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Relationship Between 4-Day Air Mass Back Trajectories and Metallic Components in PM_{10} and $PM_{2.5}$ Particle Fractions in Zagreb Air, Croatia

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Abstract This paper presents a study on the relationship between trace metal concentrations and the state of the atmosphere at the Croatian EMEP station Puntijarka, Zagreb. PM_{10} and $PM_{2.5}$ particle fractions are hazardous in terms of morbidity and hospitalization due to cardiovascular and respiratory diseases, and in terms of total mortality. In Zagreb, PM_{10} and $PM_{2.5}$ monitoring started on a daily basis at a sampling site located in the northern, residential part of the city. Trace metal concentrations were determined from daily samples. Air mass back trajectories were used to determine particulate air pollution from local and remote sources. The investigation has shown a statistically significant association between air mass back trajectories and metallic air concentration levels.

Keywords Lead · Manganese · Cadmium · Particle pollution sources

Epidemiological studies have consistently shown an association between ambient concentrations of particulate matter pollution and adverse health effects on humans (Pope and Dockery 1999). Exposure to urban particles is associated with an increase in mortality and morbidity, mainly of cardiopulmonary origin (Levy et al. 1999; Šimić et al. 2001). PM_{10} and $PM_{2.5}$ are currently perceived to be the best practical measure of particulate matter most likely to cause ill health (Donaldson et al. 1999).

Air mass back trajectories provide useful means to establish source-receptor relationships of air pollutants (Stohl 1998; Beverland et al. 2000). The long-range transport of pollutants is significantly influenced by synoptic scale meteorological patterns. If climate effects change the frequency of synoptic patterns, the frequency of pollution episodes is also likely to alter (Dorling and Davies 1995).

This paper aims to investigate the relationship between the metallic components, namely, lead, manganese and cadmium in PM_{10} and $PM_{2.5}$ particle fractions measured in Zagreb air, Croatia and corresponding 4-day backward air trajectories.

Materials and Methods

For the period 2000–2003, PM_{10} and $PM_{2.5}$ monitoring in Zagreb was performed at one sampling site located in the northern, residential part of the city (45°50′09.4″ N, 15°58′58.6″ E, 147 m ASL.), approximately 20 m from a road with moderate traffic density. Daily samples of particle fractions were collected on 90 mm diameter cellulose membrane filters from 100 m^3 of ambient air. Coarser particle fraction was removed from air stream by means of standard inertial impactor (EN12341 1999). Filters were preconditioned in desiccators for constant humidity for 24 h before and after sampling. Particle mass concentration was gravimetrically determined by weighing on Mettler Toledo MX-5 microbalance.

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Mass concentrations of metallic components were determined by atomic absorption spectrometry. Pye Unicam SP 9 flame atomic absorption spectrometer was used. All AAS measurements were carried out in an air/acetylene flame. Chemical analysis followed the same procedure as described earlier (Čačković et al. 2006). The detection limits were: 0.0015 μg m^{-3} for lead, 0.0013 μg m^{-3} for manganese, and 0.0001 μg m^{-3} for cadmium. The method recovery were 99.3–101.2% with relative standard deviation RSD <5%.

Over the same period 2000–2003, 4-day air mass back trajectories were computed daily (arrival time 12 GMT) at the Puntijarka receptor point (45°54′32″ N, 15°58′23″ E, 980 m ASL.). The 2D trajectories were calculated with a horizontal resolution of 50 × 50 km^2 in the EMEP grid (EMEP, www.emep.int). The choice of a 4-day trajectory is a compromise between the several-day atmospheric residence times of fine particles and the accuracy in calculation of trajectory. Trajectory calculations are based on meteorological data from the PARLAM-PS model with 925 hPa wind fields, developed at the Norwegian Meteorological Institute.

In order to group similar trajectories, which indicate both similar meteorology (i.e. distinct synoptic regime over the duration of the trajectory) and transport of the air parcels over the same specific emission regions, trajectories were assigned to daily sector values. The area around the receptor point was divided in eight equal sectors (Klaić and Lisac 1988). The north sector (sector 1), which was centered at 0°, spanned the angle of −22.5° to 22.5°; northeast sector (sector 2, centered at 45°) spanned the angle of 22.5° to 67.5°, etc. The criterion for the allocation of particular trajectory to a particular sector was that at least 50% of its points were found within this sector. Following this criterion, 25% of the investigated air trajectories could not be assigned to one sector alone. However, mass concentrations of pollutants for days without assigned sectors did not differ significantly from those with assigned sectors ($p > 0.05$, ANOVA, one-way). Therefore, the obtained results could be considered as representative for the entire investigated period.

Results and Discussion

Figure 1 shows the location of the PM monitoring site (Zagreb) and EMEP meteorological site (Puntijarka). Puntijarka is located near the summit of the SW–NE stretching Mt. Medvednica, while the PM monitoring site is located at the southern slope of the mountain.

Table 1 shows mass concentrations of pollutants measured in daily samples for the entire measuring period.

Figure 2 shows relative frequencies of 4-days air mass backward trajectories in relation to the incoming sector. The highest relative frequencies were observed for NW, W and N incoming sectors. This indicates the predominance of transport from W–N directions. The same is the common route of frontal systems running across the continental (inland) part of Croatia. These trajectories precede or follow cold fronts with generally strong and steady winds.

Figures 3 and 4 show PM_{10} and $PM_{2.5}$ fraction and metal concentration distributions in relation to air mass arrival direction. Overall pollutant contributions are also presented in Figures 3 and 4. They reflect the product of relative frequency of air mass trajectories and the ratio between average pollutant concentrations per sector and average pollutant concentration for all directions over the investigated period (Hršak et al. 2000; Vađić et al. 2000). The average concentrations of nearly all investigated pollutants depend significantly ($p < 0.05$, ANOVA, one-way) on back trajectory sectors, except for Mn and Cd in $PM_{2.5}$ ($p > 0.05$).

Higher concentration levels of PM_{10} and $PM_{2.5}$ were associated with SE and S back trajectories. These

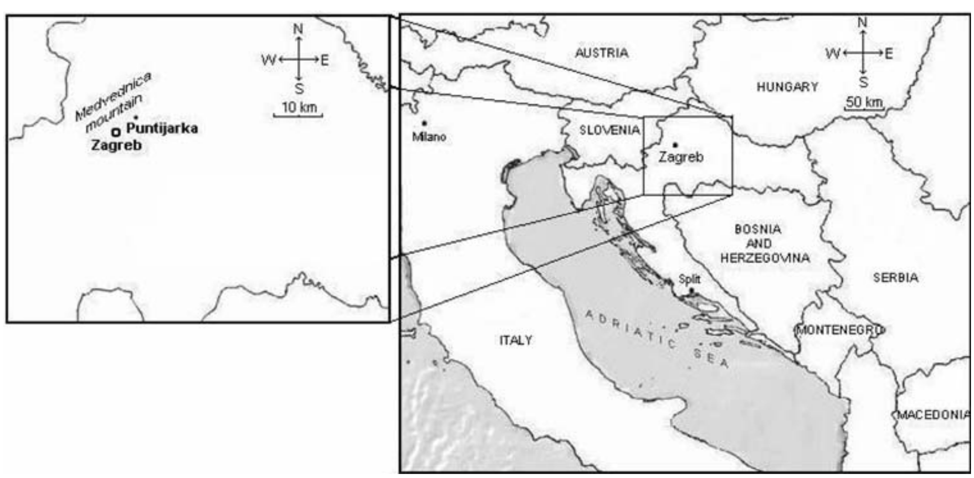

Fig. 1 Location of the Zagreb and EMEP meteorological site Puntijarka

Table 1 Mass concentrations of pollutants (μg m^{-3})

Statistical parameters	PM_{10}	Pb in PM_{10}	Mn in PM_{10}	Cd in PM_{10}
N	747	747	743	663
C_{avg}	**37.15**	**0.085**	**0.0117**	**0.00076**
SD	23.50	0.067	0.0077	0.00058
C_{50}	31.10	0.066	0.0099	0.00062
C_{max}	225.46	0.594	0.0557	0.00908
	$PM_{2.5}$	Pb in $PM_{2.5}$	Mn in $PM_{2.5}$	Cd in $PM_{2.5}$
N	747	745	740	664
C_{avg}	**27.49**	**0.076**	**0.0079**	**0.00066**
SD	20.12	0.061	0.0052	0.00040
C_{50}	21.75	0.059	0.0068	0.00058
C_{max}	200.30	0.588	0.0367	0.00427

N, number of samples; C_{avg}, average value; SD, standard deviation; C_{50}, median; C_{max}, maximum value

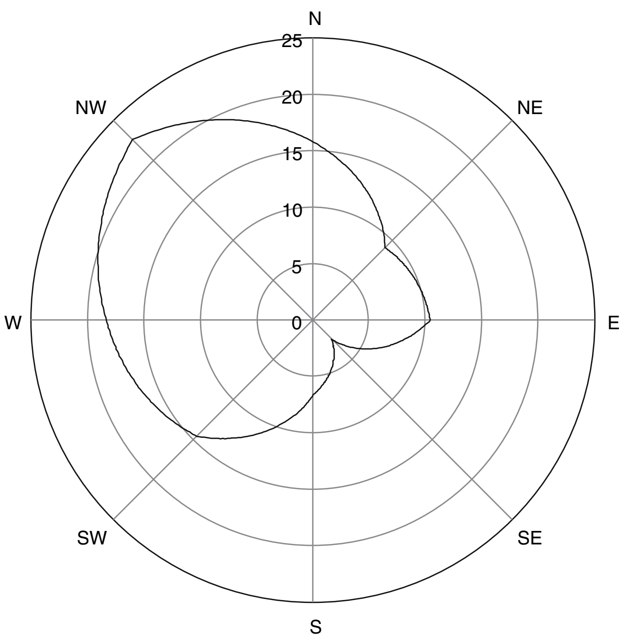

Fig. 2 Percentage of recurrence of air mass back trajectory sector (%)

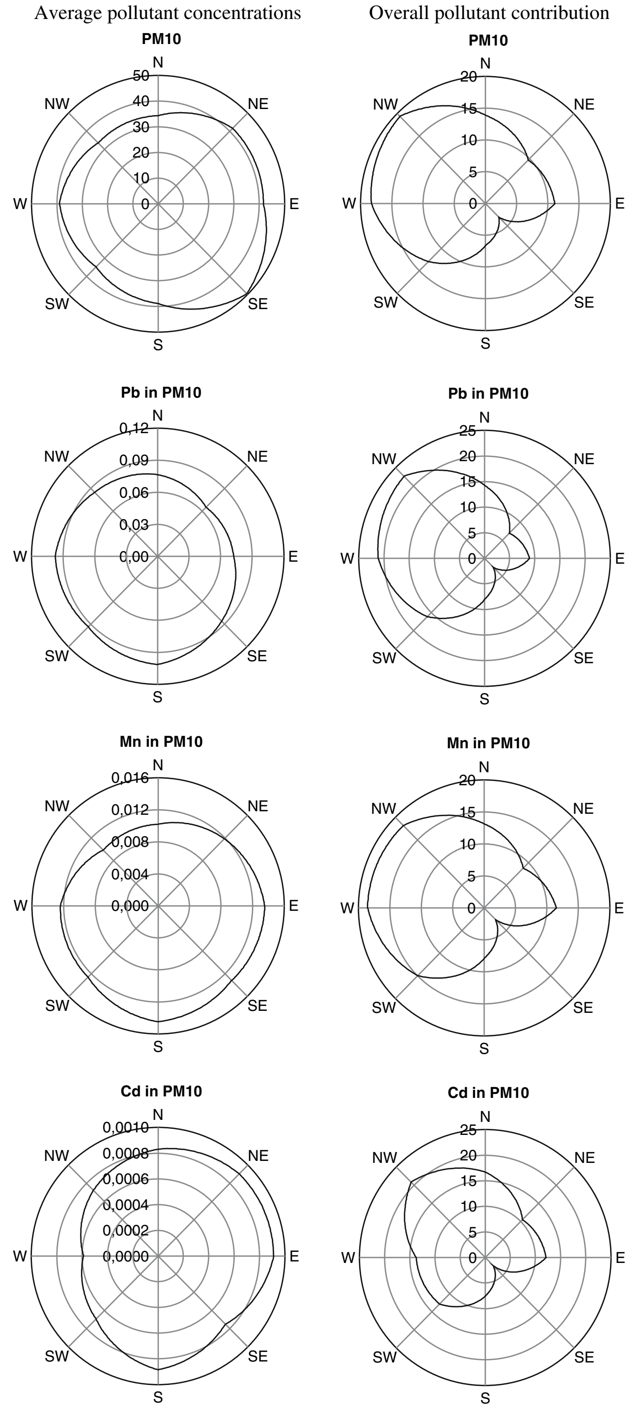

Fig. 3 Average PM_{10}, Pb, Mn and Cd concentration (μg m^{-3}) and average pollutant contribution in relation to the air mass back trajectories direction (%)

trajectories pass over the industrial zone of Zagreb (i.e. over the main local source of particle pollution), which is located in the southeastern part of the town. Considering long-range transport of pollutants, sources in Bosnia-Herzegovina might also contribute to elevated pollution levels. However, this study cannot clearly distinguish between the relative contribution of the local and remote pollution sources. Nevertheless, judging by the results of other studies of long-range transport of other pollutants to Croatia (Klaić and Beširević 1998), it is very likely that most pollution originates from the local sources.

High traffic density in the city center and the western part of the city could be the main local source of lead and manganese pollution. Higher concentration of cadmium during NE air mass trajectories may also point to a local source.

Mt. Medvednica stands as a shield from the pollution coming from the N and NW. Regardless, air mass back

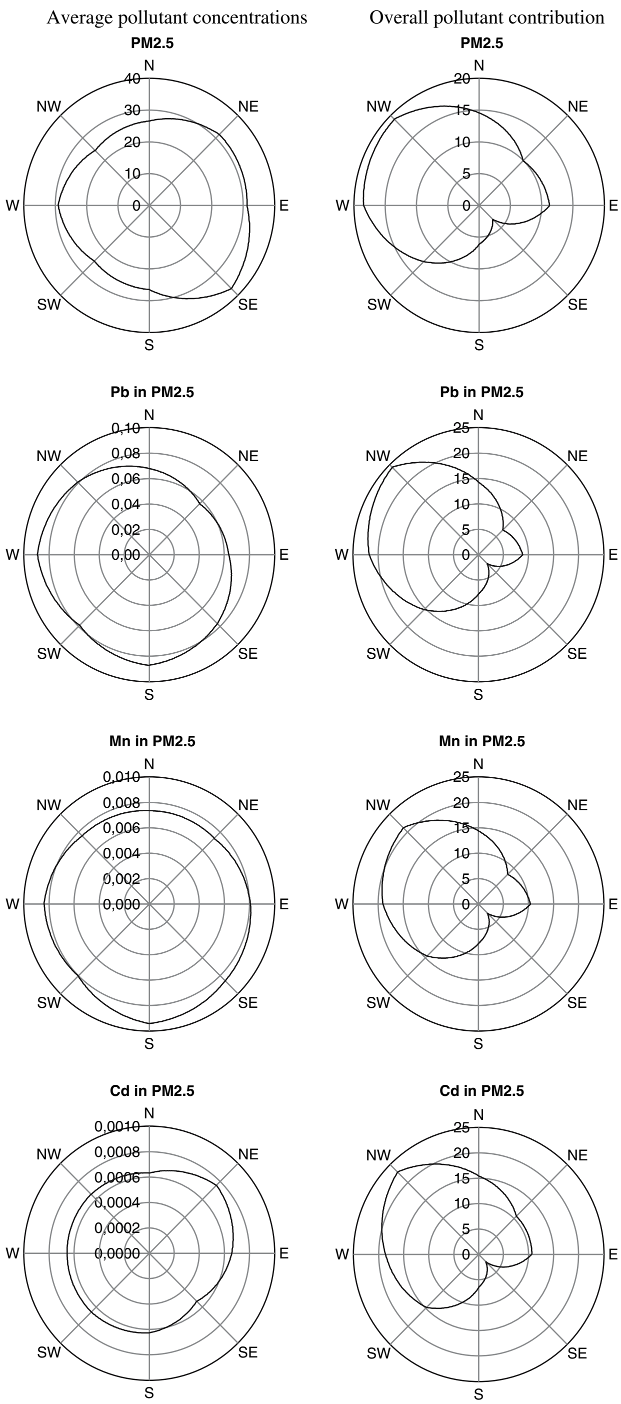

Fig. 4 Average $PM_{2.5}$, Pb, Mn and Cd concentration (μg m^{-3}) and average pollutant contribution in relation to the air mass back trajectories direction (%)

trajectories from the N, W, and NW, which are the most common, significantly contribute to overall particle pollution in Zagreb area.

This study has provided some, however limited, information about local and remote sources and their contribution to particulate air pollution in Zagreb. Main local particle sources in Zagreb include the industrial zone in the southeastern part of the city, city center with its dense traffic and numerous space heating appliances in the SE, S and SW. Our results suggest that city planners have made the right decision by situating the industrial zone in the SE. Remote sources could be associated with the N, W, and NW directions. In spite of relatively low pollutant concentrations associated with these directions, they significantly contribute to air pollution in Zagreb due to their frequent occurrence.

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