

On the impact of precipitation amount on the concentration of elements and ions in urban aerosol particles

F. Deutsch,^{1,5} M. Stranger,¹ A.E. Kaplinskii,^{1,2}
L. Samek,³ P. Joos,⁴ and R. Van Grieken¹

¹ *Micro- and Trace Analysis Center, University of Antwerp, Belgium*

² *Institute for Water and Environmental Problems,
Siberian Branch of the Russian Academy of Sciences, Barnaul, Russia*

³ *University of Mining and Metallurgy, Cracow, Poland*

⁴ *Catholic Higher School Sint-Lieven, Ghent, Belgium*

⁵ *Flemish Institute for Technological Research, Mol, Belgium*

Received May 14, 2003

The results of studying the elemental and ion composition of the ambient aerosol in and around Antwerp are presented. Four sampling campaigns covering all seasons were performed. The samples were obtained by filtration and impaction methods. Subsequently, the filters were analyzed by X-ray fluorescence spectrometry for elements, and the impactor substrates were leached with water and analyzed by ion chromatography for ions. In comparing the results of chemical analysis with the meteorological information, it was found that the concentration of certain elements and ions in aerosol samples was affected considerably by the location of the sampling site and by the meteorological conditions. In relatively less polluted places like small towns and suburbs of Antwerp, the concentrations of some elements and ions showed qualitatively a positive or negative correlation with the amount of precipitation in their time variations. Hence, we suppose that in the former case these elements and ions are contained mainly in the more hygroscopic fraction (the most apparent is the behavior of Na and Cl) and in the latter case the elements are mainly present in the less hygroscopic fraction of the ambient aerosol. However, this behavior of the elements and ions may differ for particles in different size ranges. In the highly urbanized and industrial sites close to the central and industrial parts of Antwerp, these correlations were not found. This could be connected with the high and variable local aerosol generation rate, when only heavy rains are able to provide a sufficient removal of aerosols from the atmosphere.

Introduction

The Belgian city Antwerp and its suburbs form a highly populated and industrially developed European region. Here a relatively small area concentrates the second largest petrochemical plant in the world, many chemical, metallurgical, and engineering plants, as well as a commercial port, the second largest in traffic of Europe. The population of the Antwerp agglomeration is about 700 000. The city has the developed traffic system; it is crossed by highways connecting Belgium with neighboring Germany, France, and the Netherlands. The concentration of atmospheric pollutants (gases and aerosols) is routinely measured using a network of stationary posts of atmospheric monitoring of the Flemish Environment Agency (VMM), which are located all over Flanders (the Northern Dutch-speaking part of Belgium). The state of the atmosphere has been analyzed in a number of papers,¹⁻⁴ in particular, as concerning the issues of the effect of air pollution on asthma occurrence.^{5,6}

As known, the surface concentration of aerosol particles is determined by the balance between two opposite factors, namely, the particle generation and removal from the atmosphere. New particles are generated in photochemical reactions, wind erosion of soil, evaporation of seawater splashes, and other natural mechanisms, as well as in many anthropogenic

processes. Particle removal can be connected not only with the coagulation and following deposition in the field of gravity, but also with the direct effect of meteorological processes: capture by rain and fog droplets (with possible partial dilution) and mechanical action of wind and snow. These processes were studied by many authors and reported, for example, in Refs. 7-11.

The efficiency of removal of some substances in particles is largely determined by the intensity of precipitation and the mean wind velocity. This paper presents some results of measuring the concentrations of some aerosol elements and ions in Antwerp and its suburbs in comparison with the meteorological information, which suggests some conclusions on the effect of active meteorological processes on the measured parameters.

Techniques of experiment and sample processing

In the period from November 2000 to May 2001 four campaigns of aerosol sampling were conducted in Antwerp and its suburbs. This period covered all seasons: fall (November), winter (February), spring (March), and early summer (May). Samples were collected with a filtering system and a Model PM10 three-stage impactor made by Dekati Ltd. (Finland).

Both the filtering system and the impactor used Nuclepore polycarbonate filters (in the latter case, as substrates) with the pore diameter of $0.4\ \mu\text{m}$. The cutoff size of impactor stages was 1, 2.5, and $10\ \mu\text{m}$. Thus, the substrate of the first impactor stage collected particles, whose aerodynamic diameter was larger than $10\ \mu\text{m}$, while the substrates of the second and third stages collected, respectively, particles with the diameter from 2.5 to $10\ \mu\text{m}$ and from 1 to $2.5\ \mu\text{m}$. Particles smaller than $1\ \mu\text{m}$ were collected by the Whatman output fiberglass filter. Air consumption for both of the samplers was $30\ \text{l/min}$.

Samples were collected at the five above-mentioned stationary posts of atmospheric monitoring of the Flemish Environment Agency (VMM). In Antwerp these are located in the city center (hereinafter site 1), near the port in the northern part of the city (site 2), in the industrial zone (site 3), and in suburbs (sites 4, 5). One more site (site 6) was organized on the roof of the building of the Chemical Department of the University of Antwerp that is located in the southern suburbs. As a background site (site 7), we took the stationary post in a small village Bree situated $100\ \text{km}$ to the east from Antwerp. In each site, continuous 24-h sampling was carried out, after that the samples were collected, instrumentation was transported to a new site, and the process was repeated. Thus, the total number of the sampling sites was seven, and every sampling campaign took about two weeks (less weekends).

The samples were processed in the Micro- and Trace Analysis Center of the University of Antwerp. Aerosol filters were analyzed by the method of X-ray fluorescence spectrometry for the following elements: S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Zn, and Pb. The impactor substrates and the output filter were leached in deionized water, and then the solution obtained were analyzed by the method of ion chromatography for water-soluble ions: K^+ , Ca^{2+} , NH_4^+ , Cl^- , SO_4^{2-} , NO_3^- . The results of chemical analysis were recalculated into volume concentrations of the measured elements and ions. The meteorological information needed for interpretation of the experimental data (temperature, diurnal precipitation amount, wind speed and direction) was taken from the Web site <http://www.weatheronline.co.uk> for weather posts closest to the sampling sites.

Results and discussion

The measured concentrations of elements and water-soluble ions in aerosol particles are plotted, along with the diurnal precipitation amount, as functions of time (sampling dates). These plots are shown in Figs. 1–6. Each of them is drawn based on four points and looks like a broken line. Because of the limited number of data sets in time, they cannot be considered as continuous plots of variation of the corresponding parameters with sufficient time resolution, however, measurements that are more frequent could provide for higher reliability of the following conclusions.

The plots of variation of the maximum and minimum temperature and the mean wind velocity during the same 24 hours, providing the extra information, were drawn separately. This allowed us to compare the plots, though the variability of aerosol parameters in time may be caused not only by purely meteorological factors.

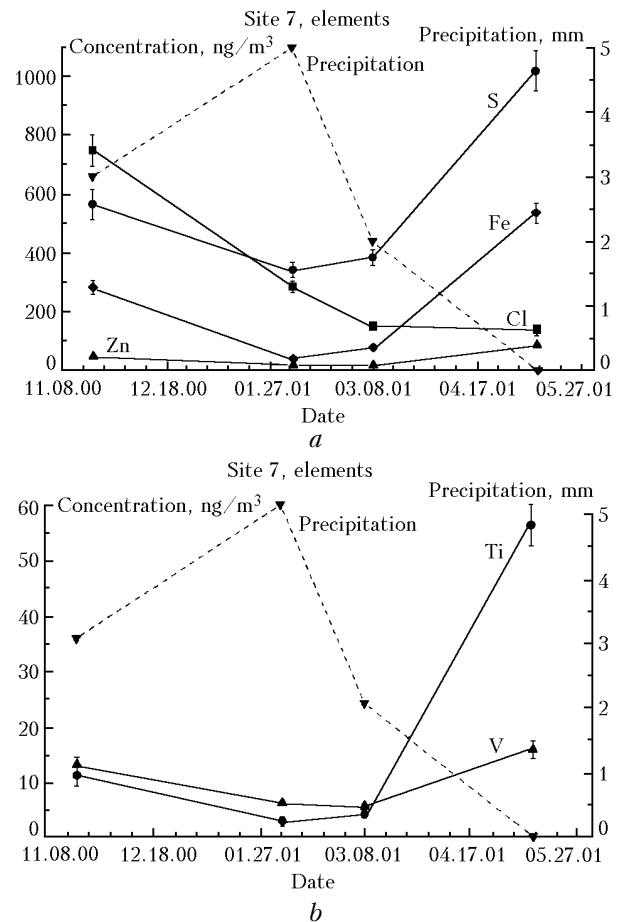


Fig. 1. Measured concentrations and precipitation amount in the background site 7: S, Fe, Cl, Zn (a) and Ti, V (b).

For example, in the village Bree (background site 7) the behaviors of the S, Fe, Zn, Ti, and V concentrations showed the qualitatively negative correlation with the diurnal precipitation amount (Fig. 1). The same is true for Ca and Pb (the corresponding plots are omitted). Presumably, these elements are contained in the weakly hygroscopic or insoluble aerosol fraction, which is scavenged by rain from the atmosphere, and the higher the precipitation intensity, the lower the measured concentrations. In early February, we observed the lowest concentrations of these elements, which corresponded to the highest diurnal precipitation amount. These facts can be explained by the relative remoteness of this site from big cities and industrial territories with high particle generation rate. Therefore, the observed variations in the concentrations of these elements could be related to almost only meteorological processes. It is worthy to note the qualitatively different behavior of Cl (Fig. 1a), which manifests itself in other sites as well.

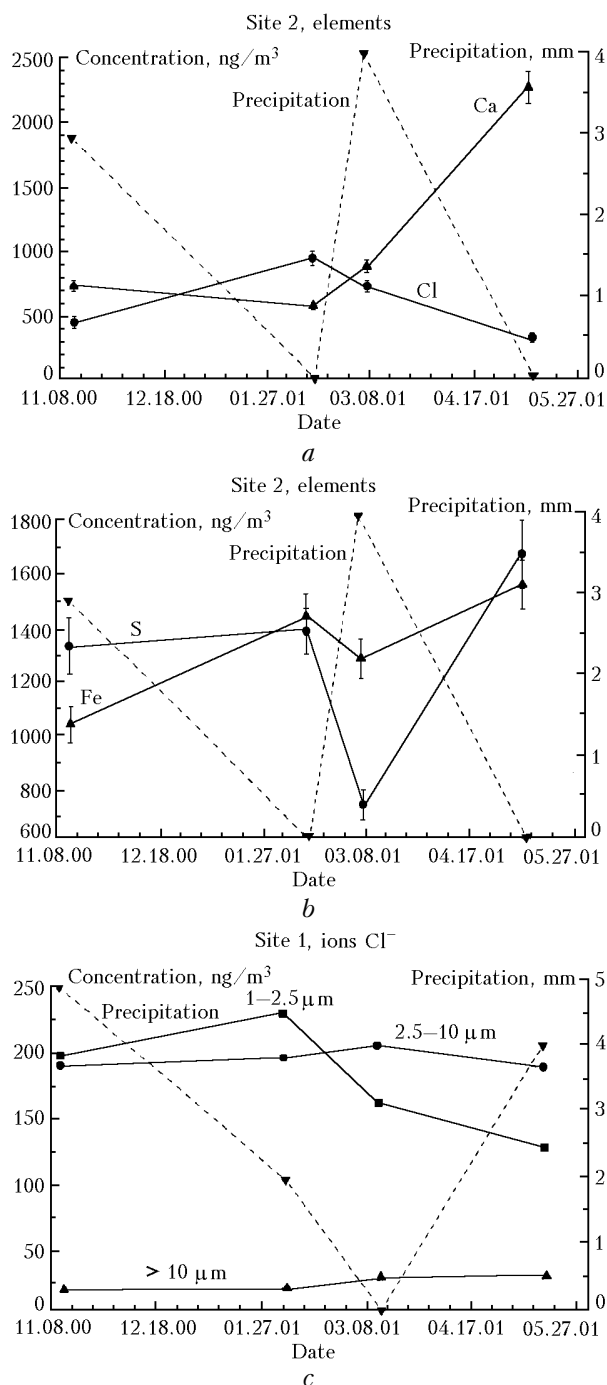


Fig. 2. Measured concentrations and precipitation amount in sites 2 and 1 (highly built-up areas): site 2 (port zone), Ca, Cl (a); in the same place, S, Fe (b); site 1 (center), Cl⁻ ions in three particle size ranges (c).

In the samples collected in sites 1 and 2 (central and port zones of Antwerp), almost no similar dependences were observed. The Ca concentration does not show the qualitative correlation with the precipitation (Fig. 2a), and only for S and Fe we can see the negative correlation in site 2 (Fig. 2b). The concentration of elemental Cl in both of the sites varied only slightly (Fig. 2a), and the concentration of Cl⁻ ions showed different dependences in different

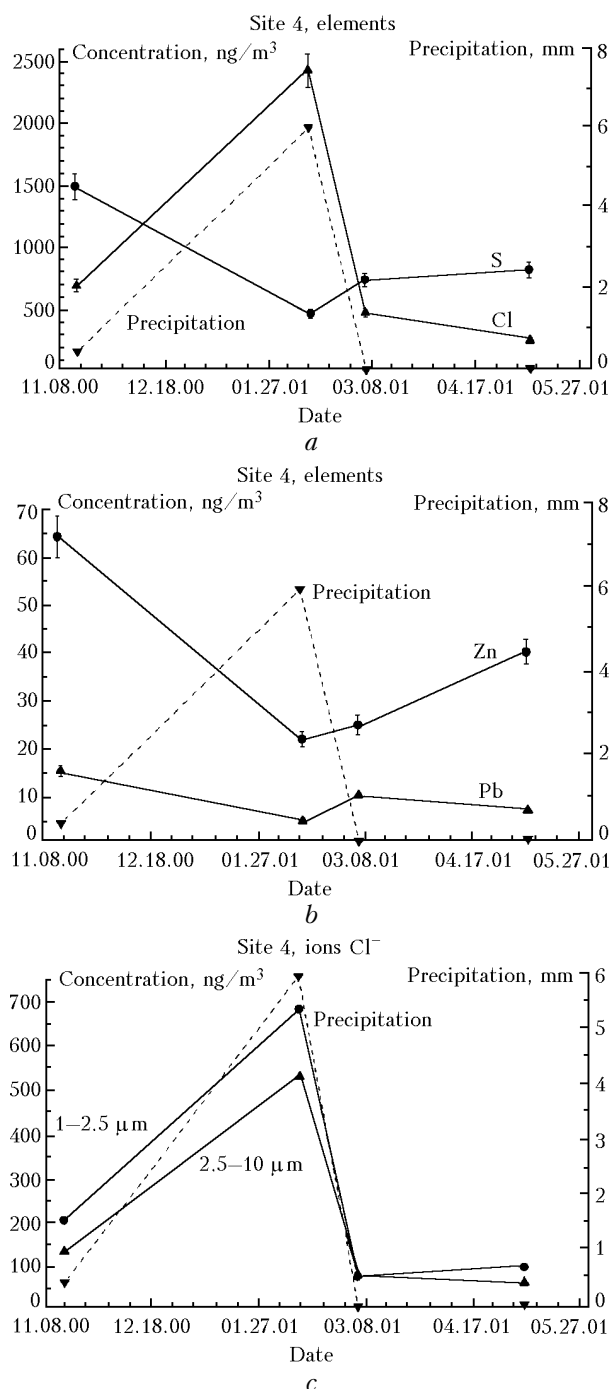


Fig. 3. Measured concentrations and precipitation amount in site 4 (northern suburbs): S, Cl (a); Zn, Pb (b); Cl⁻ ions in two particle size ranges (c).

particle size ranges, which are not connected with the behavior of precipitation amount (Fig. 2c). The same is true for other elements and ions not only in sites 1 and 2, but also in site 3 situated in the purely industrial zone near petrochemical plants. The only explanation of such a behavior of the concentrations is the high particle generation rate, because of which the effect of the precipitation amount and the wind speed and direction on the concentrations turns out to be insignificant.

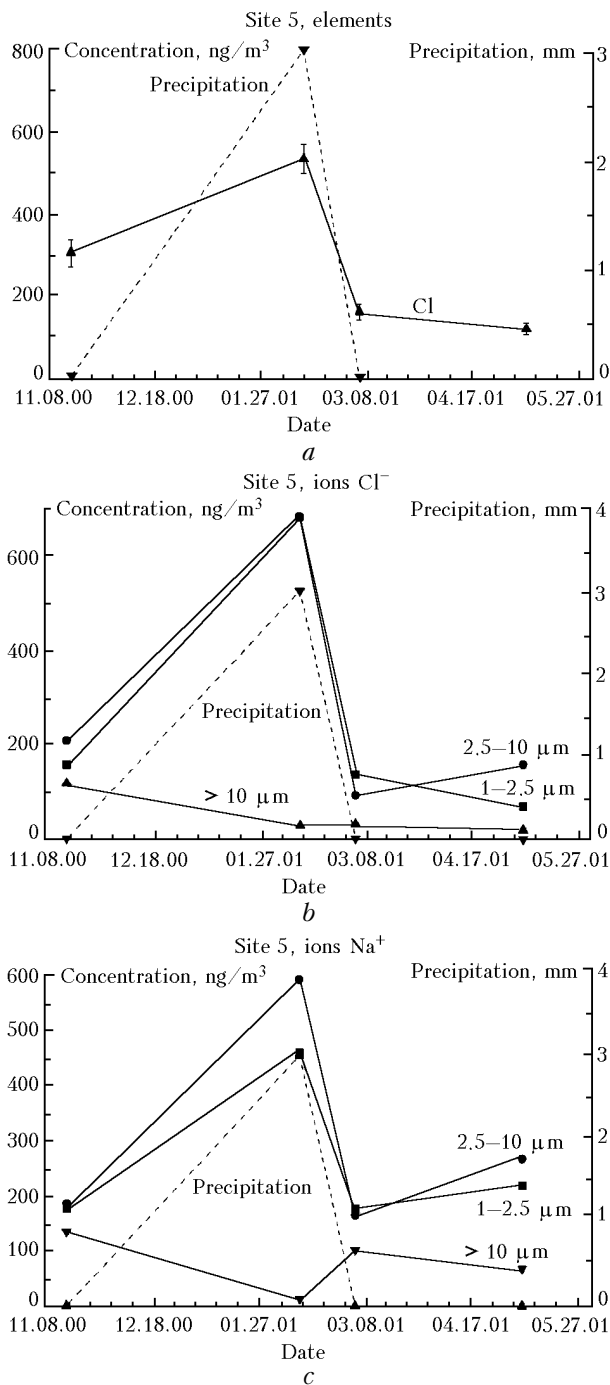


Fig. 4. Measured concentrations and precipitation amount in site 5 (northeastern suburbs): Cl (a); Cl⁻ ions in three particle size ranges (b); Na⁺ ions in three particle size ranges (c).

Sites 4 and 5 are situated in suburban villages so that in case of the winds from the western to the southern directions they are subjected to the effect of aerosol sources located in the port zone: marine engines and industrial enterprises. It is likely for this reason, that the highest values of the S, Zn, Pb concentrations (Figs. 3a and b) as well as the V and Mn concentrations (not shown) were observed in the November series of measurements in site 4 at southwestern wind direction and insignificant precipitation amount. The minimum

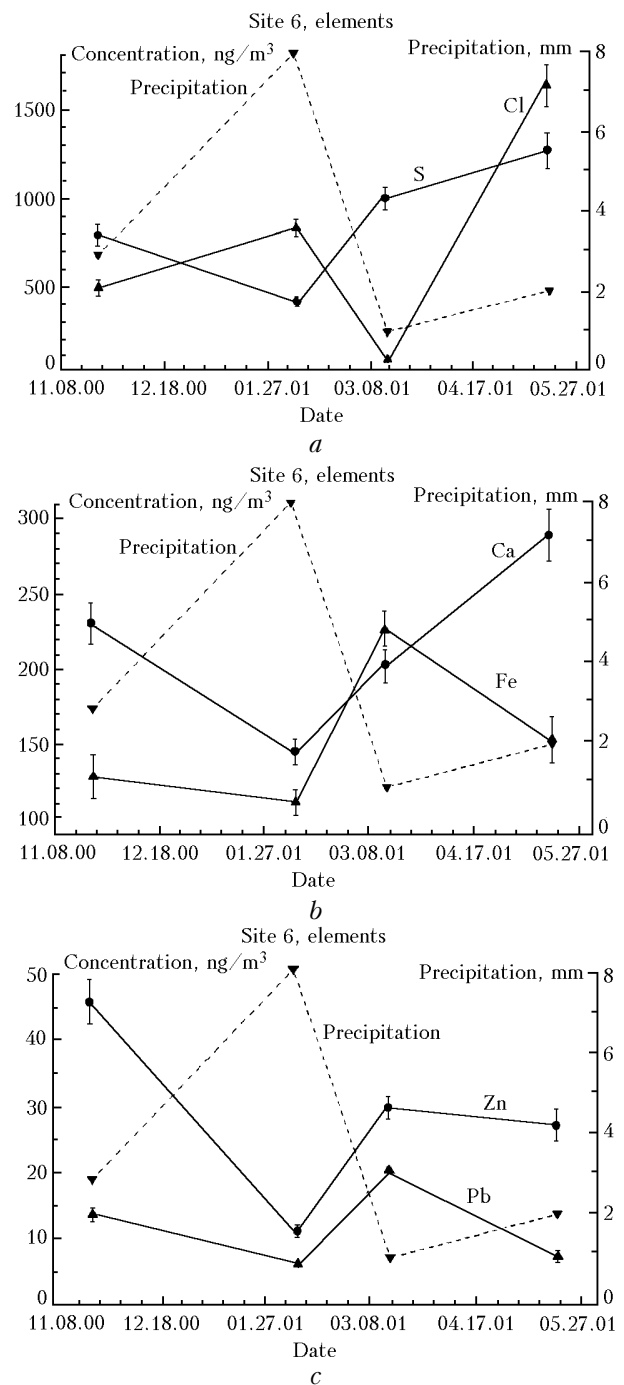


Fig. 5. Measured concentrations and precipitation amount in site 6 (southern suburbs): S, Cl (a); Ca, Fe (b); Zn, Pb (c).

concentrations of these elements were obtained in February when it rained in the day of measurements.

The behaviors of the Cl element and ion in both of the sites differed sharply from that of other elements. As can be seen from Figs. 3a,c and 4a,b, the concentration of Cl and Cl⁻ ions in the particle size range of 1–10 μm follows the precipitation amount, that is, the positive correlation is observed. The same is true for the Na⁺ ions in the same particle size range (Fig. 4c). The probable explanation is that because

the city is close to the sea, the atmospheric aerosol in Antwerp always includes a large amount of strongly hygroscopic particles of sea salt. Therefore, rain droplets contain a significant amount of the dissolved sodium chloride. When droplets strike the surface, aerosol particles enriched with sodium and chlorine ions are generated, and the higher the rain intensity, the higher their concentration. That is why the qualitatively positive correlation was observed between the concentration of these elements and their ions, on the one hand, and the precipitation amount, on the other hand.

As was noted above, in the background site 7 the behavior of the chlorine concentration was also peculiar. However, since this site is about 150 km far from the sea, the positive correlation of the Cl concentration with the precipitation amount for it is less pronounced.

As to the site 6 situated in the university campus on the southern outskirts of Antwerp, the effect of industrial sources of aerosol there was almost absent. All the four sampling periods were characterized by the rainy weather and the southern wind direction. The effect of the precipitation amount on the measured concentrations of the elements (negative correlation) is well pronounced for Fe, Zn, Pb (Figs. 5*b* and *c*), less pronounced for S and Ca (Figs. 5*a* and *b*), and absent for Ti and V.

At the same time, the concentration of the elemental Cl (Fig. 5*a*) and Cl⁻ ions in particles larger than 1 μm in this site (Fig. 6*a*) shows the positive correlation with the precipitation amount. Similar dependences were also obtained for Na⁺ ions (not shown). To a less degree, such a behavior is also characteristic of K⁺ ions in particles larger than 2.5 μm (Fig. 6*b*). However, SO₄²⁻ (Fig. 6*c*) and NO₃⁻ ions in particles larger than 1 μm show the negative correlation with precipitation. It is likely that aerosol particles containing sulfates and nitrates are less hygroscopic than sea salt particles enriched with sodium chloride. Therefore, they are less soluble in rain droplets falling from clouds, and so the corresponding ions are removed from the atmosphere just like insoluble compounds, which show themselves in the negative correlation.

Conclusions

Thus, in relatively unpolluted sites such as suburbs and countryside, the concentrations of some elements and ions in aerosol particles can show a qualitatively positive or negative correlation with the amount of precipitation during sampling. It can be supposed that in the former case these elements and ions are contained in the strongly hygroscopic aerosol fraction (which is especially obvious for sodium and chlorine), while in the latter case these are contained in a weakly hygroscopic or insoluble fraction. Hygroscopic characteristics of particles significantly affect the processes of their removal from the atmosphere and, consequently, the concentrations of

the corresponding elements and ions in the near-surface aerosol during precipitation. However, this behavior of elements and ions may be different for particles in different size ranges. The presence of sodium and chlorine in samples and the dependence of their concentrations on the precipitation amount may be connected with a significant concentration of the sea salt particles in the atmosphere of Antwerp situated near the shore of the Northern Sea.

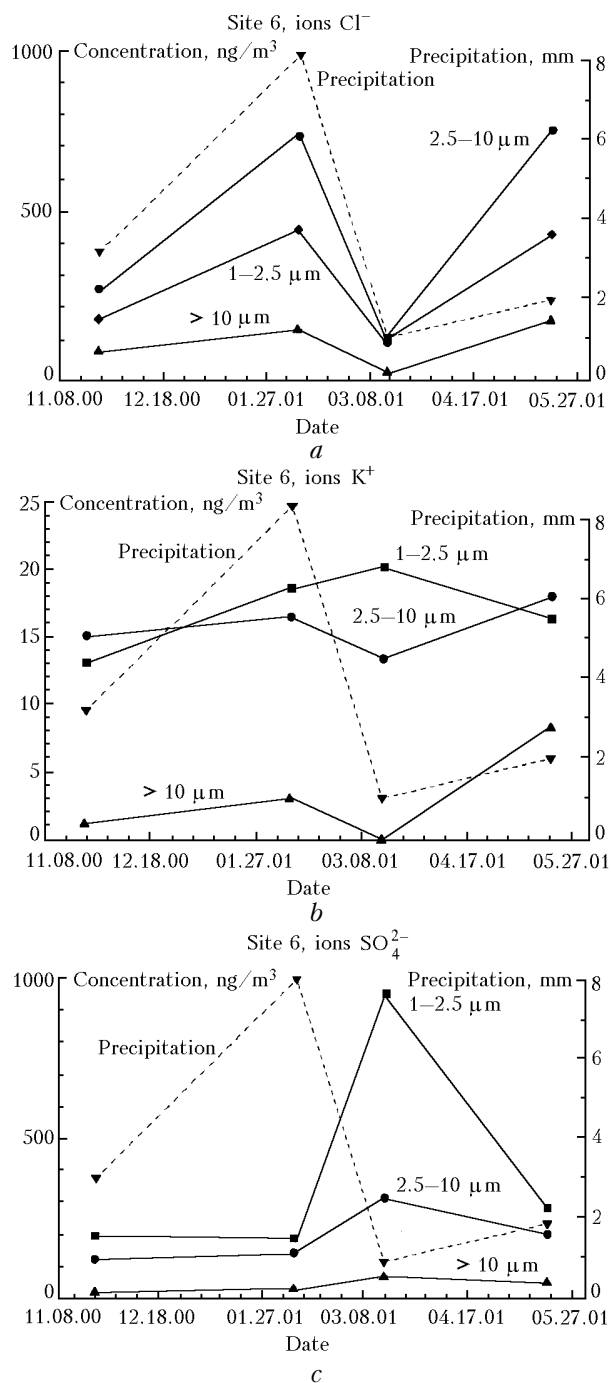


Fig. 6. Measured concentrations and precipitation amount in site 6 (southern suburbs): Cl⁻ ions in three particle size ranges (a); K⁺ ions in three particle size ranges (b); SO₄²⁻ ions in three particle size ranges (c).

At the same time, in the sites located in the industrial or densely built-up urban areas, these effects almost do not manifest themselves because of a high particle generation rate, and only heavy rains are capable of removing aerosol pollutants from the atmosphere.

Acknowledgments

The support from the Federal Ministry of Science, Research and the Arts of Belgium, University of Antwerp, and Flemish Environment Agency is acknowledged.

References

1. W.A. Van Borm and F.C. Adams, *J. Aerosol Sci.* **18**, 593–596 (1987).
2. W.A. Van Borm, F.C. Adams, and W. Maenhaut, *Atmos. Environ.* **23**, 1139–1151 (1989).
3. W.A. Van Borm, F.C. Adams, and W. Maenhaut, *Atmos. Environ.* **24B**, 419–435 (1990).
4. C. Mensink, I. De Vlieger, and J. Nys, *Atmos. Environ.* **34**, 4595–4602 (2000).
5. M.H. Wieringa, J.J. Weyler, F.J. Van Bastelaer, et al., *Europ. Respirat. J.* **10**, 1460–1466 (1997).
6. M.H. Wieringa, J.J. Weyler, V.J. Nelen, et al., *Int. J. of Epidemiol.* **27**, 630–635 (1998).
7. M.A. Byrne and S.G. Jennings, *Atmos. Environ.* **27A**, 2099–2105 (1993).
8. S.K. Mitra, U. Barth, and H.R. Pruppacher, *Atmos. Environ.* **24A**, 1247–1254 (1990).
9. A.E. Kaplinskii and I.A. Sutorikhin, *Atmos. Oceanic Opt.* **7**, No. 8, 619–621 (1994).
10. H. Sparmacher, K. Fulber, and H. Bonka, *Atmos. Environ.* **27A**, 605–618 (1993).
11. M. Väkevä, K. Hämeri, T. Puhakka, et al., *J. Aerosol Sci.* **30** (Suppl.1), S649–S650 (1999).
12. V.A. Arkhipov and V.F. Trofimov, in: *Abstract of Reports at IX Workgroup on Siberian Aerosols* (Publishing House of IAO SB RAS, Tomsk (2002), p. 22.