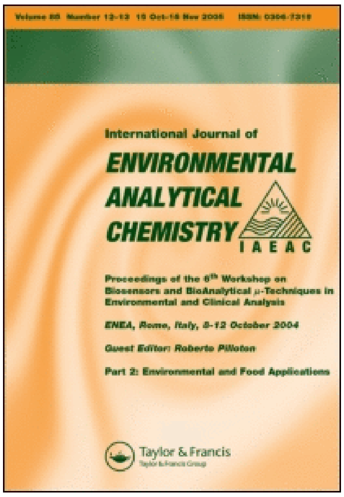

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AIRBORNE METALS IN URBAN AREAS*

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The concentration of nine metals (Tl, Pb, Mn, Fe, Cr, Zr, V, Ni, Cd) was measured by ICP in airborne particulate matter.

Two hundred samples were collected in 7 sampling sites selected according to specific emissions existing in the areas.

Results confirmed the usefulness of multi-element analyses to identify major sources of pollution.

The following associations were evidentiated. Steel plant: Fe, Mn, Cr; Urban incinerator: Cd, Mn; Traffic: Pb, Mn; Oil combustion: V, Ni; Cement plant: Tl.

The research has also given useful information about mean levels of exposure to toxic and cancerogenic metals in the quarters of Genoa.

KEY WORDS: Airborne particulate, metals, PAHs, source indicators, air quality monitoring, ICP, gas chromatography.

INTRODUCTION

In an urban area pollutants, such as SO2 and NOx, are emitted from many different kinds of sources; for this reason the analytical control of these compounds give little information about causes and sources of pollution events.

The knowledge of chemical composition of inorganic and organic constituents of airborne particulate, appears to be a useful method to identify sources of atmospheric pollution.

The concentration of some specific metals in the particulate matter may give information about possible anthropogenic sources.[1]

For example, lead is a typical component of emission from leaded gasoline motors, zirconium is relatively abundant in coal and chromium, iron and manganese characterise emissions from steel factories.[2] Also the relative abundance of peculiar elements may be related to specific sources. For example, the ratio vanadium:nickel changes according to the fuel used in combustion.

In fumes produced by combustion of light oil and coal the ratio V:Ni is about 1; this ratio is higher when heavy oil is used.

In a research carried out for air quality monitoring in the town of Genoa, we have used the following metals as emission indicators: thallium, chromium, lead, manganese, cadmium, iron, vanadium, zirconium and nickel.

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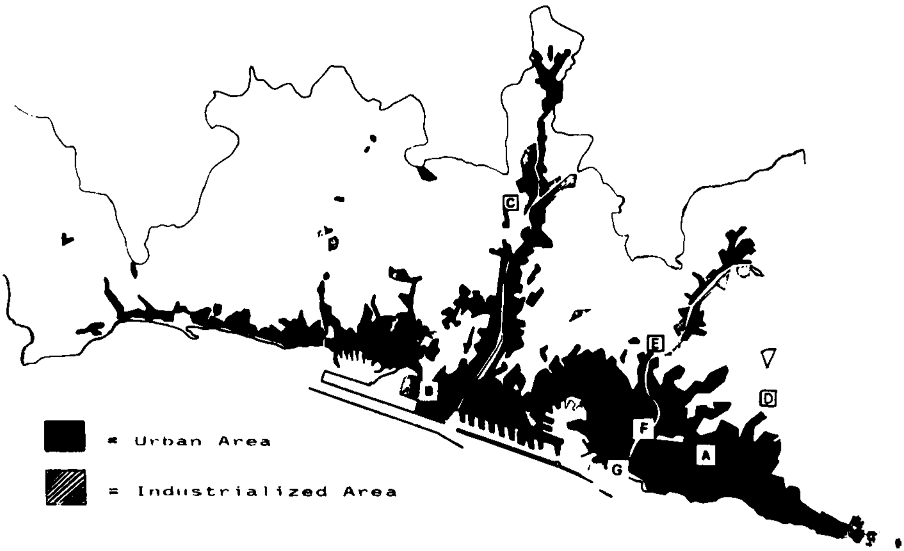


Figure 1 Map of the city of Genoa.

Metal concentration in 200 samples of particulate matter collected in seven sampling sites selected in urban, industrial and suburban areas (Figure 1) were measured and major sources of pollution were tentatively identified.

Further, according to the method suggested by Grimmer,[3] the ratio between the concentration of PAHs and benzo(e)pyrene (B(e)P) adsorbed on the particulate matter was used to confirm the indications of possible prevailing anthropogenic sources.

Cyclopenta(c,d)pyrene (Cyc) and benzo(ghi)perylene (B(ghi)P) are present in emissions from passenger cars in a higher concentration than B(e)P and PAH profiles obtained from the emissions of oil burners contain a larger amount of benzoanthracene and chrysene.

Furthermore the ratio of concentration of indeno(1,2,3-c,d)pyrene/B(ghi)P may also give useful information to identify the specific contribution of motor vehicle and domestic heating emissions (coal and oil).

According to the literature, the value of IND/B(ghi)P should be about 0.37 and 0.90 in PAH profiles obtained from automobile exhaust and domestic heating exhaust respectively.

METHODS

Samples of airborne particulate were collected using high volume samplers (metal work GHWL 2000).

About 2000 m^3 of air were filtered in 24 hours by glassfibre filter (Gelman type A/E 20 × 25 cm).

After sampling two disks of 10.4 cm^2 of surface were cut from each filter for the analysis of metals.

The particulate matter was treated with 65% HNO_3 for 5 hours at 165 °C. The residue was solubilized with 10% NHO_3 and analysed by Inductively Coupled Plasma (Spectrometer Jolin Yvon JY38—Plasma source JY3832) at the following condition:

- GAS: Plasma, 18 l/min Ar
  Carrier, 0.4 l/min Ar
  Coating, 0.4 l/min Ar
- Sample rate: 0.8 ml/min
  (trough perystaltic pump)
- Power: 2 kW
- Entrance slit: 50 u
- Exit slit: 50 u

The following metals were determinated: Tl, Pb, Mn, Fe, Cr, V, Zr, Ni, Cd.

On the rest of the filter 15 IPA were analysed. The particulate matter was solubilised with cyclohexane; the PAHs were separated by TLC and analysed by capillary gaschromatography.

The data obtained were statically elaborated by the use of geometric means and lognormal distributions.[4]

RESULTS

The following parameters were taken into account to identify anthropogenic sources of airborne pollutants.

1. Relative Abundance of Metals in Particulate Matter

The natural abundance of analysed elements in the earth's crust, expressed as ppm was used as comparison.

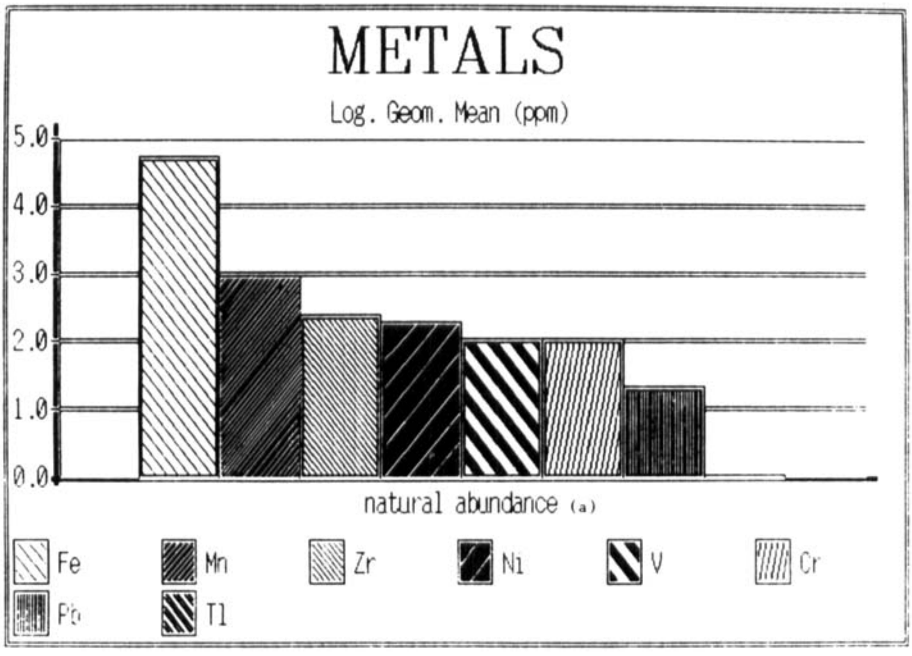
The values listed in decreasing order of occurrence are shown in Figure 2.

The geometric means of metals concentration (ppm) in airborne particulate found in studied areas were reported in the same way for comparison.

Figure 3 shows that in site D, which is on a hill in the town suburb, particularly the lead concentration was higher than expected according to its natural abundance.

In site B (Figure 4) the relative abundance of Mn and Cr reveals the presence of a big stainless-steel factory.

Site F (Figure 5) characterised by a high density of traffic, not surprisingly, is heavily polluted by lead.



(a) source: Merk Index 10th edition

Figure 2 Metals occurring in the earth's crust.

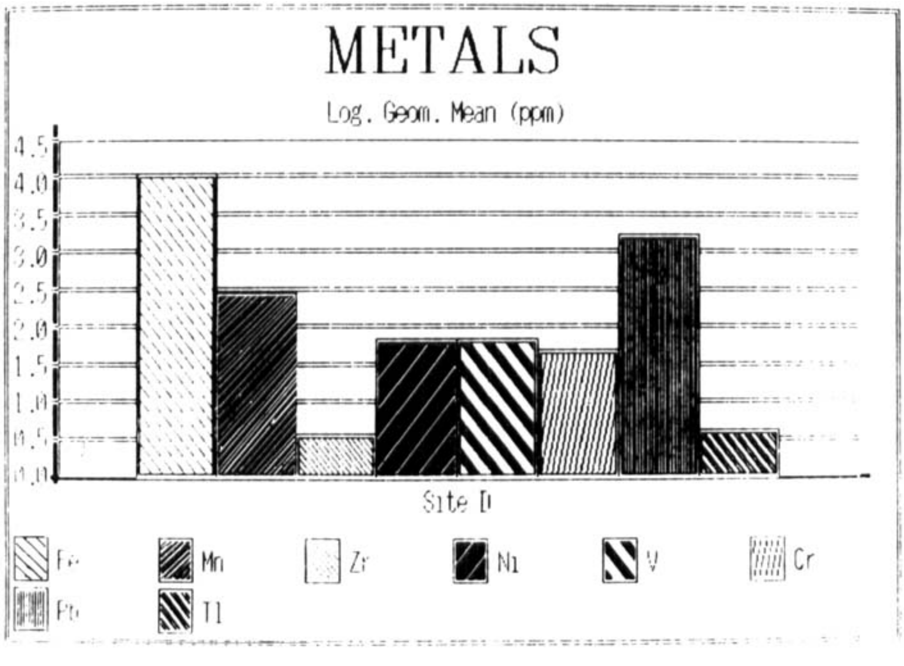


Figure 3 Relative abundance of metals in site D.

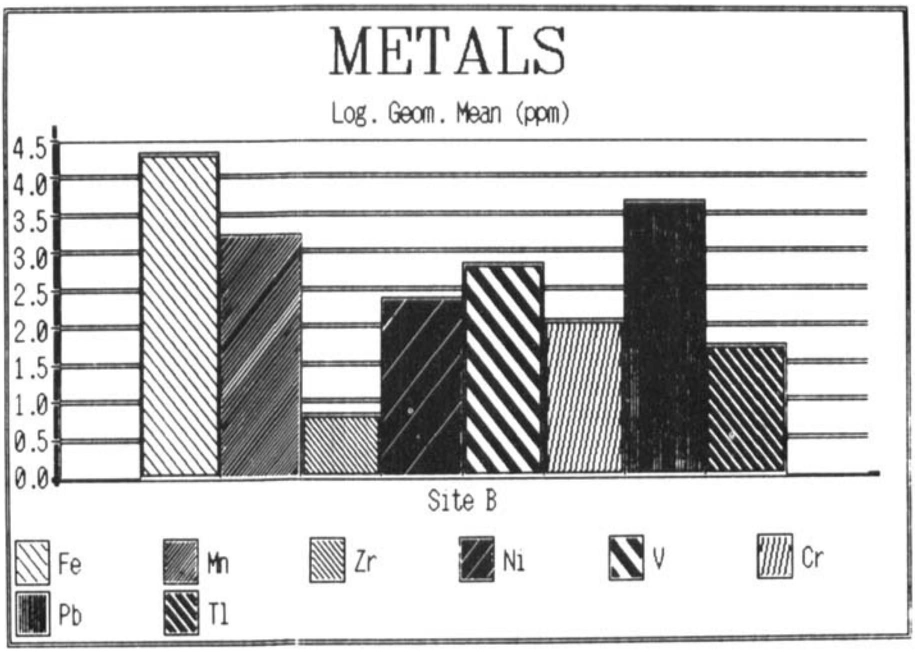


Figure 4 Relative abundance of metals in site B.

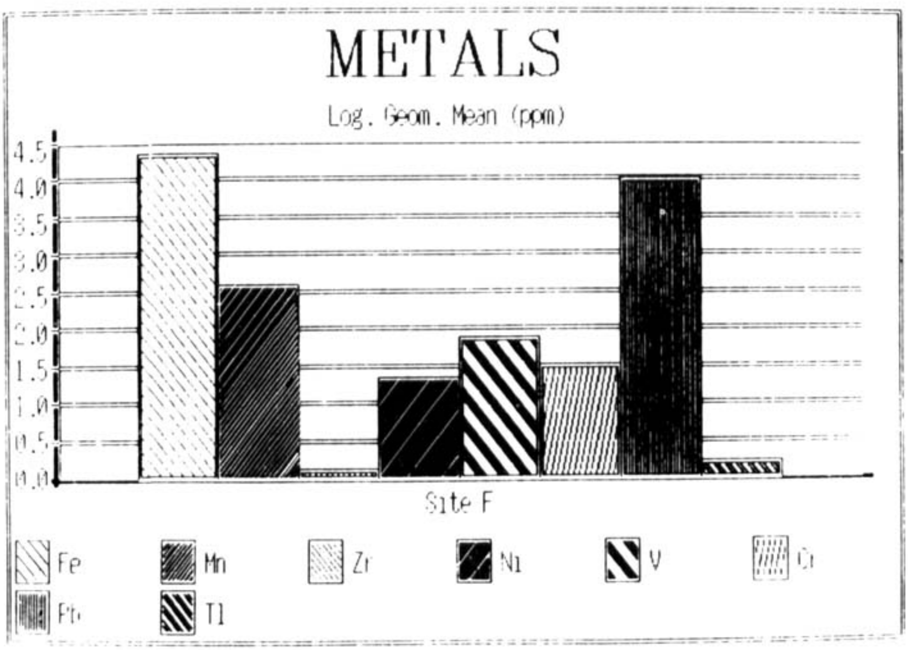


Figure 5 Relative abundance of metals in site F.

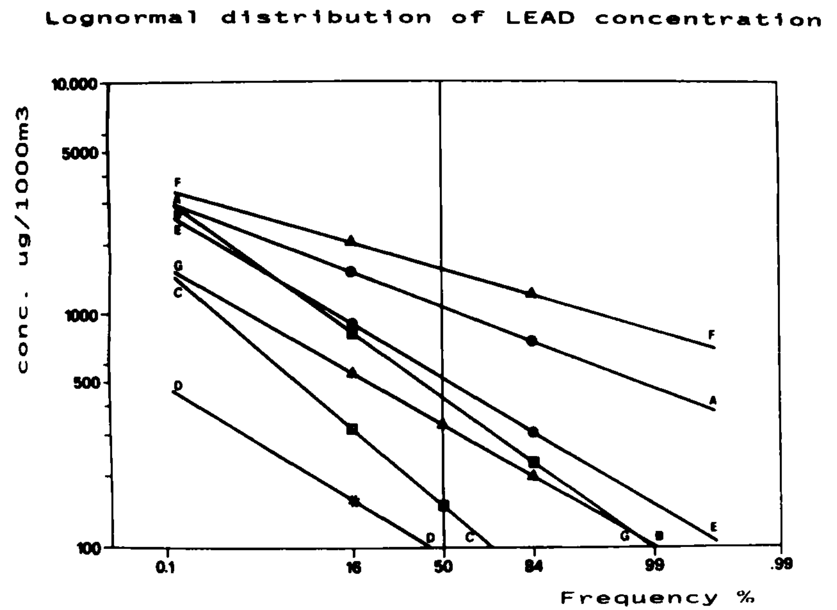


Figure 6 Cumulative frequency distribution of lead concentration.

2. Statistical Elaboration by the Cumulative Frequency Distribution

The cumulative frequency distribution, a statistical method for the elaboration of data, gives information about the presence of diffused or localized sources.

The numerical value of straight line slopes may be in fact a measure of the variability of data and may give information about the kind of source.

For example Figure 6 shows the lognormal distribution of lead concentrations in sampling sites.

In sites A and F the straight lines slope is small (A = −0.15, F = −0.11). For this it is reasonable to suppose that the primary anthropogenic source of pollution in these sites is a diffused source as automobile exhaust.

It is interesting to note that the value of two slopes are also comparable.

In site B the straight line appears to be steeper (−0.27); this suggests that in site B lead may be emitted also from a stationary source, therefore its concentration may depend on wind direction.

The use of this kind of statistical model was also useful to verify the cadmium as possible anthropogenic element emitted from urban incinerators.

In site E, in fact, high concentration of cadmium were found.

According to literature the presence of this element was correlated with a municipal incinerator operating in this area.[5]

Further research was carried out to verify this hypothesis.

Cadmium concentration was measured when the plant was closed for routine maintenance.

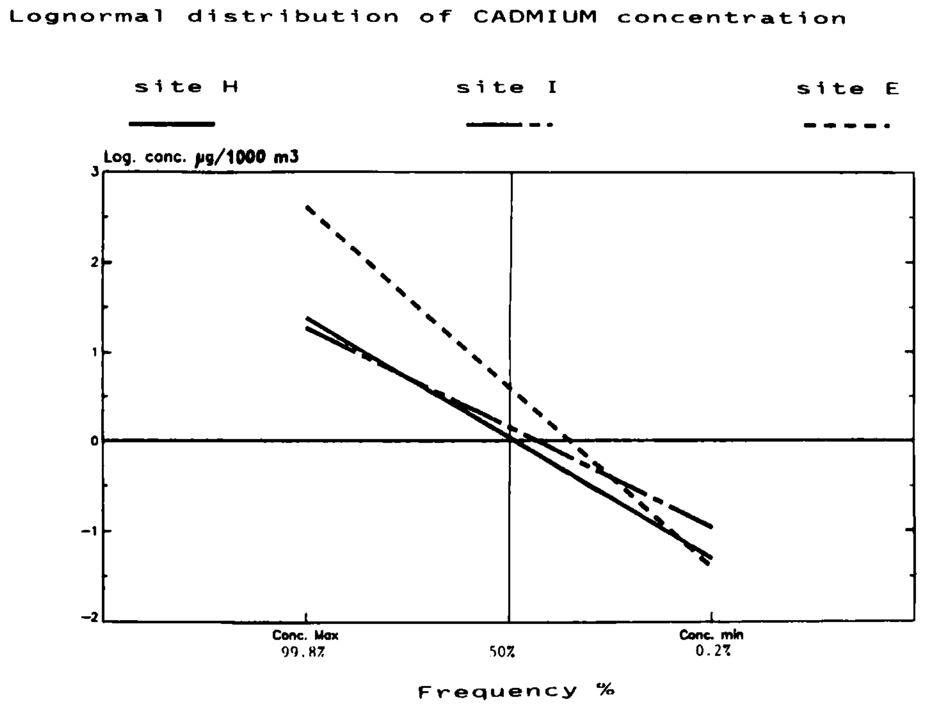


Figure 7 Cumulative frequency distribution of cadmium concentration with closed (site I and site H) and open (site E) incinerator.

Its cumulative frequency distributions calculated with open and closed municipal incinerator are shown in Figure 7.

The significant decrease of straight line slopes and a mean lower Cd concentration upon closing of the plant is in accordance with the hypothesis that the incinerator may be the main source for this metal.

3. Modification of Chemical Composition of Particulate Matter According to Prevailing Wind Direction

This kind of approach is useful to identify fixed sources and it is easily applicable to plan areas where anemological conditions are predictable.

Difficulties arise when orographical situations become complex as in our experience.

Otherwise it was possible to apply this method in the analyses obtained in site B, placed beside the sea.

Figure 8 shows the mean concentrations in site B of some metals according to the direction of prevailing wind during the sampling time.

It is interesting to note that daily concentration of Cr and Mn shows a good correlation ($p \leq 0.01$) and these metals are particularly abundant when south-west winds blow (Figure 9).

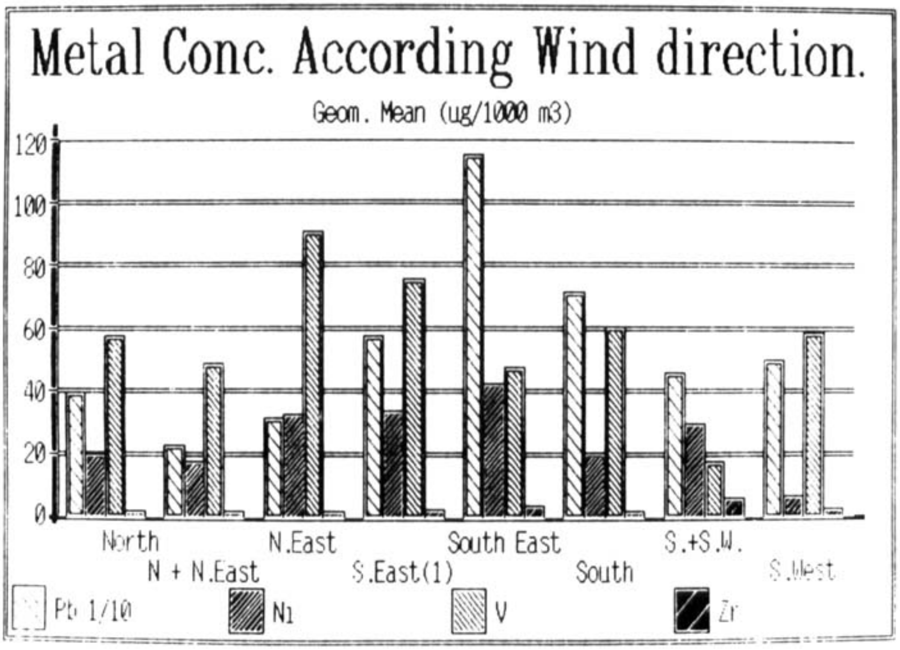


Figure 8 Geometric means of metal concentrations in site B according to wind direction.

This is in accordance with the location, in this direction, of a stainless steel factory.

On the contrary a higher concentration of lead and zirconium occurred with constant wind from south, south-east.

In this case also the PAHs analyses gave important information about the involved source: their concentrations were higher with dominant south-east winds.

In this direction the possible known sources are:

- a coke plant operating in the steel factory;
- a coal power plant in the dockyard.

The variability of data described in point "2", the zirconium abundance (element emitted by coal combustion) and an analysis of PAHs profile (Figure 10) exclude the possibility of a diffuse traffic pollution as lead presence suggests.

In site B, in fact, a good correlation ($p \leqq 0.01$) between IND and B(ghi)P concentration was found with a ratio of 1.31 ± 0.05 characterized by high traffic, as the site F, is 0.42 ± 0.13 according to literature data.[6]

The practical absence of another PAH (CYC) in the particulate matter coming from south-east confirmed that traffic was not involved in the phenomenon.

In samples from south-east, moreover, no correlation was found between Ni and V while these metals were well correlated in north-east samples ($p \leqq 0.01$) with a ratio typically found in emission from an oil-burning plant.

All these data suggest that, with a high probability, the two plants using coal might be particularly involved in the production of lead and PAHs.

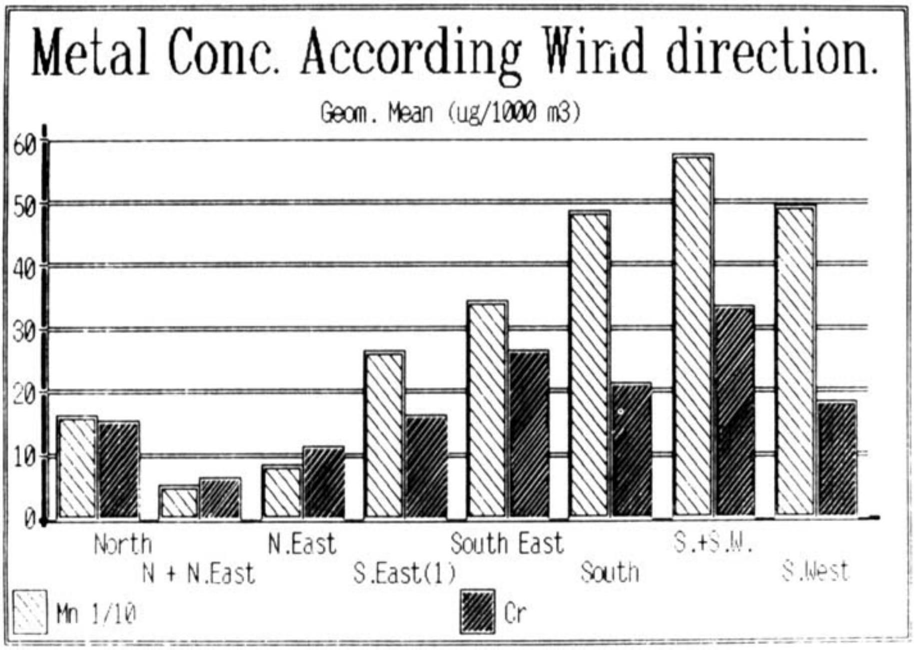


Figure 9 Geometric means of Cr and Mn concentrations according to wind direction.

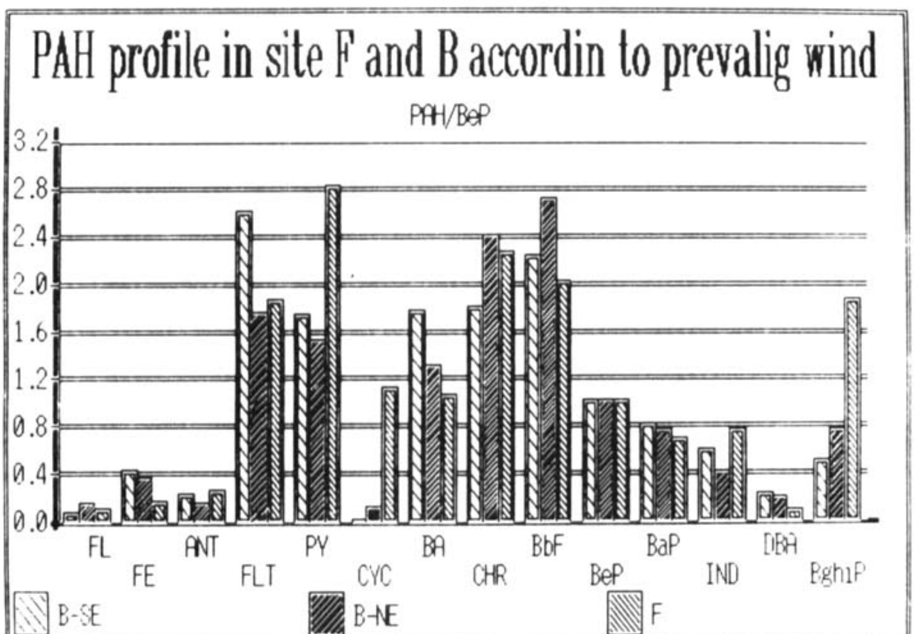


Figure 10 PAHs profile relative to a high traffic site (site F) and an industrial site (site B) according to prevailing wind.

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