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Comparative Analysis of Emissions and Diffusion of Air PAHs at a Coastal Arid Site (Patagonia, Argentina)

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The town of Puerto Madryn is on the Atlantic coast of Patagonia (42:45 S, 65:01 W) and has experienced a sustained expansion of industrial (metallurgical, fishing) activities since 1973. Environmental monitoring has been performed for several years at one of the aluminum plants in the area. As part of the monitoring program, the quality of the ambient air at the industrial sector has been continuously sampled to evaluate the potential local exposures through inhalation to various emissions.

Air particulate polynuclear aromatic hydrocarbons (PAHs) have been selected as some of the targets for these studies because, apart from usual sources in the urban environment (vehicle emissions, domestic heating, etc.), there is a single major emitting source of these compounds at the anode baking facility in the area, and the question was to evaluate the partial contribution of this source to the overall exposure in the nearby environment.

It is usually considered that the level of PAHs concentration in air particulate is an important indicator of the level of pollution by the combustion of hydrocarbons, coal, traffic emissions, etc. Due to improvements in pollution control devices in all these areas, the concentrations of PAHs have diminished from typical values of BaP (benzo(a)pyrene) such as 46 ng/m3 during 1949/51 to 4 ng/m3 in 1972/73 in London (Lauther & Waller 1978) or 50-95 ng/m3 in 1970 to 3-6 ng/m3 in Duisberg and Duesseldorf (Tomingas 1980). In most cities, the mean annual level 10 ng/m3 is apparently not exceeded (Funke et al. 1982; Tomingas 1980; Flessel et al. 1991). The BaP concentration in rural or high mountain places usually considered as "clean" has been quoted to be 0.4 ng/m3 in Schaunisland, Black Forest, Germany (Borneff and Borneff 1982) and less than 0.03 ng/m3 in a highland station in Bolivia (Cautreels & Cauwenberghe 1978).

Some PAHs have been shown to be carcinogenic. BaP is a potent carcinogen and the mechanism of its action involving monooxigenases has been described in detail (Bentley & Oesch 1977). BkF (benzo(k)fluoranthene) has been indicated as of medium

Table 1. Annual average wind direction and velocities, stabilities and persistences used to run the INPUFF model.

Winds from	Annual persistence (hr)	Average intensity (m/sec)	Pasquill stability class	Fraction annual persistence
N	754	3.98	C	0.086
N.E.	543	4.14	C	0.062
E	198	3.57	C	0.022
S.E.	407	4.57	C	0.046
S	833	5.80	D	0.095
S.W.	2367	5.93	D	0.270
W	1574	5.27	D	0.180
N.W.	1189	5.76	D	0.135
Calm	895	<0.70	B	0.102

strength and others, like BgP (benzo(ghi)perylene), have not been found to be carcinogenic (Borneff and Borneff 1982). Because PAHs consist of a large number of compounds, it has been usual to only select some of them for monitoring or environmental assessment practices. The analyses of the so called PAH profiles sometimes allow the identification of the emitting source (Smith 1984), but most usually, they result from the relative ambient stability of the different PAHs, since they are known to be degraded by sunlight and oxygen action. Valerio et al. (1987) have reported that the half lives of BaP and BkF under simulated sunlight conditions are 5.3 and 14.1 hours, respectively.

In this study, the air particulate and gaseous concentrations of BaP, BkF and BgP sampled during 1988-1991 at a monitoring station in the industrial park of Puerto Madryn are shown in comparison with several other sets of similar data in the literature during the last decade. Some of the analysis have been performed with a newly developed technique of differential spectroscopy (Ares 1992). The results have been projected to the surrounding area by means of a diffusion model which uses emission data and meteorological conditions also measured at the site. The results here presented refer to BaP, BkF and BgP, a set which has been selected to encompass a range of biological activity and environmental persistences.

MATERIALS AND METHODS

Air samples were taken during 1988-1991 with a high volume (HV) sampler (Sierra Instruments, CA. US, model 305-2000) at constant flows between 90-110 m3/hr (flow controller model 350, calibration with TEFLON flowmeter and M330 variable orifice board). After each calibration, air particles were collected on cellulose filters (Sierra C3056F) during intervals of 90-220 hr depending on the particulate load. The final sampled volume was calculated by integration of daily values read on the flowmeter,

Table 2. Comparison of PAH particulate concentrations (μg/g) in several reported cases and this study. The data of Funke (1982) were recalculated from figures.

PAH	SRM1649 Certified Value	Takada (1991)	Funke et al. (1982)	Puerto Madryn	
				Total	Inhalable
BaP	2.9±0.5	0.1±0.06	0.03	0.006±0.005	0.009±0.003
BkF	2.0±0.1	0.2±0.14	0.14	0.005±0.003	0.038±0.023
BgP	4.5±1.1	0.1±0.06	0.20	0.030±0.020	0.007±0.004

and the daily flows were computed as the average of the initial and final flow during that period. The results here presented correspond to a total sampling time of 3300 hr. Inhalable particles were collected on a duplicate HV sampler with a series 320 size selective inlet (50% collection efficiency at 15 ± 2 μ size at a wind speed of 2-24 km/hr). Gaseous components were collected at a similar HV sampler where the single cellulose filter was replaced by a 5 mm layer of activated charcoal between two filters. The stack stream which is assumed to be the major PAH emitting source near the sampling station was isokinetically sampled at regular intervals during 15 days with a FLAKT equipment. The stream was drawn directly onto a submicronic glass fiber filter (MILLIPORE RAWP 293 25) and the passing flow was bubbled through a set of impingers with cyclohexane refrigerated to maintain it just above its freezing temperature. The PAHs in the particulate samples, activated charcoal, stack particulate and impingers were analyzed by means of UV-differential spectrometry (Ares 1992) after micro-Sohxlet extraction with cyclohexane (SINTORGAN, chromat. grade). Additionally, stack particulate was analyzed with HPLC (HP1050 pump, HP UV-VIS 8245 detector at 254,278,300 and 364 nm). The elution was on a HP DDS Hypersil (5μ , 200x4.6 mm) column with Methanol-Water (2 min:40%M-60%W; 15 min gradient up to 100%W; 5 min 100%W) at a flow rate of 2 ml/min. The sample was diluted in 10 μL of cyclohexane for injection.

Modeling of stack stream diffusion in the area was achieved with INPUFF (UNAMAP) model (Petersen & Lavdas 1986) which simulates the pollutant concentration field generated by a stationary source treating the emission as a set of successive Gaussian-puffs which are dispersed according to a Pasquill-Gifford algorithm, assuming a non-degradable pollutant. The wind field data for the simulation were gathered during 1985-7 with an anemograph (SIAP) and average local values of stability classes were from Mazzeo et al.(1974). The model was calculated for a set of receptors located a 0.5 km intervals along 2 axes centered at the source and up to 3.0 km away from it at heights taken from local topographic surveys. The simulations were performed for intervals long enough (6 hr) to attain steady state concentration fields at average meteorological conditions

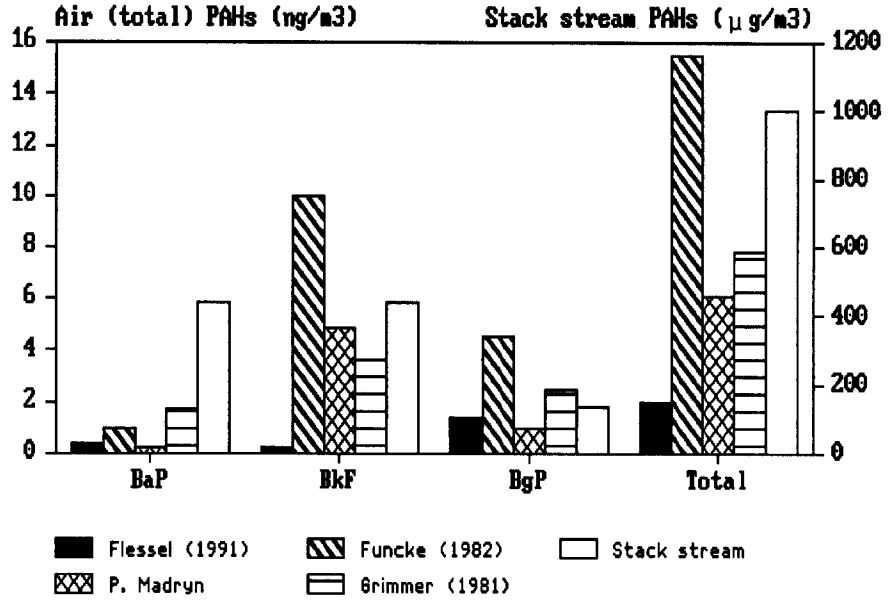

Figure 1. Comparative concentrations of PAHs in several recent studies and at Puerto Madryn.

described in Table 1. Finally, the average expected annual concentration at each receptor point was computed as a weighed sum of exposures under all conditions in Table 1.

RESULTS AND DISCUSSION

Table 2 shows a comparison of PAH concentrations in total air particulates recently reported in the literature and those obtained in this study. SRM1649 (NBS 1978) is a reference material collected at Washington DC for which PAH certified values have been formulated. The confidence limits given for results with this material correspond to the different analytical techniques used for certification and not to ambient variability. Takada (1991) data are from street urban dust at Tokyo, which has been collected with a vacuum cleaner, and might over-represent coarse particulate. Funke et al. (1982) collected with HV samplers and their results are most probably comparable to our Total Particulate figures, but the German study included 3 heavily polluted cities in the Ruhr area in 1979-1980. Furthermore, the Puerto Madryn site is arid (mean annual precipitation of 169 mm), and soil erosion dust is and important contributor to the air particulate load, which undoubtedly dilutes the PAH concentration expressed on a mass of particulate basis. Concentrations of gaseous PAHs in the air at Puerto Madryn were found to be negligible (0.1-1 % of total in

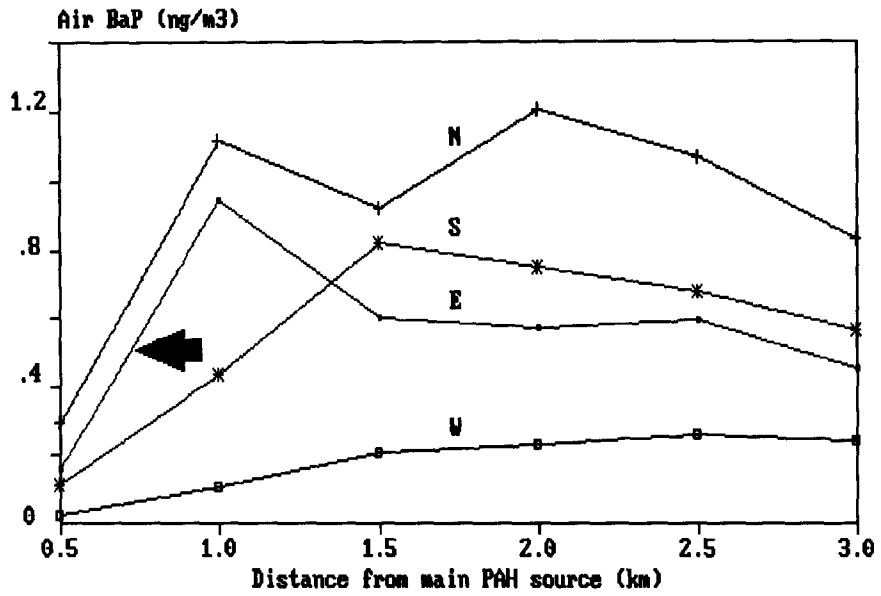

Figure 2. Profiles of air BaP concentration in the vicinity of the monitoring station (at point of arrow tip) used for this study.

particulate form).

Figure 1 shows the air PAH concentrations in this and other reported studies, and those in the stack stream at Puerto Madryn. It is observed that the values at this site are in the range of those observed at San Francisco (Flessel et al. 1991) and lower than those of Grimmer & Ixfield (1981) and Funcke et al. (1982) which correspond to sites with well developed industrial activities a decade ago. The relative proportion of BaP in immission values is lower than at the stack stream, probably reflecting a faster decay of this PAH with respect to BkF and BgP, as expectable from reported decay rates.

Figure 2 shows the profiles of computed BaP annual average concentrations for receptor sites around the source stack sampled in this study. The concentrations are lower in the immediate vicinity of the stack and increase up to a maximum which is located at varying distance depending on the local topography. It is observed that the average BaP concentrations predicted by the INPUFF model for the location of the monitoring station is very similar to that actually measured at that point (0.36 ng/m3, SD: 0.28, see Figure 1). A local average of 0.55 ng/m3 BaP can be calculated from all shown local values. The declining trends at 3 km in all directions, indicate that

average concentrations produced by this source are expected to be lower at increasing distances beyond this point. Also, the model estimates are conservative, since no decay term was included in the calculations.

It has been proposed that the best criterion to evaluate exposures to substances like PAHs is to assume a linear continuous dose-response function or higher at low exposures (EPA 1986). Moreover, it has practical interest to perform estimates of the level of additional risk which might be expected from ambient exposures to BaP. On the basis of animal carcinogenicity data, an ADI ("Acceptable Daily Intake") for BaP has been computed (Santodonato et al. 1979) as the quantity which would be associated with a 1/1000000 level of increased risk for a 70 kg adult to develop cancer. This amounts to 47 ng/day through dietary intake or 48 ng/day intratracheal. For an individual inhaling about 15 m3/day of air in the area characterized by the values shown in Figure 2, the daily intake would total 7.5 ng/day, which in turn corresponds to 0.17/1000000 increased risk. Whether this is "acceptable" or not depends on a number of factors among which the comparison with what has been feasible to attain in a number of other communities may play a role. A comparison of this type can be drawn from the application of the orientation value 10 ng/m3 BaP which on the basis of environmental preventive action has been suggested by the German Federal Agency for the Environment (Borneff and Borneff 1982), and which has apparently been attained in recent years in most communities of industrialized countries. The corresponding increased risk estimate for 10 ng/m3 is 3.1/1000000. These figures should not be interpreted as representing the total increased risk potential of air particulate (Flessel et al. 1991) nor is BaP concentration necessarily a good correlate of it (Tomingas and Pott 1978).

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