

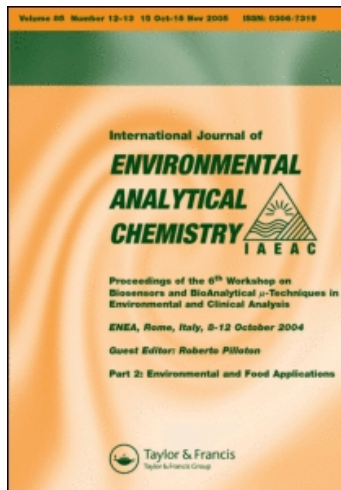
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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Chiavarini, S. , Galletti, M. , Michetti, I. , Perini, A. and Testa, L.(1994) 'Environmental Monitoring at Terra Nova Bay Station From 1989 to 1991', International Journal of Environmental Analytical Chemistry, 55: 1, 331 — 340

To link to this Article: DOI: 10.1080/03067319408026230

URL: <http://dx.doi.org/10.1080/03067319408026230>

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ENVIRONMENTAL MONITORING AT TERRA NOVA BAY STATION FROM 1989 TO 1991

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(Received, 4 July 1993; in final form, 11 November 1993)

Monitoring was carried on in the Italian Antarctic Station Terra Nova Bay. Airborne particulate matter was sampled at different Base locations during the Italian expeditions; samples were then analyzed at the ENEA laboratories for chemical characterization. The analyses were carried out by INAA (Instrumental Neutron Activation Analysis) for the determination of major, minor and trace elements (Na, K, Cs, Sc, V, Mn, Fe, Co, Zn, La) and by gas chromatography-mass spectrometry for the determination of PAH compounds. Data from the 1989-1990 and 1990-1991 campaigns are reported and discussed. Moreover, isokinetic samplings were carried out at the Base incinerator; the filters were analyzed by INAA; the V, Cr, Cu, Zn, Cd, Sb concentrations are reported.

KEY WORDS: Antarctica, pollution, airborne, PAH, INAA, gas-chromatography.

INTRODUCTION

Recently, scientists have become more and more conscious of the importance of Antarctica, not only for its unique aspects as a research laboratory, but also for its importance in tracking planetary scale phenomena. The increased human activities on this continent, particularly in some areas, and the recent growth of tourism in the last years has made the Antarctic operators aware of the need to strengthen the existing environmental protection measures. An Antarctic Treaty Special Consultative Meeting was first convened in November 1990 in Viña del Mar, then again, in Madrid to establish the Protocol on Environmental Protection to the Antarctic Treaty. Environmental monitoring is one of the most delicate and debated topics of the Protocol that is currently under examination.

To fulfill the requirements of the Antarctic Treaty System, and to be consistent with Italian policy on the matter, the monitoring of human activities at the Italian Base, started during the 1986-1987 campaign¹, was continued during the 1989-1990 and 1990-1991 expeditions. The collected samples were analyzed at the ENEA Casaccia laboratories for the determination of multi-elemental composition and of organic micropollutants (PAH).

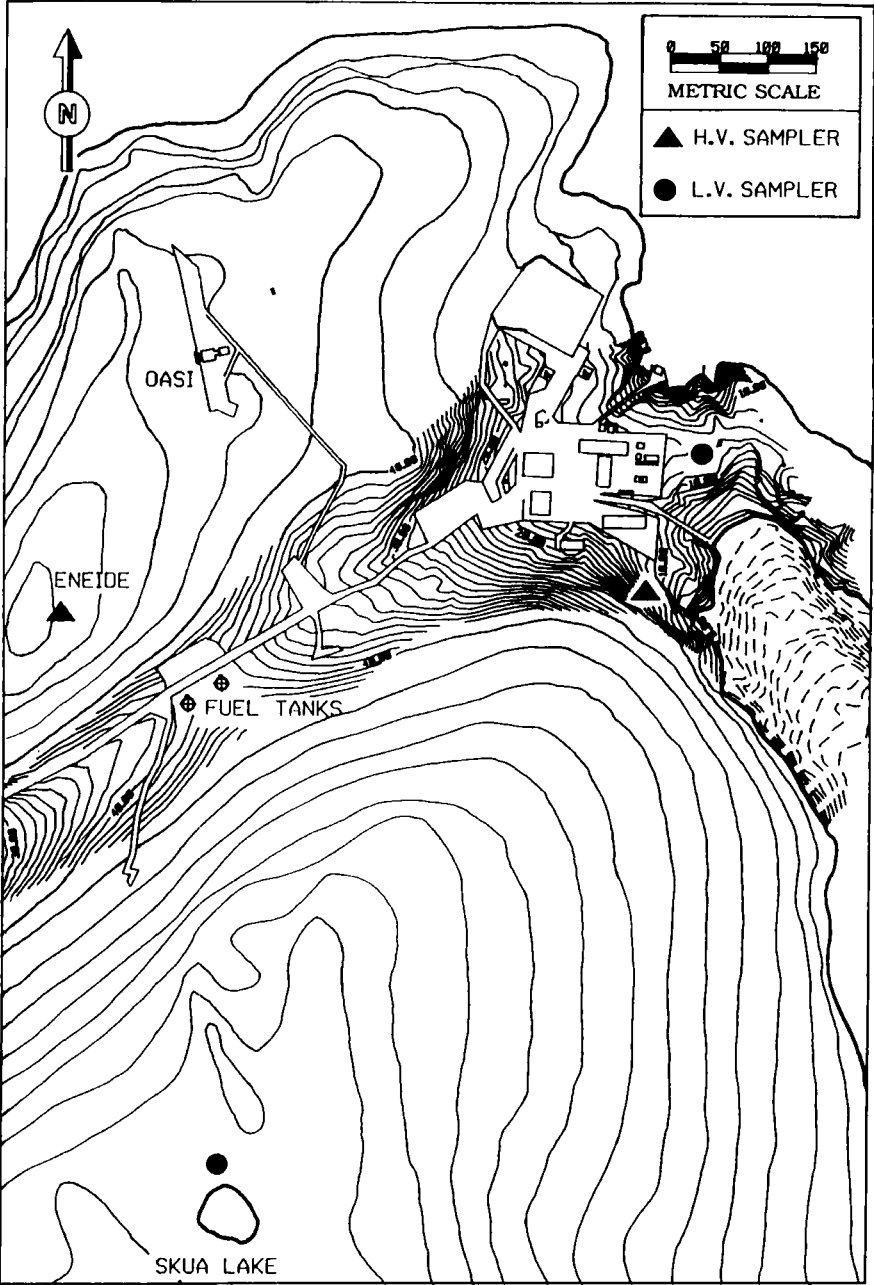


Figure 1 Sampling sites during the 1989-1990 expedition.

The experimental part of the project is described herein, and the results are compared with those obtained in the previous expeditions.

EXPERIMENTAL

During the 1989–1990 Expedition, two Andersen High Volume samplers (H.V.) and two Low Volume samplers (L.V.) APM1 operated from January 2, 1990 to February 11, 1990; the different sampling locations are shown in Figure 1. In addition, on January 27, January 31 and February 8, isokinetic samplings were performed at the incinerator according to the following procedure. An average quantity of 300 l was pumped through fiber quartz filters. A total of 11 filters were collected.

During the 1990–1991 Expedition, 4 H.V. samplers were installed as shown in Figure 2, and operated from January 2, 1991 to February 6, 1991. As can be noted the H.V. samplers were located at the four cardinal points around the main building. As in previous expeditions¹ logistic needs and the area morphology were decisive factors in the selection of the installation sites. The L.V. sampler was set up at Skua lake.

The sampling parameters, in both the expeditions, were as follows:

	H.V. sampler	L.V. sampler
sampling period	3 day	6 day
air flux	1130 l/min	20 l/min
filter	fiber quartz	membrane (0.45 μ)

All filters were analyzed for major, minor and trace elements by INAA according to the previously described procedure¹.

Five of the samples from the 1989–1990 campaign were analyzed for Cu by ETA-AAS (Electrothermal Atomization-Atomic Absorption Spectrometry); a Perkin Elmer mod. 5100 ZL was used. Digestions were carried out in closed 120 ml PTFE vessels with 2 ml of suprapure concentrated HNO₃ according to the procedure outlined by Chakraborti². A microwave oven MDS-SID by CEM was used. 10 μ l of the solution were analyzed by ETA-AAS as follows:

wavelength	324.8 nm
pretreatment temperature	1000 °C
atomization temperature	2600 °C

The fiber quartz filters were also analyzed for PAH compounds by gas-chromatography-mass spectroscopy, the methodology is described by Caricchia³.

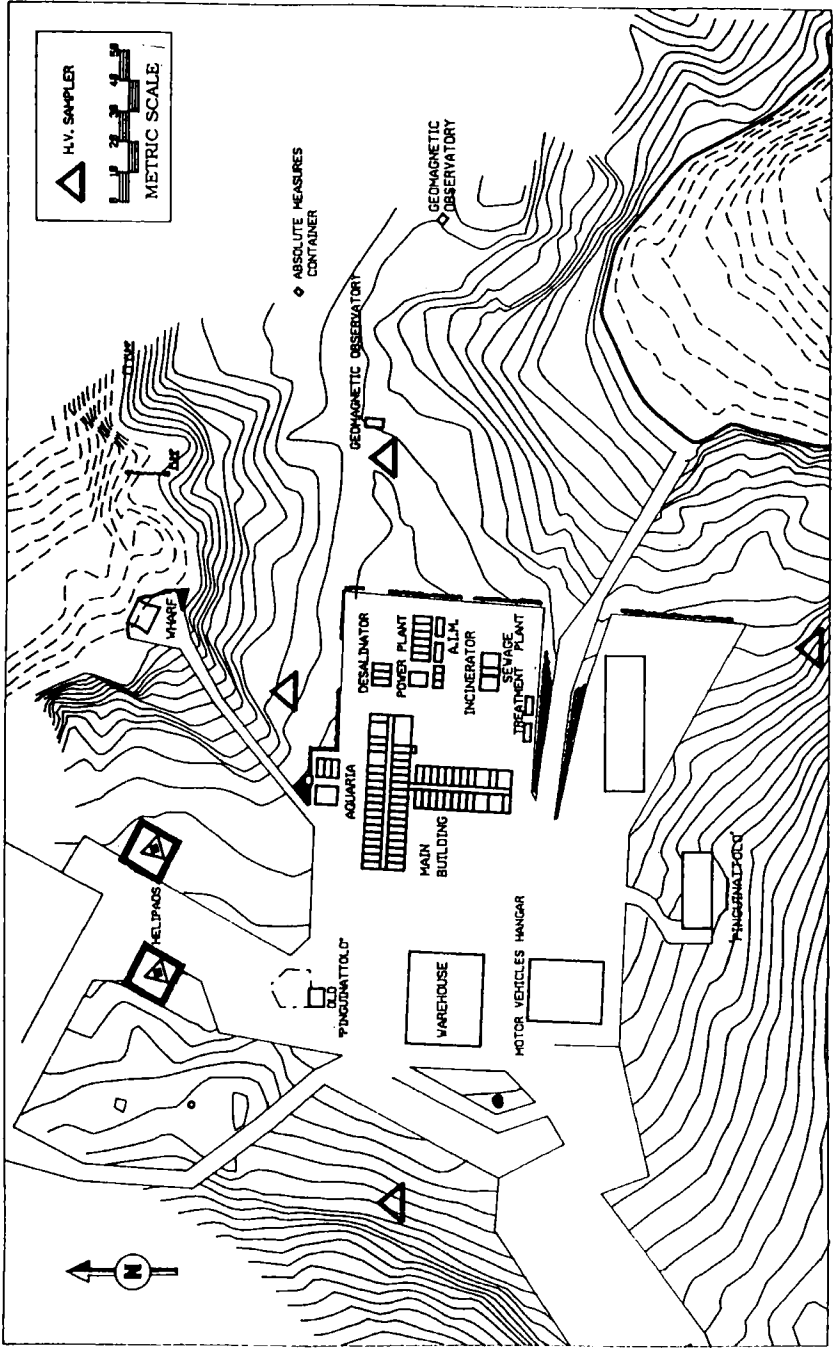


Figure 2 Sampling sites during the 1990–1991 expedition.

Table 1 Airborne particulate matter. Elemental composition measured at Terra Nova Bay Station; 1989–1990 Expedition.

Elements	Elements concentration					
	East Side Sampler			South Side Sampler		
	MIN.	MAX.	AVE.	MIN.	MAX.	AVE.
*Na	0.42±0.08	1.42±0.14	0.78±0.09	<0.50	0.53±0.08	<0.50
*K	0.36±0.05	1.06±0.27	0.71±0.16	0.20±0.10	0.49±0.20	0.33±0.11
Cs	<0.01	0.02±0.01	<0.01	<0.01	0.09±0.02	0.04±0.01
Sc	0.03±0.02	0.20±0.01	0.11±0.01	0.03±0.01	0.32±0.03	0.12±0.02
V	<1.0	3.9±0.8	2.4±0.8	1.8±0.4	7.1±0.7	4.1±0.5
Mn	<1.0	8.9±4.5	4.5±2.7	11.3±1.1	25.0±2.5	16.4±1.6
*Fe	<0.10	0.69±0.07	0.38±0.05	<0.10	1.08±0.05	0.39±0.04
Co	0.2±0.1	0.3±0.1	0.2±0.1	0.2±0.1	0.4±0.1	0.2±0.1
Cu	<20	<20	<20	22±8	147±21	84±16
Zn	9.3±1.0	12.5±1.3	10.8±1.4	19.5±2.0	38.4±4.0	27.5±2.8
La	0.2±0.1	0.7±0.1	0.4±0.1	<0.1	1.5±0.2	0.5±0.1

*Units in $\mu\text{g}/\text{m}^3$, others in ng/m^3 .

RESULTS AND DISCUSSION

Some of the elements measured are reported in Tables 1–5; the organic micropollutants (PAH) are reported in Table 8. The data refer to the 1989–1990 and 1990–1991 campaigns. During the 1989–1990 expedition, the L.V. sampler on the East side operated for a short period of time; only 3 samples were collected because the instrument subsequently broke down. The data from this station are too scanty, therefore the average is merely indicative.

The different composition of the filters used (membrane filter for the L.V. sampler and fiber quartz filter for the H.V. sampler) results in different detection limits for the elements that are macroconstituents for the relative filters. For this reason, Na, K and Al have higher detection limits for the fiber quartz filters than for membrane filters.

Table 2 Airborne particulate matter. Elemental composition measured at Terra Nova Bay Station surroundings; 1989–1990 Expedition.

Elements	Elements concentration					
	Skua Lake Sampler			Eneide Sampler		
	MIN.	MAX.	AVE.	MIN.	MAX.	AVE.
*Na	0.21±0.04	0.95±0.09	0.45±0.07	<0.50	<0.50	<0.50
*K	0.11±0.03	0.33±0.13	0.19±0.08	<0.30	0.59±0.18	<0.30
Cs	<0.01	<0.01	<0.01	<0.01	0.03±0.01	0.03±0.01
Sc	0.02±0.01	0.07±0.03	0.03±0.01	<0.01	0.04±0.01	0.04±0.01
V	<1.0	2.6±0.5	1.4±0.4	<1.0	11.4±2.0	4.7±0.5
Mn	<1.0	2.8±1.0	1.3±0.8	5.2±2.7	18.5±1.9	12.0±2.0
*Fe	<0.10	0.17±0.03	0.09±0.02	<0.10	0.20±0.04	0.11±0.03
Co	<0.1	0.20±0.10	0.12±0.05	<0.10	0.40±0.10	0.20±0.10
Cu	<20	<20	<20	<20	90±18	—
Zn	2.7±0.6	9.9±1.0	6.3±0.8	7.5±1.3	27.0±2.7	18.7±2.5
La	0.2±0.1	0.3±0.1	0.2±0.1	<0.1	0.2±0.1	<0.1

*Units in $\mu\text{g}/\text{m}^3$, others in ng/m^3 .

Table 3 Airborne particulate matter. Elemental composition measured at Terra Nova Bay Station surroundings; 1990–1991 Expedition.

<i>Elements concentration Skua Lake Sampler</i>			
Elements	MIN.	MAX.	AVE.
*Na	0.26±0.04	0.73±0.07	0.42±0.06
*K	<0.20	0.24±0.05	<0.20
Cs	<0.010	0.060±0.005	0.010±0.005
Sc	0.010±0.00	0.070±0.004	0.010±0.003
V	<1.0	3.3±0.7	<1.0
Mn	<1.0	36±7	<1.0
*Fe	0.04±0.02	0.25±0.01	0.07±0.01
Co	<0.05	0.20±0.05	0.11±0.05
Zn	1.3±0.4	1474±74	67±7
La	0.10±0.05	0.30±0.05	0.10±0.05

*Units in $\mu\text{g}/\text{m}^3$, others in ng/m^3 .**Table 4** Airborne particulate matter. Elemental composition measured at Terra Nova Bay Station; 1990–1991 Expedition.

<i>Elements concentration</i>						
<i>Elements</i>	<i>West Side Sampler</i>			<i>East Side Sampler</i>		
	MIN.	MAX.	AVE.	MIN.	MAX.	AVE.
*Na	<0.50	<0.50	<0.50	<0.50	0.69±0.10	<0.50
*K	<0.20	<0.20	<0.20	<0.20	0.41±0.12	<0.20
Cs	<0.010	0.030±0.005	<0.010	<0.010	0.030±0.005	<0.010
Sc	<0.01	0.10±0.01	0.03±0.01	<0.01	0.10±0.01	0.02±0.01
V	<1.0	3.1±0.6	2.4±2.0	<1.0	3.6±0.5	1.4±0.6
Mn	<1.0	19±2	13±3	<1.0	15±4	<1.0
*Fe	0.04±0.01	0.30±0.01	0.14±0.01	<0.02	0.19±0.04	0.06±0.01
Co	<0.05	0.20±0.05	0.08±0.02	<0.05	0.10±0.02	<0.05
Zn	<1.0	<1.0	<1.0	<1.0	15.2±1.5	<1.0
La	<0.10	0.20±0.05	<0.10	<0.10	<0.10	<0.10

*Units in $\mu\text{g}/\text{m}^3$, others in ng/m^3 .**Table 5** Airborne particulate matter. Elemental composition measured at Terra Nova Bay Station; 1990–1991 Expedition.

<i>Elements concentration (ng/m^3)</i>						
<i>Elements</i>	<i>South Side Sampler</i>			<i>North Side Sampler</i>		
	MIN.	MAX.	AVE.	MIN.	MAX.	AVE.
*Na	<0.50	0.79±0.12	<0.50	<0.50	<0.50	<0.50
*K	<0.20	0.24±0.05	<0.20	<0.20	<0.20	<0.20
Cs	<0.010	0.020±0.005	<0.010	<0.010	0.040±0.005	<0.010
Sc	<0.010	0.050±0.005	<0.010	<0.010	0.100±0.010	0.040±0.006
V<1.0	3.3±0.6	1.2±0.6	<1.0	4.2±0.6	2.2±0.6	
Mn	<1.0	14±3	<1.0	<1.0	20±5	12±3
*Fe	<0.02	0.18±0.02	0.05±0.01	<0.02	0.36±0.02	0.14±0.01
Co	<0.05	0.07±0.03	<0.05	<0.05	0.10±0.05	0.07±0.02
Zn	<1.0	8.7±0.9	<1.0	<1.0	8.6±1.7	<1.0
La	<0.10	<0.10	<0.10	<0.10	0.30±0.05	0.10±0.05

*Units in $\mu\text{g}/\text{m}^3$, others in ng/m^3 .

For each element the minimum, maximum and average values have been reported, so that an idea of the range of variability during the entire period of human presence can be given.

The uncertainties of the measurements have been calculated on the basis of the detection limit of the method for each element, and on the sampling conditions.

From the data obtained, the following considerations can be drawn.

The Na values at Skua Lake reported during the 1989–1990 Expedition were confirmed by those found during the subsequent campaign (about $400 \pm 50 \text{ ng/m}^3$). They are higher than the concentrations measured at the same site during the previous years ($230 \pm 35 \text{ ng/m}^3$). The same trend has been observed at the Base. The values measured in 1987–1988 and 1988–1989 were $438 \pm 45 \text{ ng/m}^3$ and $127 \pm 30 \text{ ng/m}^3$, respectively. No variation was found for elements such as La, Fe and Co in either period under study. Mn shows its highest value ($4.5 \pm 2.7 \text{ ng/m}^3$) in 1989–1990.

In 1989–1990, the V concentration also increased. The highest average value was found at Eneide: $4.7 \pm 0.5 \text{ ng/m}^3$; during that particular season there was ongoing building activity in the Eneide vicinity. Nevertheless, these values are lower than those measured in industrialized areas, and are comparable to those measured in other remote areas, such as Plateau Rosa and Pantelleria⁴. During the 1990–1991 Expedition lower levels ranging from $<1.0 \text{ ng/m}^3$ up to $2.4 \pm 2.0 \text{ ng/m}^3$ were determined. It should be pointed out that the Skua Lake sampler was powered by the electric generators at the Base.

During the 1990–1991 campaign, Zn generally was detected in very low concentrations, except at the Skua Lake site where many high values were determined; this resulted in a high average value $67 \pm 7 \text{ ng/m}^3$.

Unusually high anomalous values were found for Cu. In Table 2, which refers to the Eneide sampler, the Cu average value has not been calculated because the data for this site are variable and scanty.

To better compare different methodologies, five of the samples collected during the 1989–1990 Expedition were analyzed both by INAA and by ETA-AAS; the results are shown in Table 6. The data reported are consistent and suggest the need for further investigation to explain the Cu trend. The Cu concentrations measured during the 1990–1991 campaign have not been reported because most of them fall in a range lower than the detection limit of the method used ($<20 \text{ ng/m}^3$).

Table 6 Cu concentrations (ng/m^3) measured by INAA and by ETA-AAS; 1989–1990 Expedition.

Sample	INAA	ETA-AAS
1	<20	17 ± 1
2	<20	4.0 ± 0.1
3*	0.14 ± 0.01	0.13 ± 0.01
4*	<0.020	0.013 ± 0.001
5	<20	10 ± 1

*number 3 and number 4 are isokinetic samplings at the incinerator; the concentration unit is mg/m^3 .

Table 7 Data from the isokinetic sampling at the incinerator.

Date	V	Elements concentration (mg/m ³)				
		Cr	Cu	Zn	Cd	Sb
27/1/90	<0.001	0.008±0.001	0.067±0.010	1.60±0.11	0.003±0.001	0.030±0.003
31/1/90	<0.001	0.010±0.001	0.039±0.011	0.48±0.01	0.006±0.002	0.067±0.006
8/2/90	<0.001	0.012±0.002	0.097±0.014	0.89±0.10	0.002±0.001	0.016±0.002

Table 7 shows the most representative elements present in the incinerator emissions. The concentration values are the averages of the daily measurements. It should be pointed out that the average waste composition is the following:

paper	50%
organic wastes (kitchen)	30%
wood (not chemically treated)	20%

The V data have been reported to show the incinerator load on the environment.

Table 8 reports all of the data obtained for PAH's; the concentrations measured for each compound are low and comparable to the lowest levels documented in remote sites. The electric generators seem to be the major source of PAH's; in fact, during this sampling period the incinerator was used only once. The incinerator is powered with diesel fuel; the consumption is 600 l/day; the post-burning gas temperature is 1100°C; the gas temperature at the chimney is 120°C; gases are washed by means of a recycling water system; the chimney is about 3 m high and the inner diameter is about 20 cm. Compounds such as benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene are only detectable in samples collected while the incinerator was operating. A preliminary look at wind direction and intensity in that period leads to the conclusion that the sea is the ecosystem most affected by PAH pollution. Nevertheless, the data available at present are scanty and need corroboration through further samplings and investigations.

CONCLUSIONS

From the data collected since 1986–1987 it can be concluded that the human presence in Antarctica has only slightly altered the environment. The changes are temporary and depend on the types of activities carried out at the Base. The trend of some element concentrations traced over the years seems to support these considerations.

The concentrations of elements such as V, Fe and Mn measured at the different sampling sites show high values during one campaign that may decrease during the following campaign.

It should be pointed out that toxic and noxious elements such as As, Sb, Cd have never been detected; the concentrations of these elements have always been under the detection limit of the methods used.

Table 8 Concentration (pg/m³) of PAHs in the atmospheric particulate matter; 1990–1991 Expedition.

(*** data not available)

A = phenanthrene

B = anthracene

C = fluoranthene

D = pyrene

E = benzo(a)anthracene

F = crysene

G = benzo(bjk)fluoranthenes

H = benzo(a)pyrene

I = indenopyrene

L = dibenzo(ah)anthracene

M = benzo(ghi)perylene

Period from to	Station	A	B	C	D	E	F	G	H	I	L	M	Total PAH
2/1 4/	North	29.3	3.5	16.7	24.7	4.9	11.1	17.1	16.4	31.9	n.d.	40.8	196.4
	South	45.9	2.7	19.9	23.9	3.7	8.0	16.5	15.5	29.3	n.d.	35.5	200.9
	East	51.5	4.5	24.6	23.3	1.9	5.0	7.9	5.2	14.8	n.d.	19.5	158.2
	West***												
5/1 7/	North	53.7	3.5	28.8	24.8	18.4	33.9	86.4	24.9	84.9	n.d.	96.3	455.6
	South	43.6	2.6	20.3	16.0	3.3	7.7	7.9	6.1	10.4	n.d.	11.9	129.8
	East	41.5	3.2	13.7	11.9	n.d.	4.4	1.9	n.d.	n.d.	n.d.	n.d.	76.6
	West***												
8/1 10/1	North	16.7	3.0	7.3	8.5	3.6	8.9	15.3	13.0	n.d.	n.d.	15.4	91.7
	South	8.7	2.0	6.0	7.0	5.6	7.8	28.4	6.5	45.1	n.d.	40.7	157.8
	East***												
	West***												
11/1 13/1	North	51.7	5.2	21.0	19.6	2.9	13.6	14.0	11.0	n.d.	n.d.	10.0	149.0
	South	32.8	2.9	14.0	14.5	4.3	14.7	15.8	1.9	n.d.	n.d.	5.5	106.4
	East	18.6	2.6	11.0	10.5	1.8	9.8	8.3	6.2	n.d.	n.d.	n.d.	68.8
	West	46.0	7.1	15.3	12.2	2.3	6.4	11.6	6.7	n.d.	n.d.	6.5	114.1
14/1 16/1	North	41.2	4.6	16.9	12.7	n.d.	4.4	2.0	n.d.	n.d.	n.d.	n.d.	81.8
	South	21.2	3.2	15.3	14.5	9.8	17.6	n.d.	n.d.	n.d.	n.d.	n.d.	81.6
	East	53.3	6.1	31.8	22.5	n.d.	n.d.	53.2	n.d.	n.d.	n.d.	n.d.	166.9
	West	48.4	5.1	18.5	16.4	n.d.	n.d.	5.5	n.d.	n.d.	n.d.	n.d.	93.9
17/1 19/1	North	54.5	6.7	26.6	19.3	13.2	26.0	64.5	54.6	n.d.	n.d.	54.9	320.3
	South	42.0	4.7	19.5	11.2	n.d.	21.4	38.5	19.9	26.1	n.d.	32.0	215.3
	East	35.7	4.1	15.7	9.8	n.d.	n.d.	4.7	n.d.	n.d.	n.d.	n.d.	70.0
	West	57.6	4.6	22.6	15.3	n.d.	n.d.	15.1	n.d.	n.d.	n.d.	n.d.	115.2
20/1 22/1	North	22.0	1.7	12.9	6.0	n.d.	9.0	10.8	n.d.	n.d.	n.d.	n.d.	62.4
	South	23.4	1.5	13.0	6.0	n.d.	10.5	n.d.	n.d.	n.d.	n.d.	n.d.	54.4
	East	37.2	3.3	21.4	16.0	n.d.	26.3	20.5	n.d.	n.d.	n.d.	n.d.	124.7
	West	34.6	n.d.	11.7	7.9	n.d.	n.d.	11.0	n.d.	n.d.	n.d.	n.d.	65.2
23/1 25/1	North	49.7	3.3	23.0	15.9	n.d.	20.0	13.8	n.d.	n.d.	n.d.	n.d.	125.7
	South	50.6	4.1	21.1	14.5	n.d.	n.d.	5.9	n.d.	n.d.	n.d.	n.d.	96.2
	East	41.4	6.1	35.6	28.3	40.3	71.6	139.7	44.0	66.1	n.d.	93.7	566.8
	West	30.1	3.1	17.4	12.5	n.d.	n.d.	6.3	n.d.	n.d.	n.d.	n.d.	69.4
26/1 28/1	North	27.9	2.0	19.0	11.6	n.d.	18.4	n.d.	n.d.	n.d.	n.d.	n.d.	78.9
	South	21.5	2.2	15.7	12.9	n.d.	n.d.	7.2	n.d.	n.d.	n.d.	n.d.	59.5
	East	31.4	4.5	30.1	36.2	31.2	96.5	112.0	30.3	n.d.	n.d.	33.2	405.4
	West	30.4	2.9	19.0	11.9	n.d.	n.d.	2.9	n.d.	n.d.	n.d.	n.d.	67.1
29/1 31/1	North	21.8	1.4	16.0	11.5	1.7	6.2	6.4	0.9	6.2	0.6	12.7	85.4
	South	17.0	n.d.	9.7	6.1	n.d.	n.d.	2.8	n.d.	n.d.	n.d.	n.d.	35.6
	East	46.5	4.5	50.9	42.8	57.7	92.3	169.0	34.5	82.7	7.6	100.2	688.7
	West	5.7	n.d.	5.5	4.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.4
1/2 3/	North	36.4	3.5	22.0	18.8	n.d.	26.6	16.3	n.d.	n.d.	n.d.	n.d.	123.6
	South	33.2	0.9	13.3	8.3	n.d.	n.d.	6.5	n.d.	n.d.	n.d.	n.d.	62.2
	East	35.0	2.7	15.8	14.3	n.d.	21.7	28.9	n.d.	n.d.	n.d.	n.d.	118.4
	West	33.2	2.3	11.8	7.5	n.d.	12.6	6.1	n.d.	n.d.	n.d.	n.d.	73.5
4/2 6/	North	33.1	3.4	20.4	13.3	n.d.	23.9	55.3	33.2	13.6	n.d.	n.d.	196.2
	South	26.6	2.7	24.6	15.3	9.6	16.4	48.3	8.8	46.7	n.d.	133.3	332.3
	East***												
	West	23.8	1.5	13.4	9.6	n.d.	9.3	13.7	n.d.	n.d.	n.d.	43.5	114.8

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