

Nitric acid and particulate matter measurements at Athens, Greece, in connection with corrosion studies

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Abstract. For a long time, scientists have been concerned about the effects of air pollution on materials and especially on the monuments of the cultural heritage. The EU funded a project, entitled MULTI-ASSESS, to determine these effects and to develop dose-response functions appropriate for the new multi-pollutant environment. The University of Athens participated in this effort as a targeted field exposure test site. In the present paper, the measurements of the passive samplers, which were exposed during the same period with the samples for corrosion studies, at the Athens station, are presented. The results have shown that only 16.5% of the deposited mass was water soluble. The vertical distribution of passive particle collectors has led to the conclusion that the height of maximum deposition of each ion is different. In addition, a variation of the water-soluble mass to total deposited mass between 8% and 31% was observed.

1 Introduction

Air pollution is a multi-component problem for billions of people all over the world, especially for the residents of urban areas (Kondratyev and Varotsos, 1995a, b, 1996, 2001, 2002; Monks et al., 2000; Friess et al., 2006; Heard et al., 2006; Methven et al., 2006; Chandra and Varotsos, 1995). The impacts of this problem can be noticed on living organisms as well as in many other fields (Efstathiou et al., 1998; Feretis et al., 2002; Cracknell and Varotsos, 2007; Tzanis and Varotsos, 2008; Varotsos, 2002; Gernandt et al., 1995). Our material cultural heritage is affected by air pollution which behaves as a complex system (like many geophysical systems) exhibiting a long memory effect (Varotsos and Kirk-Davidoff, 2006; Varotsos et al., 1996, 2005b;

Varotsos, 2005a). Structural materials of monuments, statues, even paintings are spoiled by the interaction with the man-made primary and secondary corrosive pollutants of the atmosphere, the wind and precipitation. The knowledge of how air pollutants and climate parameters lead to material corrosion and which pollutant causes the greatest damage in each region is particularly important for the protection of the historic and cultural monuments as well as for the selection of the appropriate materials for new structures.

In the past, sulphur dioxide has been defined as the fundamental agent causing the corrosion of the materials. Many countries have strived to reduce the concentration of sulphur dioxide in the atmosphere, but the increasing motorized traffic, among other reasons, has caused an increase in the concentrations of nitrogen compounds, ozone and particulate matter. The last leads to a new multi-pollutant situation, which was analyzed by Varotsos et al. (2005a) using measurements that were taken in Athens during the period 1987–2003. The results of this analysis clearly showed that the temporal evolution of air pollution exhibits a long memory effect and particularly persistent long-range power-law correlations from about 4 h to 9 months for PM₁₀.

We have a new pollution situation in Europe today when particle and sulphur dioxide emissions have been reduced substantially. There have been very few measurements of nitric acid because of the high costs of measurements. The emission of nitrogen oxides in Europe has not decreased much and from the few published works on nitric acid it appears that its concentration has not decreased very much either. The relative importance of nitric acid for the corrosion of ancient buildings and artifacts has therefore increased.

Europe is a place with a rich cultural heritage. This fact has sensitized the EU to this contemporary problem. The EU funded a project entitled MULTI-ASSESS (Kucera et al., 2005) with the objective of improving this situation. In this project, 34 European sites from all over Europe as well as one from Canada participated. The project focused on the



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degradation of materials due to air pollution and climate. The primary objective was the development of multi-pollutant deterioration and soiling models of wet and dry deposition of gases and particulates on materials used in objects of the European cultural heritage. In addition, the previously developed dose-response functions, quantifying the impacts of the pollution on specific materials, were modified to correspond to the new pollution situation. These functions can be used by the EU to implement new tolerance levels of pollution in order to minimise the pollution effects on historic and cultural monuments. The measurements of the project were also going to be used to map pollution over Europe and locate the high risk areas (Tidblad et al., 2005).

The University of Athens participated in this effort on behalf of Greece. Athens is a contemporary city suffering from severe air pollution (Cartalis and Varotsos, 1994; Jacovides et al., 1994; Varotsos et al., 2003; Tzanis, 2005; Tzanis et al., 2008). Additionally, in this city there are many historical invaluable monuments, like the Acropolis and the Parthenon. This fact implies the need for monitoring air pollution and further study of its impact on this heritage.

It should be mentioned here that the purpose of the project was not to analyse the particle composition in Athens, but only to analyse those particles that have a high deposition velocity to surfaces and only to analyse the compounds that have a high risk for increasing the corrosion rate. A simple passive particle sampler was developed for this purpose. It was tested in Athens, Rome and London and has now been used all over Europe and at many sites in Asia. The deposition rates of particulate matter as well as other pollutants and climate parameters are being compared to measured corrosion rates at all sites. The particle depositions from individual sites have not been published, but the correlation equations between atmospheric parameters and corrosion rate for different materials. The study in Europe was repeated in 2005/2006 and is now being repeated again. We know from other projects that urban aerosols contain a lot of insoluble matter such as oxides of silicon and aluminium. They can contribute to the soiling which we also measure, but not to the corrosion rate. Water soluble salts, however, are hygroscopic and form electrolytes that can increase the corrosion rate. This and previous studies have therefore focused on the water soluble fraction of the particles with high deposition rates.

2 Experimental

The project was divided into seven work packages (WPs). Athens has participated in WP1, WP2 and WP4 so far. WP1 and WP2 took place during 2002–2004. For the needs of these work packages a station was installed at Patisision Street, in central Athens ($37^{\circ}59'57''$ N, $23^{\circ}43'59''$ E) on the roof of the Ministry for the Environment, Energy and Climate Change building. In this part of the project, the de-

nuder technique for measuring HNO_3 was tested against a new diffusive sampler, which was earlier developed by the Swedish Environmental Research Institute (IVL) (Ferm, 2004). At this kind of passive samplers the gas to be measured is trapped on a filter impregnated with a water-soluble substance. The filter is mounted at the back of a short, wide, tube; gas is transported to the sorbent by molecular diffusion. In the open end of the tube, a stainless steel mesh acts as a wind and insect screen. A $1\ \mu\text{m}$ Teflon filter is located behind the mesh to prevent aerosol from impacting onto the impregnated filter. The accuracy, after the two methods had been compared on a monthly basis, was about $\pm 25\%$, which is acceptable in the EU directives (EU, 1999). The modified median absolute difference estimator (MMAD) and the coefficient of variation (CoV) were $0.16\ \mu\text{g m}^{-3}$ and 24% , respectively. When the two methods were compared on a bi-monthly basis the MMAD was $0.11\ \mu\text{g m}^{-3}$ and the CoV was 18% (Ferm et al., 2005). The average overestimation for Athens was 16% . Due to these results, it was finally decided to use passive samplers for the rest of the project. Besides the good results, passive samplers have some great advantages compared to other methods. They have low cost and there is no need for electricity, technical personnel or field calibration. In addition, passive samplers are ideal for sampling near the objects of interest because they are noiseless and their exposure can be made inconspicuously.

WP4 took place during 2003–2004. For the needs of this part of the project, a new station was installed at Aristotelous Street, in central Athens, on the building of the Ministry for Health and Social Solidarity ($37^{\circ}59'16''$ N, $23^{\circ}43'39''$ E). The building is located at a crossroads, close to the “ring road”. One facade of the building is facing south while the other faces east. At this station, in addition to other specimens, two kinds of samplers were placed: passive particle collectors and diffusive passive samplers. Some of these samplers were exposed on the roof, both in unsheltered and sheltered positions, while the rest were distributed on specific levels at 3 m, 6 m, 9 m, 15 m, 18 m and 21 m height above the ground (ground floor, 1st, 2nd, 4th, 5th and 7th floor, respectively) as sheltered, in order to interpret corrosion and soiling effects on materials as a function of height.

The sheltered samplers were situated at the facade of the building which is facing south, at about 10 m away from the center of the crossroads with an exception for the samplers at the 2nd floor which were placed about 20 m away from the center of the crossroads. The street canyon is about 16 m wide and has an east-west orientation while the traffic is one-way. The prevailing wind direction in this area was NNE. Along the street canyon, at both sides, there are buildings of about 15–30 m height. In front of the sampler location there is a building of about 30 m height.

For the HNO_3 concentration measurements, diffusive passive samplers were used. They were mounted under a rain shield attached to a pole ca 2 m above ground on the rack used for exposing corrosion specimens, on the roof. The

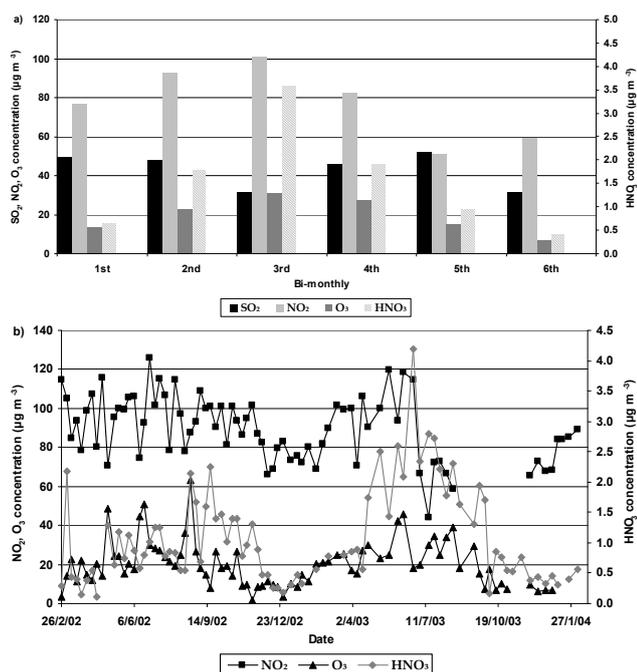


Fig. 1. (a) Comparison between SO₂, NO₂, O₃ and HNO₃ (made by passive samplers) concentrations on a bi-monthly basis at the Aristotelous Street station. (b) Concentration of HNO₃ obtained by denuder technique and the corresponding concentrations of NO₂ and O₃ at the Patisson Street station.

exposure lasted two months for each pair of samplers, for a total period of one year. After the exposure, samplers were sent to IVL for further analysis and obtaining of the results. The main purpose of these measurements was to correlate the nitric acid concentration with the corrosion or degradation rate of the exposed specimens.

Passive particle collectors were used to quantify the deposition of particles. This kind of collector uses a rectangular Teflon filter which is wound around a 10-mm-diameter PVC tubing and is held in place by a small clip. The exposed area is 6.28 cm². This area is used to calculate the deposition. Since there were exposed materials both as sheltered and unsheltered, passive particle collectors were also exposed in the same way. A collector was exposed in an unsheltered position, partly protected from rain but not from wind and it was replaced every two months for a period of one year. Two collectors were exposed as sheltered at each level, just beside the materials specimens, for a whole period of one year. In addition, two other collectors were exposed as sheltered in an aluminium box with open bottom on the main rack on the roof.

The measurements of SO₂, NO₂ and O₃ concentrations were made with conventional analyzers and obtained by the National Service for Air Pollution Monitoring.

Table 1. Start and stop dates for each bi-monthly period.

Exposed period	Start date-Stop date
1st	16/1/2003–18/3/2003
2nd	18/3/2003–20/5/2003
3rd	20/5/2003–21/7/2003
4th	21/7/2003–22/9/2003
5th	22/9/2003–24/11/2003
6th	24/11/2003–16/1/2004

3 Monitoring

3.1 Nitric acid measurements

The results of the six bi-monthly exposure periods for the concentration of HNO₃ obtained by the passive samplers and the corresponding SO₂, NO₂ and O₃ concentrations are shown in Fig. 1a, while the dates of each period are presented in Table 1. In this figure what is obvious, is the maximum concentration of HNO₃, NO₂ and O₃ in summer which indicates that photochemical formation is the important factor for the annual variation. The bi-monthly average HNO₃ concentration is 1.54 μg m⁻³ with standard deviation ±1.17 μg m⁻³. It should be mentioned here that NO₂ and O₃ measurements were made with continuous instruments (APOA, HORIBA Inc., chemiluminescence and UV absorption, respectively) with time resolution 30 s and accuracy ±2 μg m⁻³. Figure 1b presents the concentrations of HNO₃, NO₂ and O₃ at the Patisson Street station for the experimental period which started on 26 February 2002 and ended on 18 February 2004. The measurement of HNO₃ was based on the denuder technique (Ferm et al., 2005). The NaCl coated denuders with an impregnated filter behind were exposed for specific periods during the whole experimental period and after the exposure, they were sent to IVL for analysis. The NO₂ and O₃ concentrations refer to the corresponding exposure period of each denuder.

In Fig. 2a, HNO₃ concentrations, obtained by the passive sampler technique on a bi-monthly basis, are compared to the corresponding NO₂ concentrations. The annual average HNO₃/NO₂ ratio is 1.35% on a molar basis, which is lower than the average ratio of 2.7% of all the urban sites which participated in this project. The equation for the regression line is HNO₃ = 0.05*NO₂ – 2.28 ($r^2 = 0.66$, statistically significant at 95% significance level). In Fig. 2b HNO₃ concentrations, obtained by the denuder technique, are compared to the corresponding NO₂ concentrations. The annual average HNO₃/NO₂ ratio is 0.92% on a molar basis while the equation for the regression line is HNO₃ = 0.005*NO₂ + 0.63 (no statistically significant correlation).

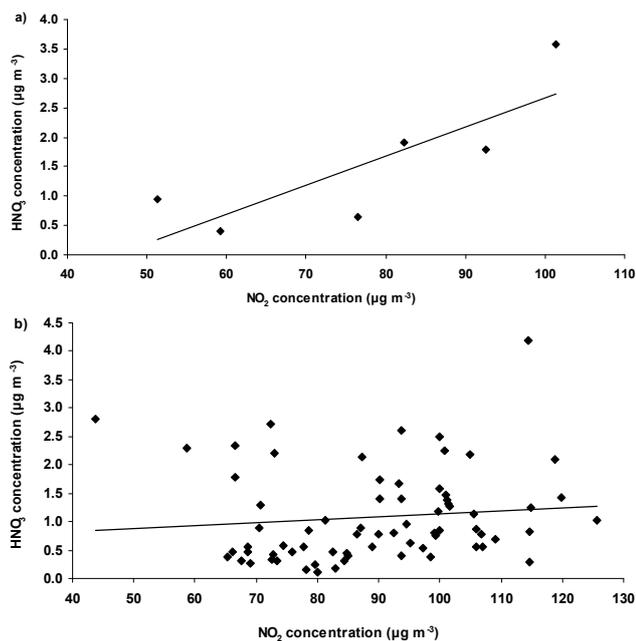


Fig. 2. (a) Nitric acid concentration, obtained by passive samplers, as a function of nitrogen dioxide concentration. (b) Nitric acid concentration, obtained by denuders, as a function of nitrogen dioxide concentration.

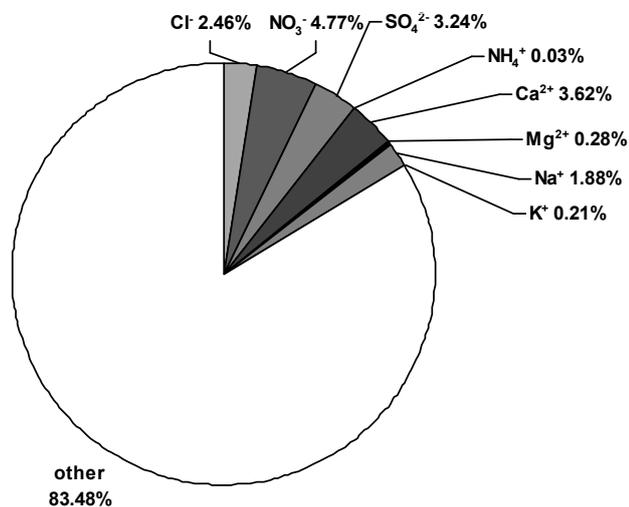


Fig. 3. Average chemical composition (percentage mass) of the deposited mass.

3.2 Particle deposition on unsheltered collectors

The deposited mass varied between $31 \mu\text{g cm}^{-2} \text{ month}^{-1}$ and $157 \mu\text{g cm}^{-2} \text{ month}^{-1}$ with an average of $87 \mu\text{g cm}^{-2} \text{ month}^{-1}$ on a bi-monthly basis. In Fig. 3 the average chemical composition of the deposited mass is shown, while in Fig. 4 the mass of ions/water-soluble

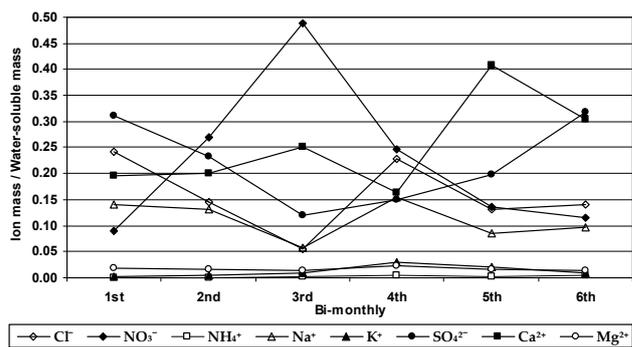


Fig. 4. Mass of ions/water-soluble mass obtained from bi-monthly measurements.

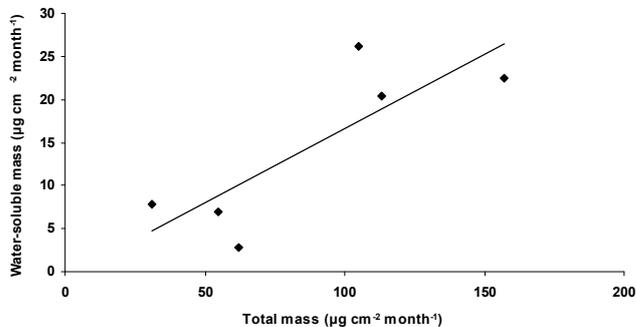


Fig. 5. Comparison between water-soluble mass and total mass on a bi-monthly basis.

mass during the sampling period is presented. It should be noted here that we find a very low content of ammonium compared to other ions such as sodium and calcium all over Europe. The reason for this is that ammonium is only found in accumulation mode particles that have the lowest deposition rate of all modes. Sodium and especially calcium belong to the coarse mode which is more readily deposited near the source. The concentrations of water soluble ions in the air (moles per cubic metre) show the opposite pattern and ammonium dominates.

The mass of the analyzed water-soluble ions seems to have poor correlation with the total mass ($y = 0.17x - 0.55$, $r^2 = 0.66$, statistically significant at 95% significance level) on a bi-monthly basis (see Fig. 5). The unidentified mass on average is 83.5% on a bi-monthly basis. This mass is believed to consist mainly of water-insoluble material. Since the filters were weighted at 50% RH, this difference means that the unidentified mass may also contain water mass along with the water-insoluble material.

In Fig. 6 the average ion balance is shown. The excess of cations of about 27% can be explained by the fact that coarse particles have higher deposition velocities than fine particles and are normally alkaline and are likely therefore to contain carbonate (Ferm et al., 2006). However, equipment

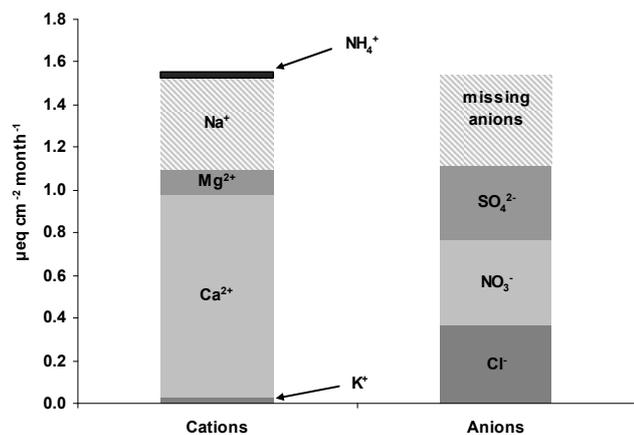


Fig. 6. Average ion balance between analyzed cations and anions in unsheltered position.

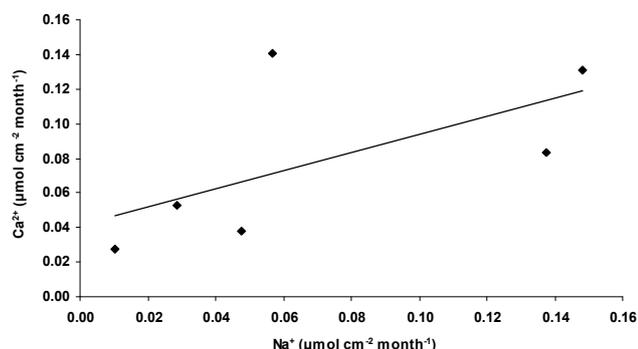


Fig. 7. Calcium deposition as a function of sodium deposition.

to analyse the carbonate content was not available and the sample amount was too small for the analysis of the alkalinity. Another parameter which was not analyzed is the organic anion content.

Figure 7 illustrates the calcium deposition against the sodium deposition ($y = 0.52x + 0.04$). There is poor correlation between them ($r^2 = 0.39$, not statistically significant) while the average $\text{Ca}^{2+}/\text{Na}^+$ ratio is 1.6 on a molar basis. Figure 8 shows the correlation between deposited calcium and nitrate ($y = 0.66x + 0.03$). The result implies good correlation between them ($r^2 = 0.93$, statistically significant at 99% level). Calcium had an average $\text{Ca}^{2+}/\text{NO}_3^-$ ratio of 2.5 on a molar basis. Figure 9 shows the sulphate deposition against the calcium ion deposition and it is evident that the sulphate deposition is poorly correlated with the calcium ion deposition ($y = 0.28x + 0.01$, $r^2 = 0.52$, not statistically significant). The average $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio is 0.39. However, the chloride deposition is very well correlated with the sodium deposition ($y = 0.8x + 0.003$, $r^2 = 0.92$, statistically significant at 99% level) on a molar basis, see Fig. 10. The average Cl^-/Na^+ ratio is 0.89. According to Fig. 11 the Mg^{2+} deposition is also well correlated with the Na^+ depo-

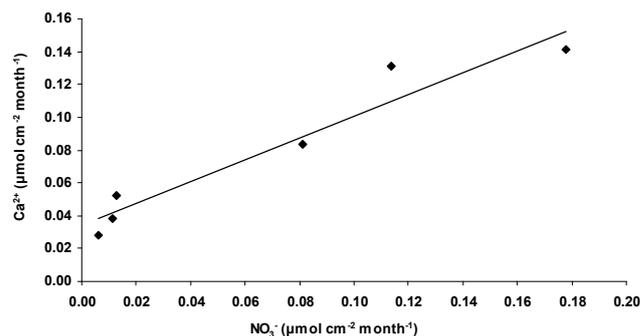


Fig. 8. Calcium deposition as a function of nitrate deposition.

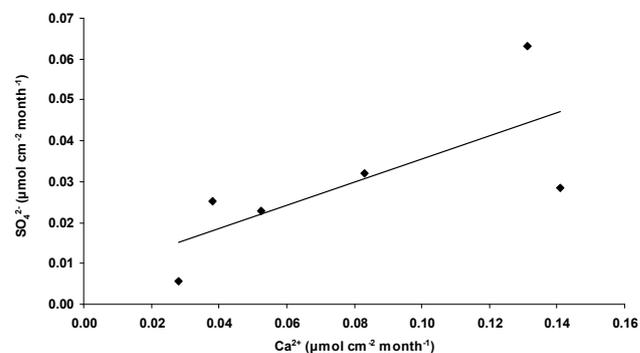


Fig. 9. Non-marine sulphate deposition as a function of non-marine calcium deposition.

sition ($y = 0.12x + 0.002$, $r^2 = 0.91$, significant at 99% level). The average $\text{Mg}^{2+}/\text{Na}^+$ ratio is 0.15.

3.3 Particle deposition on sheltered collectors

The average total mass of deposited particles inside the box was only 24% of the average mass in the unsheltered position. Figure 12 presents the average chemical composition of the deposited mass measured by the two passive particle collectors which were placed in the box. The average deposition rate (amount per unit area and time) of water-soluble compounds in the unsheltered position is 2.65 times the deposition rate of water-soluble compounds in the sheltered position. Figure 13 shows the average ion balance. It can be seen that anions are missing. This is expected, considering the average ion balance for the unsheltered collectors. The deficiency is about 22% (in $\mu\text{eq cm}^{-2} \text{ month}^{-1}$).

Figure 14 presents the profile of the deposition of the ions according to the experimental values, as measured by the diffusive passive samplers at each level. A maximum deposition for the Na^+ , Mg^{2+} , K^+ , NH_4^+ , Cl^- and SO_4^{2-} is observed at the fifth floor level. The deposition of all ions is increased in the range of 15% to 240%. A smaller excess is also observed at the first floor level where deposition of Ca^{2+} and NO_3^- have their maximum value. The fact that the electrical properties, e.g. conductivity, dielectric constant etc., depend on

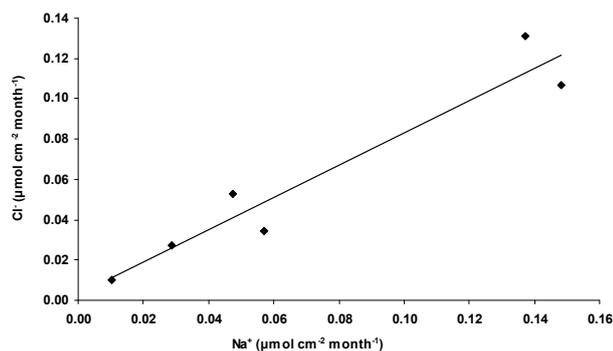


Fig. 10. Chloride deposition as a function of sodium deposition.

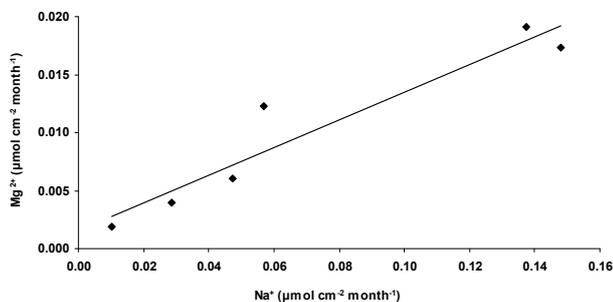


Fig. 11. Magnesium deposition as a function of sodium deposition.

temperature and pressure (Varotsos and Alexopoulos, 1980a, b, 1981; Varotsos et al., 1982) plays a crucial role in the presented observations. It should be mentioned that this is the first study of its kind where the vertical pattern of the particle deposition is measured. There are no similar studies to compare the data with yet. In the other studies measurements were only made at one site per city.

Figure 15a presents the profile of the total deposited mass and the water-soluble mass as a function of height. In this figure the variation of the water-soluble mass as a percentage of the total deposited mass is obvious. This percentage varied between 8% and 31%. These differences in the amount of the analysed mass could explain the profile of the deposited ions shown in Fig. 14. Figure 15b shows the profile of the percentage of each ion mass to water-soluble mass. According to Fig. 15b, a maximum deposition for the Mg^{2+} , NH_4^+ , Na^+ and Cl^- is observed at the fifth floor level. Calcium has maximum deposition at the ground and fourth floor level, while SO_4^{2-} has maximum deposition at the second floor. The maximum deposition of the NO_3^- is observed at the ground floor level while potassium has steady deposition at each level.

The average Cl^-/Na^+ ratio was 0.93 on a molar basis which is close to 0.89 for the unsheltered position. It should be noted that individual sites cannot be representative of an entire city or region. In addition, measurements taken in one year are not adequate for the research of the corrosion of the materials in general.

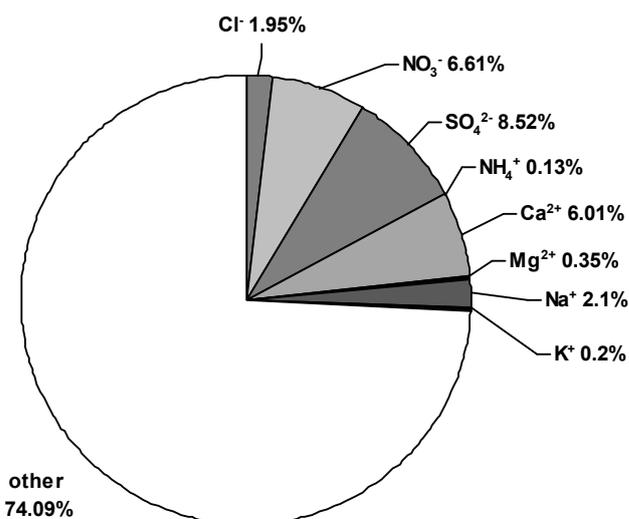


Fig. 12. Average chemical composition (percentage mass) of the deposited mass in sheltered position.

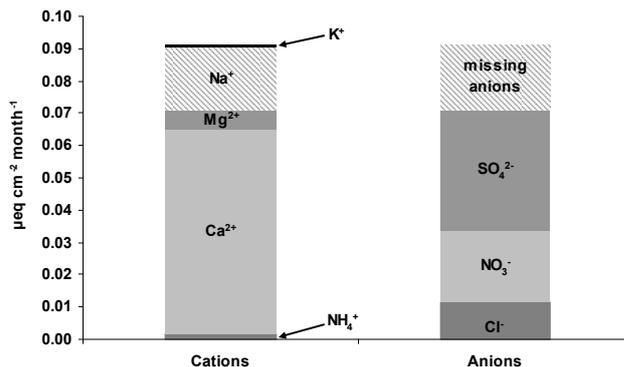


Fig. 13. Average ion balance between analyzed cations and anions in sheltered position.

4 Conclusions

Passive particle collectors were used for the study of the deposited mass. These collectors were weighed before and after their exposure in order to calculate the deposited mass. The quantitative chemical composition of the deposited mass was investigated by the chemical analysis of the water soluble part of the deposited mass, and it was found that it consists of Na^+ , Ca^{2+} , K^+ , NH_4^+ , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^- ions. On the sheltered and unsheltered collectors, 26% and 16.5% of the total deposited particle mass, respectively, was water-soluble. The results indicate that the main part of the deposited particle mass has an unknown chemical composition and further study is required in order to specify its composition. The vertically distributed passive particle collectors have shown that at the fifth floor level the concentration of the water-soluble mass is increased. At this level Na^+ , Mg^{2+} , NH_4^+ and Cl^- have maximum deposition, while

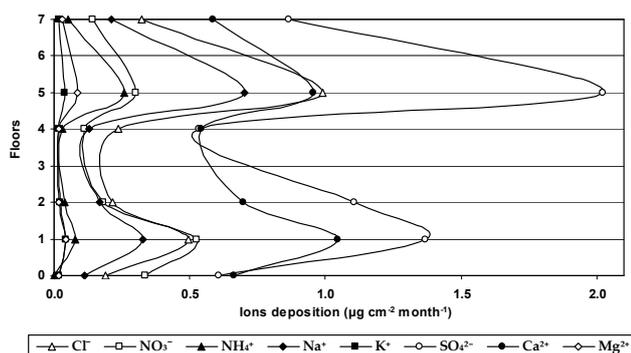


Fig. 14. Ions deposition of the analyzed water-soluble mass as a function of height.

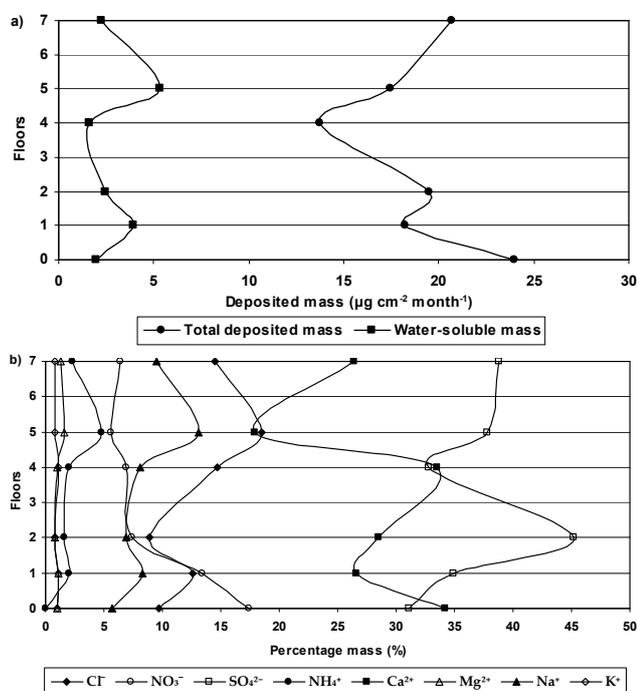


Fig. 15. (a) Total deposited mass and water-soluble mass and (b) percentage of each ion mass to water-soluble mass as a function of height.

Ca^{2+} has maximum deposition at the fourth and ground floor level. SO_4^{2-} has maximum deposition at the second floor and the NO_3^- at the ground floor level. Potassium has the same deposition at each level. For a better understanding of this result there is the need for broad-field measurements for a longer period, because the vertical distribution of particles may vary depending on many factors such as meteorological parameters, sources, transportation and the structure of the city (Chan and Kwok, 2000; Janhäll et al., 2003; Varotsos, 2005b). We are working on the latter and the results obtained will appear elsewhere in due course.

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