International Journal of Occupational Medicine and Environmental Health, Vol. 14, No. 3, 261—265, 2001

SPATIAL VARIABILITY AND TRENDS IN AMBIENT AIR CONCENTRATIONS OF METALS IN CRACOW, POLAND

KRYSTYNA SZAFRANIEC and WIESŁAW JĘDRYCHOWSKI

Chair of Epidemiology and Preventive Medicine
Collegium Medicum, Jagiellonian University
Cracow, Poland.

Abstract. Even though the air quality has been improving since the beginning of the 1980s, Cracow still belongs to the most polluted cities in Poland. The air pollution originates mainly from industry, small-size emission sources and transport. Metals in ambient air have been monitored since 1992 by 4 stations located within the city.
The aim of the study was to determine the city areas where the national limits of heavy metals in suspended particles are exceeded and to assess the trends for the years 1992-1999. The monthly mean and maximum values of lead, zinc, chromium, copper, cadmium, nickel and iron were used in the analysis.
Between 1992 and 1999, the level of most monitored metals in suspended particles was much below the national standards. Only the concentration of lead exceeded the limits by 50% in the area with the station monitoring traffic air pollution. However, the substantial variability in concentrations of monitored metals observed within the city was most pronounced around the metallurgical plant.
Nowadays a new factor prevails: heavy traffic has resulted in a substantially enhanced concentration of lead across the city.

Key words:
Air pollution, Heavy metals, Trends

INTRODUCTION

Clean air is considered to be a basic requirement for human health and well-being. Airborne particulate matter (PM) has been a concern for at least the last century, initially as a nuisance dust and more recently as the effects resulting in acute mortality and morbidity [1]. Industrialization, widespread use of coal as a fuel and transportation in particular increased PM air pollution and caused multiple serious pollution episodes. The principal motivation for health concerns about particles include their expected patterns of deposition in the human lung and their tendency to be associated with some trace metals and other chemicals. The epidemiological results point to several subpopulations as being at special risk for particulate matter exposures: children, individuals with pulmonary and cardiovascular diseases and the elderly. Although the mechanisms of PM responses remain poorly understood, the results of the acute and chronic exposure studies are complementary. However, a number of uncertainties exist in interpreting the literature on the effects of particulate matter, and especially in estimating the risks of current ambient PM concentration. The uncertainties include among others the role of various specific chemical

The paper presented at the Conference ”Metal in Eastern and Central Europe: Health effects, sources of contamination and methods of remediation”, Prague, Czech Republic, 8–10 November 2000.
Address reprint requests to Prof. W. Jędrychowski, Chair of Epidemiology and Preventive Medicine, Collegium Medicum, Jagiellonian University, Kopernika 7, 30-034 Cracow, Poland.

species in triggering health responses and, ultimately, in increasing morbidity and mortality. These chemical species include acidic compounds, trace elements, and highly reactive toxic substances. Thus future research is needed to identify mechanisms by which PM could contribute to life shortening and to assess PM chemical characteristics associated with different health effects.

MATERIALS AND METHODS

Study period

The long-term trends study of air pollution expressed as black smoke and sulphur dioxide covered a 20-year period (1978–1997) while the study of concentrations of heavy metals in ambient air spread over the years 1992–1999.

Study area

Cracow is the third large town in Poland populated by 800,000 inhabitants. It is situated in the Vistula river valley which favours atmospheric inversions with frequent trappings of moisture and fog. Topography and weather conditions are responsible for cumulating air pollution close to the earth surface for about 100 days during a year. A big metallurgical plant and a coal fired power station are the dominant sources of industrial air pollution. The local and individual coal operated stoves for household heating are another important source of air pollution especially in the old part of the city and in wintertime. An additional source of elevated concentration of air pollution is heavy traffic passing through the city center.

Air pollution data

The exposure time series data under study concerned daily measurements of black smoke and sulphur dioxide for assessing long-term trends in air pollution concentrations. Reflectometric method was used to determine black smoke concentration in ambient air and calorimetric method was employed to analyse SO_2 samples. The measurements from 15 monitoring stations operating within the city in 1978–1997 were taken. The data from the same stations were used for the whole study period.

In the evaluation of variability and trends of concentrations of heavy metals in ambient air, the samples of PM10 measurement were taken from the air pollution automatic network run by the Regional Inspectorate for Environmental Protection in Cracow. Particulate matter concentrations were measured at two residential areas, one industrial site, and a heavy traffic road. Daily, 24-hour PM10 samples were collected once a week during 1992–1999. Each sample was then analysed for a variety of chemical components (Pb, Zn, Cr, Cu, Cd, Fe), using the Smith-Hieftje 22 atomic absorption spectrophotometer (Thermo Jarell).

Statistical modeling

The time-series of monthly averages for air pollution indices (black smoke and SO_2) and concentrations of metals were constructed. The linear regression and the LOESS regression methods were employed for evaluating time trends in air pollution indices. The degree of association between time and air pollution concentrations was estimated by coefficient of determination (R^2). Pearson correlation coefficients were used to determine pairwise association between metals and ”classical” air pollutants (PM10, CO and SO_2). In order to compare the changes in mean concentration of metals in two different periods of time, 1992–1994 and 1997–1999, the non-parametric Mann-Whitney test was exploited.

RESULTS

As for the trends in air pollution levels over the period of 20 years (1978–1997), the data showed a clear decreasing trend in the concentrations of black smoke and SO_2 (Fig. 1). The reductions were greater for black smoke than for SO_2. Black smoke declined slightly faster in winter than in summer when quite strong stability of this trend has been noticed. Recently, starting from the 1990s, we have also observed stability in the level of black smoke concentration in wintertime due to replacing coal by gas in the heating system of individual apartments. It is important to notice that the commonly used 95 percentile of the distribution of the black smoke concentration is now lower than the mean value observed 15 years ago. The case of SO_2 is not so clear. The trend is more robust in both seasons.

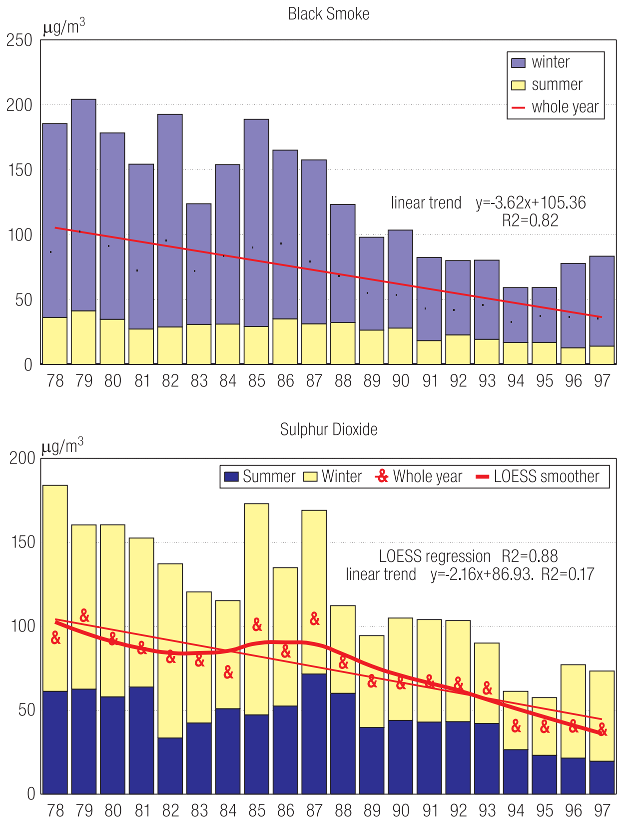

Fig. 1. Trends in air pollution in Cracow over 20 years.

The results showed that SO_2 concentration have declined linearly starting from the end of the 1980s.

The analysis of concentrations of trace metals in ambient air showed that, except for lead measured along heavy traffic roads, the median values of all metals concentrations considered were below the national standards. However, the variability in concentration ranges of various metals and also the spatial variability especially for lead and cadmium were pronounced.

The variability in the concentration of heavy metals is shown in Table 1. The differences in the level of concentrations of trace metals between residential areas, industrial site and traffic roads, and the variability for a given element at a particular kind of the site are striking. There is a difference of nearly three orders of magnitude in the concentration of cadmium, the least abundant element, and iron, the most abundant element.

Comparing median values of concentrations of metals in ambient air in two periods, 1992–1994 and 1997–1999, a significant reduction in concentrations was observed for lead, zinc and iron (40%, 31% and 44%, respectively). In

Table 1. Concentration ranges of various metals associated with particulate matter in the atmosphere. The Cracow study, 1992–1999

Metal	Concentration range (µg/m^3)		
	Residential area	Industrial area	Roads
Chromium (Cr)	0.0002–0.106	0.001–0.154	0.0006–0.148
Cadmium (Ca)	0.0002–0.013	0.0003–0.043	0.0004–0.0104
Copper (Cu)	0.006–1.615	0.021–0.520	0.025–0.417
Iron (Fe)	0.006–5.635	0.008–35.2	0.0141–14.435
Lead (Pb)	0.006–0.434	0.016–0.739	0.021–1.147
Zinc (Zn)	0.014–1.443	0.015–1.935	0.034–1.122

the case of copper an essential increase of 14% was noticed. The concentration of cadmium and chromium was at the same level during the study periods (Fig. 2). However, in different areas of the city these changes differed substantially. In particular, the analysis of air samples collected between 1992 and 1994 showed that lead concentrations in air declined from 0.133 µg/m^3 to 0.079 µg/m^3 by 1999 (Fig. 3). Lead concentrations measured along the major streets decreased from 0.303 µg/m^3 during 1992–1994 compared to 0.126 µg/m^3 in 1997–1999. A road sampling site had the highest concentration of 1.147 µg/m^3. From 1995, the concentrations have gradually decreased, which could be attributed to a lower content of lead in petrol sold in the recent years.

Current data on the chromium concentration in the ambient air are apparently inadequate to depict the trends. All stations, except for the traffic one, had annual mean concentrations between 0.0077 and 0.009 µg/m^3. However it is important to point out that during the period 1997–1999 the concentration range widened, which means occasional excess of high emission. The pattern of cadmium was

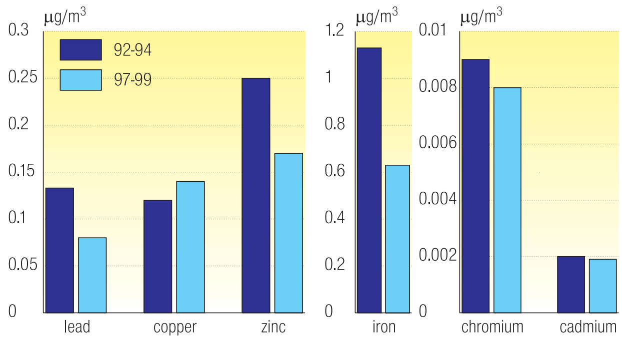

Fig. 2. Changes in the concentration of various metals measured in suspended particulate matter over time in Cracow.

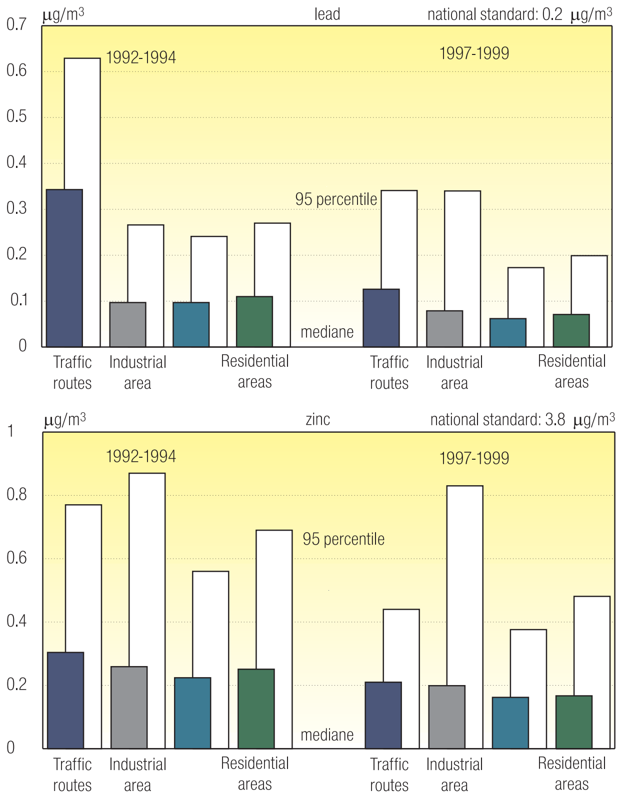

Fig. 3. Pattern of exposure to various metals (Pb, Zn) measured in suspended particulate matter in different city areas over two time periods.

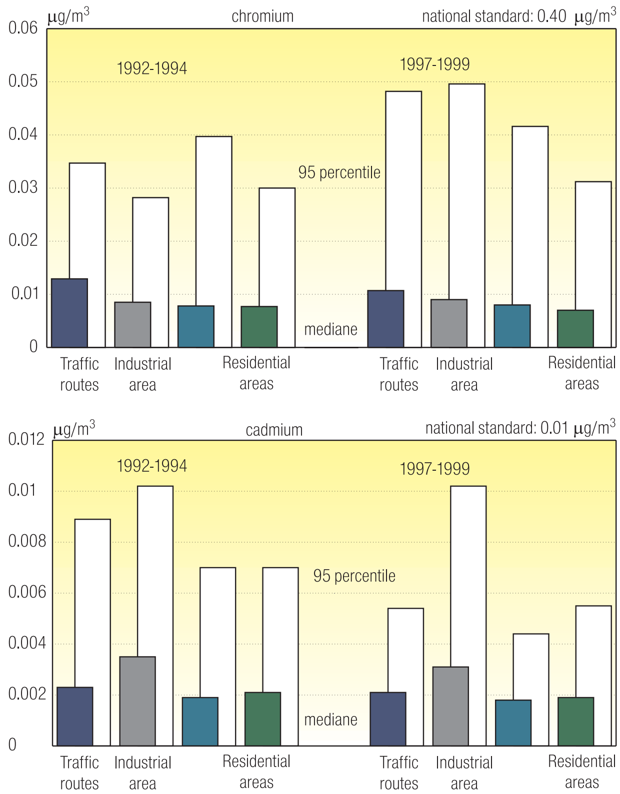

Fig. 4. Pattern of exposure to various metals (Cr, Cd) measured in suspended particulate matter in different city areas over two time periods.

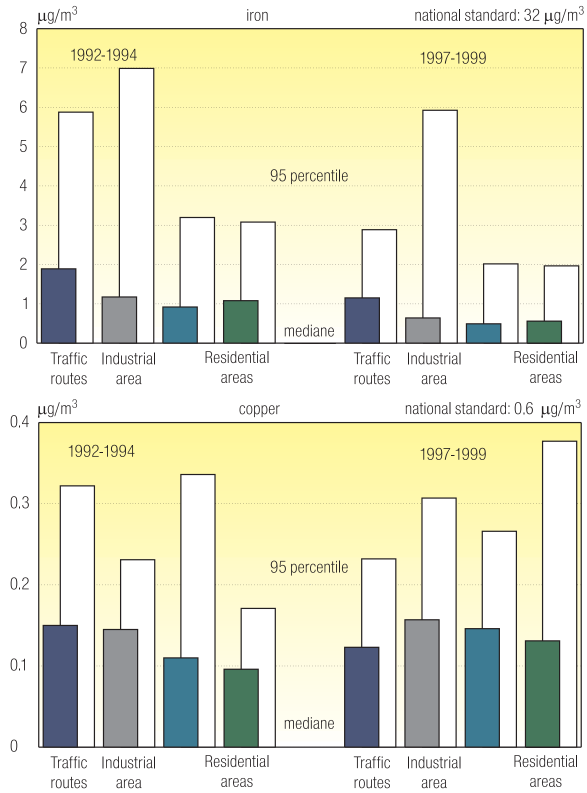

Fig. 5. Pattern of exposure to various metals (Fe, Cu) measured in suspended particulate matter in different city areas over two time periods.

similar to that observed in the industrial area with the highest concentrations (Fig. 4).

No statistically significant differences were observed in concentration of zinc measured in different parts of the city although substantial reduction in time was noted (Fig. 3). When comparing the two periods under study a significant reduction in the iron concentration became evident, regardless of the sites (Fig. 5).

Considering the association between heavy metals and ”classical” air pollutants, it is worthy to point out that the correlation coefficients were highest between lead and traffic-induced air pollutants (0.54 for PM10 and 0.66 for CO).

DISCUSSION

The analysis of concentrations of heavy metals in ambient air in Cracow showed that, except for lead measured along heavy traffic roads, the levels of all metals considered were below the national standards. It is somehow alarming that the concentration of lead is still above maximum admissible levels.

It is estimated in other studies [2] that about 80% of the total emissions of lead to the atmosphere come from the combustion of leaded petrol, which is closely related to the traffic density. Lead exposure of traffic routes spreads over the neighbouring areas and impacts essentially the mean value for the whole city (Fig. 6).

The other major lead emissions into the atmosphere come from lead smelting and solid waste disposal [3]. Lead wastes are remelted in secondary smelters and non-recycled lead-containing consumer products such as battery castings, products painted with lead pigments and bottle caps are burned in municipal incinerators.

Another striking fact is that the concentration of chromium did not change within the study period. This might happen because coal from many sources usually contains as much chromium as soils and rocks, so the burning of coal can contribute to the air concentration of chromium and is probably responsible for its large amount in the city ambient air. It is likely that the cement producing plant, located on the outskirts of Cracow, is an additional source of chromium in the air. Chromium and its compounds are used in the metallurgical industry, particularly in the production of ferrochromium alloys and stainless steel. Another important source of chromium in the atmosphere are asbestos particles emitted by the wearing of brake linings [4].

As to other heavy metals like cadmium, copper, zinc and lead, it turns out that the production of iron and steel contributes to their emissions to the atmosphere, and zinc is the major supporter to the total emission. Incineration of solid waste, located nearby, also results in the emission of these elements.

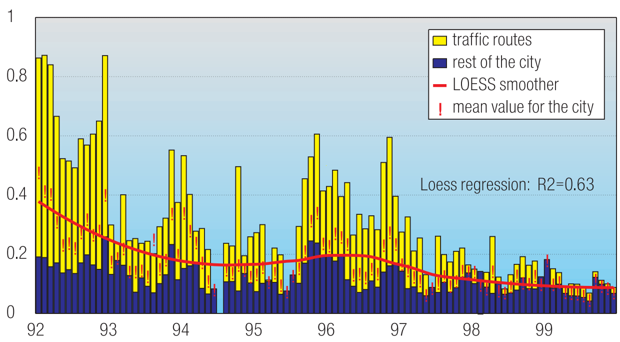

Fig. 6. Changes in lead exposure measured in suspended particulate matter considering an impact of traffic sources, Cracow, 1992–1999.

CONCLUSIONS

1. Over the last 20 years exposure pattern of air pollution in Cracow has changed substantially and now the communal pollutants fall within annual national standards although excess of extremely high exposure, lasting 1–2 days, still occurs.
2. Decline in the communal air pollution has induced a significant decrease in the level of heavy metals, however, on road-emission must be controlled to reduce the concentration of lead in ambient air.
3. The lower levels of air pollution in the Cracow residential area should lead to the decline in long-term morbidity and mortality rates from acute and chronic cardio-respiratory diseases.

ACKNOWLEDGMENT

The authors would like to thank the Regional Inspectorate for Environmental Protection in Cracow for providing them with air pollution data.

REFERENCES

1. McClellan RO, Miller FJ. *Critical Issues in Placing Particulate Matter Risks into Perspective.* In: Vostal JJ, editor. *Health Effects of Particulate Matter in Ambient Air*, Prague; 1998.
2. Stanners D, Bourdeau P, editors. *Europe's Environment*. European Environmental Agency, Copenhagen; 1995.
3. Fishbein L. *Environmental metallic carcinogens: an overview of exposure levels.* J Toxicol Environ Health 1976; 2: 77–109.
4. *IARC Monographs on the Evaluation of the carcinogenic risk of chemicals to humans. Some metals and metallic compounds*. Vol. 23. Lyon, IARC; 1980.

Received for publication: January 25, 2001
Approved for publication: August 20, 2001