanthrene levels (31.1 ng/g) in the urban farm are about 100 times lower than those found in grasses located at 4 m of a Lorraine highway (Bryselbout et al., 2000). It is therefore suggested that PAHs from point sources, e.g. vehicle exhausts, could be rapidly diluted by winds in the vicinity of the point source, then reach the average background level of the atmosphere. Further, in grasses, the predominance of low molecular-weight PAHs and the absence of high molecular-weight PAHs, e.g. perylene, benzo[b]fluoranthene, and benzo[a]pyrene (Figure 1) are in agreement with the distillation effect proposed by Bryselbout et al. (2000) to explain the behaviour of PAH concentrations near highways.

Table 1. Concentrations of polycyclic aromatic hydrocarbons in grass and milk from urban and rural areas, expressed in ng/g grass dry weight, ng/g milk fat.

	Na	Fluo	Phe	Ant	Flut	Pyr	B[a]A	Chry
RURAL GRASS	3.2	14.5	20.7	1.4	7.1	10.0	n.d.	n.d.
	3.8	12.2	21.7	1.3	7.7	13.2	n.d.	n.d.
	2.7	10.7	19.9	1.6	5.3	7.4	n.d.	n.d.
	5.1	10.0	15.7	1.5	5.9	4.2	n.d.	n.d.
	16.8*	22.5*	46.1*	4.8*	17.4*	11.5*	n.d.*	n.d.*
Average	3.7±1.0	11.9±2.0	19.5±2.6	1.5±0.1	6.5±1.1	8.7±3.8		
	Sum of PAH concentrations : 51.8 ± 10.6							
URBAN GRASS	4.9	14.8	33.8	2.0	16.0	18.3	2.3	5.1
	3.8	14.1	34.0	2.3	13.5	10.8	2.2	5.1
	4.0	14.3	35.6	3.2	13.0	12.4	2.4	4.8
	2.9	10.2	26.1	2.5	11.0	13.5	n.d.	4.5
	7.3	9.9	25.9	2.6	12.2	5.8	2.1	4.3
Average	4.6±1.7	12.6±2.4	31.1±4.7	2.5±0.4	13.1±1.8	12.2±4.5	2.2±0.2	4.8±0.4
	Sum of PAH concentrations : 83.1 ± 16.1							
RURAL MILK	6.6	n.d.	7.2	2.6	n.d.	n.d.	n.d.	n.d.
	8.4	n.d.	11.4	4.4	n.d.	5.1	n.d.	n.d.
	8.6	n.d.	21.1	3.5	7.2	14.7	n.d.	n.d.
	5.5	n.d.	7.3	2.6	1.5	3.7	n.d.	n.d.
	15.5	n.d.	15.0	3.6	4.2	7.1	n.d.	n.d.
Average	8.9±3.9		12.4±5.9	3.3±0.8	4.3±2.9	7.7±4.9		
	Sum of PAH concentrations : 36.6 ± 18.4							
URBAN MILK	n.d.	n.d.	11.2	2.2	n.d.	14.8	n.d.	n.d.
	6.5	n.d.	9.7	3.6	n.d.	n.d.	n.d.	n.d.
	8.1	n.d.	11.5	7.1	n.d.	4.8	n.d.	n.d.
	5.8	n.d.	5.8	2.3	n.d.	2.6	n.d.	n.d.
	7.1	n.d.	9.1	3.1	n.d.	4.2	n.d.	n.d.
Average	6.9±1.0		9.5±2.3	3.7±2.0		6.6±5.5		
	Sum of PAH concentrations : 26.7 ± 10.8							

Na : naphthalene, Fluo : fluorene, Phe : phenanthrene, Ant : anthracene, Flut : fluoranthene, Pyr : pyrene, B[a]A : benz[a]anthracene, Chry : chrysene. n.d. : not detected. *statistically anomalous values not taken into account for averaging.

3.2 PAH in milk and grasses

PAH concentrations in urban and rural milk are not statistically different, suggesting a similar source (Table 1, Figure 1). On the contrary, comparison of PAH distributions in grasses and milk show notable differences. Indeed PAH distributions in milk show higher relative concentrations of naphthalene, and the absence of high molecular weight PAHs. This result could be partly explained by the higher water-solubility of naphthalene favouring its selective concentration during digestion. This hypothesis is supported by food chain studies showing that the absorption of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDF), compounds of close chemical properties as PAHs, decreases with molecular weight (McLachlan, 1995). Nonetheless, several yet unknown processes may account for the PAH distribution in milk. Moreover, there are alternative, presumable sources of milk PAHs such as field drinking water (about 40 l/day), breathing air, and soil (about 600 g/day) ingested with grass.

Figure 1

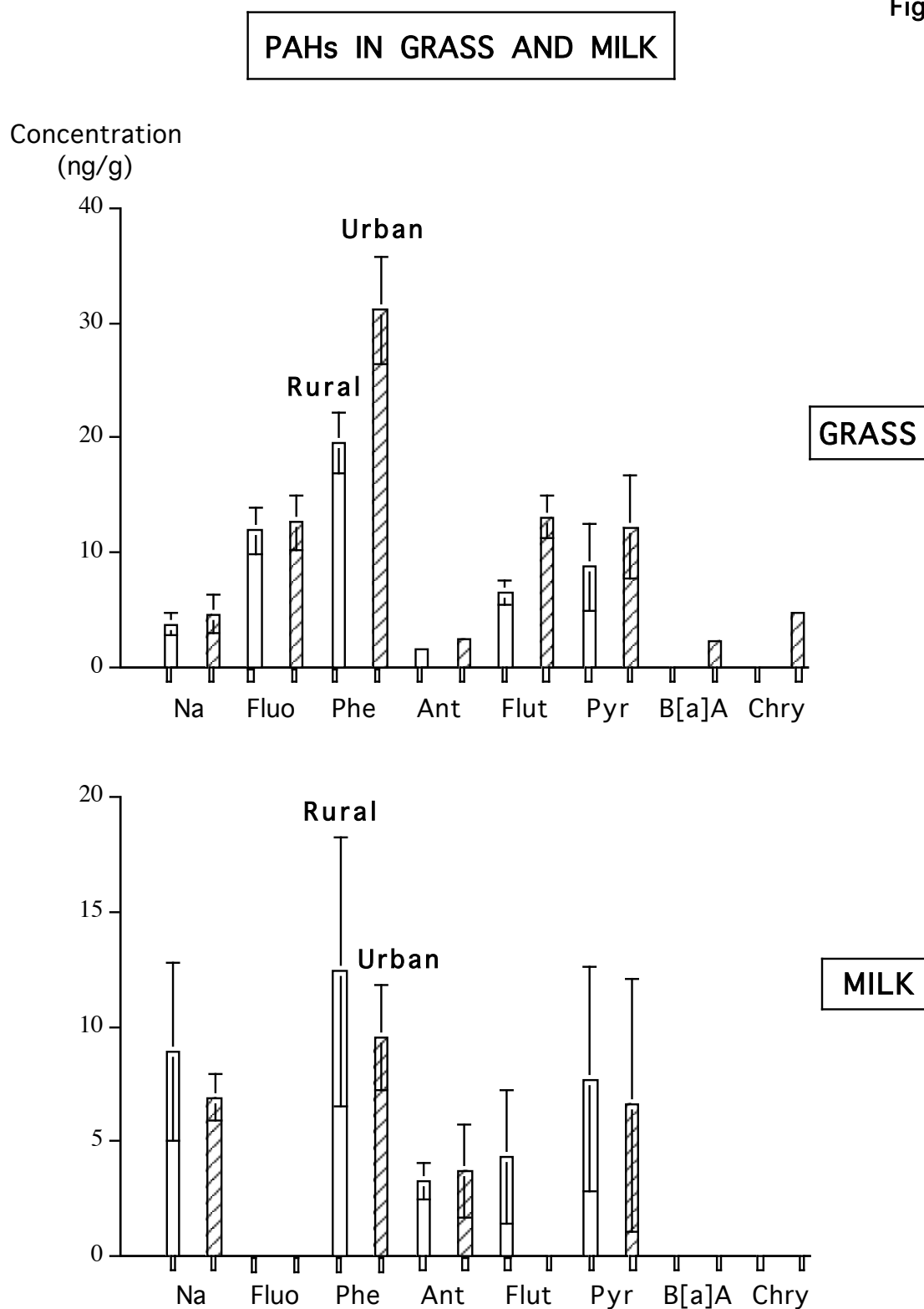


Figure 1. PAH concentrations in grasses and milk from rural and urban farms.

4. Conclusion

PAH concentrations in grass are only slightly higher in urban versus rural farms, suggesting a rapid dilution of atmospheric PAH point sources. PAH concentrations in urban and rural milk are statistically equal. Further work is under way to pinpoint the origin of milk PAHs using isotope tracers.

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