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Polycyclic Aromatic Hydrocarbons in Surface Waters of Alessandria District, South Eastern Piedmont (Italy)

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Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. Because of the high toxicity of some polycyclic compounds, such as benzopyrenes, the determination of their levels in air, water, soil and aquatic organisms was the object of several papers.

Anthropogenic pyrolitic and combustion processes, related to industrial plants, domestic heating, automobile traffic, are the major sources of these compounds; from these sources they enter atmospheric environment where their concentration is reduced by scavenging during precipitation events: rain, snow and fog in urban areas usually show high contents of PAHs (Leuenberger et al., 1988; Broman et al., 1987).
Dry and wet atmospheric polluted depositions, direct oil spills, municipal and industrial effluents transport appreciable amounts of PAHs to aquatic environment, where they are rapidly taken up and accumulate by both fish and shellfish (DoubAbdul et al., 1987; Rainio et al., 1986).
Alessandria District, in South-Eastern Piedmont (Italy), lies in the middle of Torino-Milano-Genova industrial area: in addition to local sources, a relatively long range transport of polluted air masses may conduct to this region atmospheric contaminants, such as polynuclear compounds, that can enter fluvial environments through meteoric precipitation.
The object of this work was to evaluate PAH content in surface waters flowing across the described territory. Samplings were carried on during winter season, when the concentration of these pollutants usually reaches the highest levels (Leuenberger et al., 1988).

MATERIALS AND METHODS

The determination of PAHs was performed using a rapid

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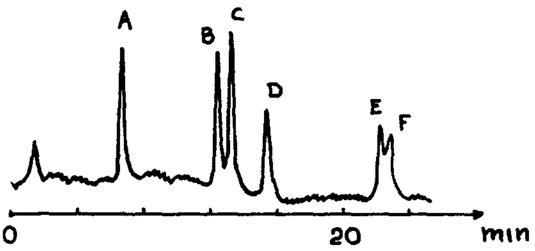

Figure 1. Chromatogram of an extract of spiked river water: (A) fluoranthene (0.02 ug/L), (B) benzo(b)-fluoranthene (0.02), (C) benzo(k)fluoranthene(0.02), (D) benzo(a)pyrene (0.04), (E) indeno(123-cd)pyrene (0.02), (F) benzo(ghi)perylene (0.08).

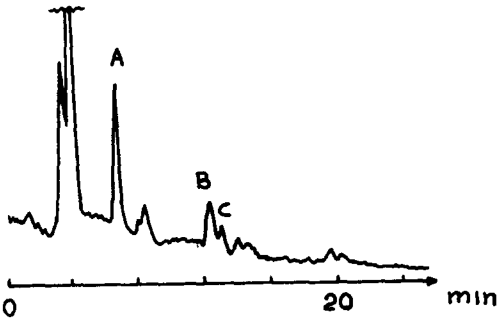

Figure 2. Chromatogram of a real sample (river water) : (A) fluoranthene, (B) benzo(b)fluoranthene, (C) benzo(k)fluoranthene.

method derived from the one described in a previous work (Cossa et al., 1988). PAHs were extracted from the sample (2 L) in a separatory funnel, using 70 ml of distilled ciclohexane; after elimination of water, the funnel was washed with 30 ml of fresh extraction solvent; then, the organic phase (70+30 ml) was dried by means of anhydrous sodium sulfate and evaporated to dryness by a rotary evaporator at 60°C under vacuum conditions. The residue was dissolved in 0.5 ml of tetrahydrofuran and analyzed by HPLC using the external standard method; chromatographic conditions are listed

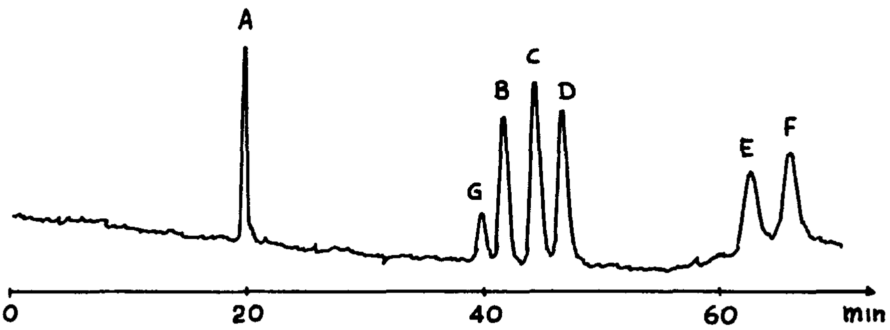

Figure 3. Chromatogram of a standard solution obtained using a MeOH / THF / water eluent (see text). (A) fluoranthene, (G) perylene, (B) benzo(b)-fluoranthene, (C) benzo(k)fluoranthene, (D) benzo-(a)pyrene, (E) indeno(123-cd)pyrene, (F) benzo(ghi)-perylene.

below:
Liquid Chromatography Varian Mod. 5000 equipped with Fluorimetric Detector Varian Mod. Fluorichrom TM (wavelenght filter - excitation: 7-54/7-60; emission: 4-76/3-71). Column: Merck 100CH-18/2, particle size 5 microns, l=250 mm, i.d.=4 mm; Guard Column Merck C18; Eluent: acetonitrile 90% - water 10%, flow=1 ml/min. Injection: 10 microliters. The described method reached the sensitivities reported in Table 1, while recoveries vary within 95-100%.

Table 1. Minimum detectable concentration (MDC) (ug/L) and mean % recovery (MR%) + SD.

PAH	MDC	MR%	+	SD
FLUORANTHENE	0.002	94.8	+	5.2
BENZO(b)FLUORANTHENE	0.002	98.7	+	3.9
BENZO(k)FLUORANTHENE	0.002	94.7	+	6.2
BENZO(a)PYRENE	0.004	98.0	+	6.4
INDENO(1,2,3-cd)PIRENE	0.002	99.9	+	8.5
BENZO(ghi)PERYLENE	0.008	100.5	+	9.1

In Figure 1 a chromatogram of an extract obtained from river water, previously purified by extraction and then spiked with six PAHs, is shown. Taking into consideration that WHO (World Health Organization) reccomends a maximum level of 0.2 ug/L for total PAHs (where the sum refers to the six searched pollutants) for drinking water, the obtained sensitivities,

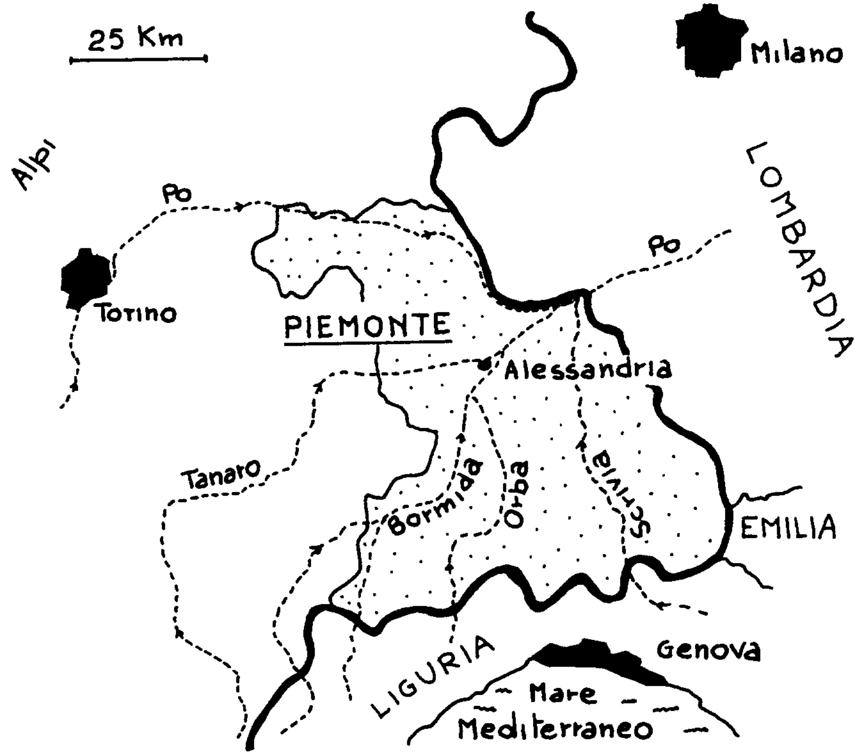

Figure 4. Localization of Alessandria District (South - Eastern Piedmont, Italy) and of the most important investigated rivers.

improvable using more complex methods, as described by Cartoni et al. (1986), were considered satisfactory to evaluate surface water pollution.

The determination of polynuclear compounds was performed on 38 samples: in Figure 2 a chromatogram of a real sample (river water containing an appreciable amount of some PAHs) is reported. A more complex eluent (methanol 60%, tetrahydrofuran 15%, water 25%; flow: 0.7 ml/min) can be used to improve chromatographic analysis. By this way some critical separations, such as the one between benzofluoranthenes and perylene (a natural occurring PAH), can be obtained (see Figure 3). However, because of the long retention times, the ternary eluent was only applied to confirm the occurence of benzofluoranthenes. Blanks were analyzed in parallel with the samples to elucidate interferences.

RESULTS AND DISCUSSION

A map of the District is in Figure 4: the sampling sites (38) are localized on 16 different water streams. The most important ones are the Po, Tanaro and Bormida rivers: in particular the valley where the last one flows was proclaimed "High Environmental Risk Area" by the Italian Government because of several dangerous industrial plants located in this region.

Table 2. PAH levels in surface waters of Alessandria District (South-Eastern Piedmont, Italy, Winter 1989-1990) arranged in arbitrary classes with the percentage (%) of incidence.

PAH	RANGE (ug/L)	N	%
FLUORANTHENE	<0.002	0	0
	0.002-0.005	10	26.3
(max.value 0.063)	0.005-0.0075	12	31.6
	0.0075-0.010	8	21.0
	0.010-0.0125	1	2.6
	0.0125-0.015	1	2.6
	0.015-0.0175	2	5.3
	0.0175-0.020	0	0
	0.020-0.0225	1	2.6
	>0.0225	3	7.9
BENZO(b)FLUORANTHENE	<0.002	20	52.6
	0.002-0.005	8	21.0
(max.value 0.018)	0.005-0.0075	5	13.2
	0.0075-0.010	2	5.3
	0.010-0.0125	2	5.3
	>0.0125	1	2.6
BENZO(k)FLUORANTHENE	<0.002	36	94.7
	0.002-0.005	2	5.3
(max.value 0.0035)			
BENZO(a)PYRENE	<0.004	38	100.0
INDENO(1,2,3-cd)PYRENE	<0.002	36	94.7
	0.002-0.005	2	5.3
(max.value 0.0023)			
BENZO(ghi)PERYLENE	<0.008	38	100.0

Table 2 reports the occurred PAHs concentrations arranged in arbitrary classes with the percentage of incidence. Looking at the data, the following statements are possible:

1) fluoranthene was present in each analyzed sample; it was the most abundant polycyclic hydrocarbon, perhaps because of its higher stability
2) benzo(b)fluoranthene occurred in several cases (47,4%) but the measured values were lower than the ones found for fluoranthene
3) benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene were detectable in only two samples and at very low level (the maximum found concentrations were respectively 0.0035 and 0.0023 ug/L)
4) benzo(a)pyrene and benzo(ghi)perylene were never detected at reported sensitivities in the considered sampling sites.

Finally, the results of this paper indicate that a diffuse pollution due to PAHs occurred in every water stream considered; the concentrations are comparable with data reported by Cartoni et al.(1986), Xu et al.(1984) and Crane et al. (1981) for surface waters.
The contamination is very far from the danger level established by WHO. The limit of 0.2 ug/L for total PAHs content was never reached and the most dangerous compounds, such as benzo(a)pyrene, were never found in the analyzed samples while others (benzo(k)fluoranthene) were only occasionally detected.

REFERENCES

Broman D, Colmsjo A, Naf C (1987) Characterization of the PAC profile in settling particulates from the urban waters of Stockholm. Bull Environ Contam Toxicol 38: 1020-1028.
Cartoni G, Coccioli F, Ronchetti M, Simonetti L, Zoccolillo L (1986) Determination of Polycyclic Aromatic Hydrocarbons in natural waters by thin-layer chromatography and high-performance liquid chromatography. J Chromatog 370: 157-163
Cossa G, Trova C, Gandolfo G, Scamuzzi M R (1988) Determinazione di Idrocarburi Aromatici Policiclici nelle acque ad uso potabile: individuazione di una metodica rapida e dati relativi alla provincia di Alessandria. Boll Chim Igien 39: 243-253.
Crane R I, Fielding M, Gibson T M, Steel C P (1981) A survey of Polycyclic Aromatic Hydrocarbons levels in British Waters . U.K. Water Research Centre Technical Report. 158.
DouAbdul Ali A Z, Abaychi J K, Al-Edanee T E, Ghani Ali A, Al-Saad H T (1987) PAHs in fish from the Arabian Gulf. Bull Environ Contam Toxicol 38: 546-552.
Leuenberger C, Czuczwa J, Heyerdahl E, Giger W (1988) Aliphatic and Polyciclic Aromatic Hydrocarbons in urban rain, snow and fog. Atmospheric Environment 22: 695-705.

Rainio K, Linko R R, Ruotsila L (1986) Polyciclic Aromatic Hydrocarbons in mussel and fish from the Finnish Archipelago Sea. Bull Environ Contam Toxicol 37: 337-343.

Xu X B, Jin Z L (1984) High - Performance Liquid Chromatographic studies of environmental carcinogens in China. J Chromatog 317: 545-555.

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