

***Interactive comment on* “Chemical
characterization of the inorganic fraction of
aerosols and mechanisms of the neutralization of
atmospheric acidity in Athens, Greece” by
E. T. Karageorgos et al.**

E. T. Karageorgos et al.

Received and published: 7 March 2007

This manuscript presents a series of results and 3) Sampling: the results were obtained from two different periods: 10 days in August 2003 and 10 days in March 2004.

We would like to thank the referee for his/her constructive comments on our paper, which aided its improvement. We would also like to point out that there appear to exist misconceptions on some aspects of our sampling campaigns. The referee has understood that our campaigns were either 10-days long (S6732; 3rd of the detailed comments) or that we have obtained only 10 daily samples (S6733; lines 3-4). However, as is clearly stated in the manuscript, (Page 12393; Lines 6-7) “Aerosol

sampling took place during two periods, the first between 7 and 27 August 2003 and the second between 8 and 28 March 2004” while later (Page 12394; Lines 16-18), it is cleared out that “Every sampling day was divided into two periods; a morning period from 07:00 to 19:00 and an evening period from 19:00 to 07:00”. Due to space limitations, we have truncated the referee’s comments in our current reply. –

There is a cloud of uncertainty on the sampling methodology -to- Was the flow constant during the 12h or 24h sampling?

Flow-control and measurement data have been carefully documented during sampling. The following paragraph has been prepared for addition in the related part of the manuscript. “For the flow-control and measurement, four new 810C Mass-TraksTM (Full Model No.: 810C-CE-DR-2; SIERRA Instruments, Inc.) were used. The devices have an accuracy of $\pm 1\%$, while they have a maximum systematic reading error of $\pm 0.2\%$. All four devices had been calibrated with air (ref1). At the flow-rate of 6.0L/min, that was employed during our campaigns, the 50% efficiency cut-off point is $10.1 \pm 0.5 \mu\text{m}$ for the DSFU pre-impactor, and $2.8 \pm 0.2 \mu\text{m}$ for the upper 12 μm filter[ref2]. The flow-rate was essentially constant, varying within approx. $\pm 2\%$, throughout the 12-h measurement sessions.” **References**

1. Sierra Series 101 Cal-Bench Automated Primary Calibration System, based on the US National Institute of Standards and Technology method)
2. Luhana L., H. Mao, Sokhi, R.S., 2001. Laboratory and field evaluation of UH Dichotomous Stacked Filter Units (DSFU), University of Hertfordshire. SAPPHIRE Report (EVK4-2001-00192). –

The authors go into excessive detail -to- remove these samples from their dataset.

We would like to thank the referee for pointing out this omission in our manuscript. All the FPM filter samples that were found broken were excluded from the subsequent statistical analysis. The following line has been added in the end of the 1st paragraph, Page 12395: "The broken FPM filters have been excluded from the subsequent calcu-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

lations and statistical analysis". –

The analytical part is given very well -to- due to a number of reasons which are not well quantified (R. Gehrig, et al., 2005). And Page 12400, line 3-10: The conclusion that PM10 concentrations -to- different measuring methods (DSFU and BAPA).

The point of small sample size (10 daily samples) has already been answered (vide supra). The term “daily” in Page 12400, lines 13 and 14 was erroneously used and might have contributed in this misconception. Half-hourly PM10 values obtained with Beta Attenuation were averaged over the respective 12-hour periods corresponding to gravimetric (DSFU) sampling sessions, for the whole of the 21-day long campaign.

Our primary focus in the related section of the manuscript (section 3.2.1, Page 12399, last paragraph) has been the discrepancy observed on our gravimetrically obtained PM-mass between the two sites and heights above ground. The two paragraphs in Page 12400 have been rephrased to better depict this. The comparisons with EU-imposed PM10 levels and the pertinent discussion are due to two facts; firstly, PM mass concentrations in the breathing-zone have not been previously reported for the very centre of Athens and, secondly, as is shown in our study, they are significantly higher than values reported by ministerial reports and other studies at storey or roof-levels, as well as the values obtained at our building-roof-located second site. Following this, comes the difference between PM10 obtained gravimetrically at 1.5 m above ground, and BAPM10, obtained at 5 m above ground. We consider the above discussion useful, as it demonstrates the need to obtain more within-breathing-zone measurements for the centre of Athens.

The discrepancies in the results obtained by use of different methods for sampling PM10 has been addressed in a series of studies, especially for northern European sites. Gravimetrically obtained PM10 concentrations have usually been found to be higher than the ones obtained by TEOM, which entails heating of the filter to as much as 50°C. However, it has also been found that the discrepancies in the results obtained with the different methods decrease with increasing ambient temperature and with

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

decreasing relative humidity (Charron et al., 2005). In addition to this, comparisons between sites in the UK and Germany and sites in Spain have indicated that in warmer climates with lower RH, the agreement between the results obtained with the different methods is usually better (Noack et al., 2001; Williams et al., 2001).

With regard to our employment of different sampling methods (Beta Attenuation and gravimetric) to obtain PM₁₀ mass concentrations in our Athinas St. site, the referee cites a study by Gehrig et al., (2005) to be taken into account. While offering very useful discussion and results on using the two methods, this study, in our opinion, lacks some information on certain aspects regarding how these results were obtained, in order to assure that the discrepancies observed between gravimetric and B-Attenuation PM₁₀ mass concentrations were solely due to the different methods employed. Specifically, a number of definitions are missing from the paper by Gehrig et al.: a) sampling heights above ground; b) information on whether both inlets were next to or at the same heights with each other. c) detailed information on the influences by meteorological conditions on each site.

In addition to the above, referring to the paper by Gehrig et al., the referee mentions that “Gravimetric and beta attenuation PM₁₀ measurements are found to display a ratio between 0.8 and 1.6”, which is not accurate. As is clearly presented on the paper by Gehrig et al., the range of ratios obtained is: (beta attenuation PM₁₀/Gravimetric PM₁₀) = 0.8 - 1.06. In the paper by Gehrig et al. one can observe that ratios of BA-PM₁₀/Grav-PM₁₀ very close to unity (1.02 and 1.06) were obtained for the two sites largely affected by mineral dust/soil. This makes sense in light of two facts: Firstly, no significant volatilisation losses, due to the warming of the sampling line and filter are to be expected for traffic-(re)suspended mineral dust. A known issue of this kind is the dissociation of semi-volatile NH₄NO₃, which in certain aerosol systems across the globe has been found to constitute a significant fraction of the aerosol, yet in other, ammonium-poor systems like ours its formation is not favoured (vide-infra). Another reason that might be responsible for discrepancies between BA and gravimetric PM₁₀ is the loss of water mass, for the same reason

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

as above. We believe that a number of factors including: a) the employment of a method like BA, entailing warming of the filter at 25-30°C (much lower than 50°C); b) in a heavily influenced by soil/re-suspension site like Athinas St., influenced by widespread construction activity; c) under relatively high T and moderate-to-low RH; d) in an ammonium-poor environment where the formation of NH₄NO₃ is not favoured, support our approach to attempt a comparison and statistically identify significantly higher 1.5m-GravPM₁₀ values than the respective 5m-BAPM₁₀, at the same site. The pertinent paragraphs on page 12400, from line 3 and onwards now read as follows:

“A direct comparison of the Athinas St. and AEDA DSFU-PM₁₀ (calculated as the sum: CPM+FPM) (Table 6.b. and Fig. 4.b) shows that the PM₁₀ mass concentrations in the breathing zone, at a height of 1.5 m above ground are significantly higher than the ones at 25 m above ground. It is also shown that morning CPM mass concentrations in Athinas St., are approximately 30% higher than the evening CPM concentrations, while the respective difference for the FPM fraction is approximately 22%. Roughly 35% of the particulate mass is found in FPM and 65% in CPM in Athinas St. Additionally, the morning Athinas St. CPM mass concentrations are approximately 43% higher than the respective ones in AEDA. The difference for the morning FPM concentrations is approximately 28%. Corresponding evening differences are 26% and 17% for the CPM and FPM respectively.

A series of studies have reported discrepancies in the PM masses obtained with different sampling methods such as TEOM or Beta Attenuation (hereafter referred to as BA) and filter-sampling with gravimetric quantification (Allen et al., 1997; Charron et al., 2005 and references therein). Gravimetrically obtained PM masses are usually found to be higher than the corresponding masses obtained with the continuously monitoring methods, and the main reason for this is the warming of the sampling line and filter, which results in the loss of semi-volatile compounds like NH₄NO₃ and water. However, it has also been found that the discrepancies in the results obtained with the different methods decrease with increasing ambient temperature and with decreasing relative

humidity (Charron et al., 2005). In a recent study (Gehrig et al., 2005), comparison of results obtained with Beta Attenuation and filter-samplers for two sites largely affected by mineral dust/soil showed a very close to unity BA-PM10/Grav-PM10 ratio (1.02 and 1.06). This makes sense in light of the fact that no significant volatilisation losses, due to the warming of the sampling line and filter at approx. 25-30°C inside the BA, occurred for traffic-(re)suspended mineral dust. In our study, in addition to the primary focus of directly comparing gravimetric PM mass concentrations obtained in the two sites, comparison of the PM masses obtained with the different methods in Athinas St., is considered applicable due to a number of reasons. Firstly, Athinas St. was a heavily influenced by soil/re-suspension site, with widespread construction activity taking place. Secondly, the weather conditions in the region during the campaign were characterized by relatively high temperatures and moderate-to-low relative humidities. Thirdly, as will be further discussed below, the region under study is an ammonium-poor environment where the formation of semi-volatile NH₄NO₃ is not favoured. In light of the above, half-hourly PM10 values obtained with BA (BAPM10) in Athinas St. were averaged over the respective 12-hour periods corresponding to gravimetric (DSFU) sampling sessions and the BAPM10 were found to be significantly lower than the gravimetric DSFU-PM10 concentrations measured at the same site. Comparative results are shown in Table 6.a. and Fig. 4.a. Examination of the morning and evening values in Table 3, for BAPM10 and DSFU-PM10 shows that the morning mass concentrations are generally much higher than the evening ones.

References

- Allen, G., Sioutas, C., Koutrakis, P., Reiss, R., Lurmann, F.W., Roberts, P.T., 1997. Evaluation of the TEOM method for measurement of ambient particulate mass in urban areas. *Journal of the Air and Waste Management Association* 47, 682-689.
- Charron, A., Harrison, R.M., Moorcroft, S., Booker, J., 2004. Quantitative interpretation of divergence between PM10 and PM2.5 mass measurement by TEOM and gravimetric (Partisol) instruments, *Atmospheric Environment* 38 (3), 415-423.
- Noack, Y., Floch, M.L., Robin, D., Leopold, A., Alary, C., 2001. Comparison of PM10

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

concentration measurements by TEOM and Partisol instruments in two sites of South of France (in French). Pollution Atmosphérique 171, 413-425.

Williams, M., Bruckmann, P., 2001. Guidance to member states on PM10 monitoring and intercomparisons with the reference method. EC Working Group on Particulate Matter

–

Finally, the authors despite... -and- In my opinion -to- collected aerosol.

The issue regarding the number of our samples has been addressed above. All conclusions derived and indications mentioned, have been established upon examination of inter-ionic correlations per sample and not from mean ionic concentrations. In addition to the 12-hour duration of the sampling sessions in our campaigns, the moderate-to-low RH and relatively high temperatures in the area under study, accounting of the possibility for sampling artefacts has been mentioned in the first paragraph of section 3.2.3. This section is principally based on literature cited, including the study by (H. Kouyoumdjian and N. A. Saliba, 2006) that the referee suggests. This paragraph (Page 12403, Lines 11) has been considered for change and it now reads as follows:

“The absorption of SO₂ on particles collected on filters, which could lead to sulfate artefacts, has been found to be negligible for ammonium poor environments (Pathak et al., 2004). The above can be assumed to be applicable in the present study, given the moderate-to-low SO₂ concentrations obtained at two sites nearest to ours during the March campaign (29 ug m⁻³ in Patision and 22 ug m⁻³ in Aristotelous; PERPA; Hellenic Ministry of Environment”.

Apart from the above, we agree with the referee that a specifically-setup experiment, entailing sampling and analysis of gaseous species, with, perhaps, the combined use of modelling, would be required in order to fully assess the neutralization “closure”. The current study, however, does not present a “closure approach” accounting for all (solid and gaseous) species involved in the neutralization processes, it does not report any modelling results upon the neutralization of all acidity existent in the Athenian at-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

mosphere, nor is it entitled “- and the neutralization of atmospheric acidity”. Instead, it proposes certain “mechanisms”, demonstrating the chemical attitude of specific compounds, in relation to the neutralization of atmospheric acidity. It does so based on ionic abundances, inter-ionic ratios and correlations, as well as on aerosol-system-specific thermodynamic predictions. It is therefore carefully entitled “- and mechanisms of the neutralization of atmospheric acidity”. We believe that our data do suffice for this and total omission of this discussion would probably “hide” information that can be derived from the data. –

DETAILED COMMENTS 1) The authors mention the use of OPCs and DMPS -to-removed.

Reference to this instrumentation has been subtracted from the revised ms. –

2) Introduction, line 25 the authors report data about the vehicle fleet in Athens -to-added.

The data presented are based on various reports (in Greek) and personal communication with the pertinent Ministries. To date, we have unfortunately not found any, complete from every aspect, state report on the Athens vehicle-fleet, that would be in English and citable. However, we cite a Ph.D. manuscript containing related information, albeit in Greek. **References** Simmeonidis, P., “Study of atmospheric pollution and its sources by use of GIS”, Ph.D. Thesis, Aristotle University of Thessaloniki, 2002 –

Page 12392 line 5 there are a number -to- that could be mentioned

In addition to the studies already cited in the lines mentioned, we have included the following references: *M. Sillanpaa et al., 2005, Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe, Atmos.Chem.Phys., 2005* and *Markus Sillanpaa et al., 2006, Chemical composition and mass closure of particulate matter at six urban sites in Europe, Atmospheric Environment 40 S212-S223–*

4) Elemental analysis: ISO 17025 -to- it should be mentioned.

The laboratory is accredited for PIXE. This will be included in the revised ms. –

5) *Results and discussion: page 12398, line 25: the authors state -to- for S high values.*

By 2003 and 2004, automotive diesel in Greece, used by buses and taxis in Athens, was officially the richest in sulphur, in the EU [ref1], while, realistically, it is expected to have been even richer due to adulteration with other kinds of diesel [ref2]. Notwithstanding the implementation of measures for the widespread introduction of low-sulphur-content diesel, sulphur concentrations are believed to still be higher by as much as an order of the magnitude than the 50 ppm limit (Ministry of Environment, Ministry of Transportation, personal communication).

References

Quality of petrol and diesel fuel used for road transport in the European Union, REPORT FROM THE COMMISSION, Second annual report (Reporting year 2003), COM(2005) 69

S. Kalligeros, F. Zannikos, S. Stournas, E. Lois and G. Anastopoulos, A survey of the automotive diesel quality in the Athens area, INTERNATIONAL JOURNAL OF ENERGY RESEARCH, Int. J. Energy Res. 2001; 25:13811390 (DOI: 10.1002/er.764)

The lines the referee mentions on page 12398, line 22 and on, have been changed as follows:

"A "trend" of the prevalence of evening over morning values for FPM S and Cu in both fractions is worth mentioning, as well as the fact that an increase in the concentration of the latter has been recently reported compared to the late 80's (Manalis et al., 2005 and references therein). Such an increase was seen in the August campaign, when in Athinas St FPM Cu mean concentration has more than doubled compared to the one reported by Scheff and Valiozis, (1990), but not during the March campaign. During the March campaign, AEDA Cu concentrations were found to be only slightly higher to the ones reported by Scheff and Valiozis, (1990). The respective March 2004 Athinas St. concentration was lower than the one obtained in the August 2003 campaign in

the same site, lower than the one obtained in AEDA in the same campaign, and lower than the one reported by Scheff and Valiozis (1990). It can thus be derived, that Cu-enrichment sources during the August 2003 were less active or influencing the Athinas St site during March 2004, which is to be further researched in the future. A similar seasonal pattern is observed for higher in August and overall high sulphur concentrations. Significant contribution to the sulphur-concentrations is believed to be due to the high sulphur-content of diesel for road-transport in Greece [ref1 and 2], in addition to the major contribution by fossil-fuel combustion for domestic heating during the March 2004". –

Page 12399, line 10: No increase is observed for Cr according to the data shown in Table 5a.

Table 5.a. compares Athens Cr concentrations with other recent studies for other major cities of Europe. No older Cr values for Athens are mentioned in table 5.a. This point is derived by comparison with the ones of previous studies (Manalis et al., 2005 and references therein) which has been clarified in the revised ms. –

Page 12401, line 5-20: How does the agreement with previous PM10 measurements at 25 m above ground support the fact that the concentrations in Athens are higher in the breathing zone?

The lines the referee points out should be read within the context of the related section "3.2.1". Specifically, another study (Valavanidis et al., 2006), with sampling carried out during approximately the same period, in a nearby to AEDA site, and at a similar height above ground (25m), has reported very similar PM10 mass concentrations and distribution of mass in the two fractions, to the ones we gravimetrically obtained at the AEDA site. These values (ours and of Valavanidis et al., 2006) are reasonably close to the values presented in a series of other recent studies for Athens, for the years 2001-2003, in the references mentioned in the lines 5-20. These measurements were carried out in nearby to Valavanidis et al., sites as well as in a couple of other Ministry Sites,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

at heights above ground level mentioned in the text. The above, as well as the fact that our Athinas PM10 values, at 1.5 m above ground, have been found to be significantly higher than the AEDA site values, and, consequently, to the ones reported in the other authors' studies cited, support the fact that near-ground, within-breathing-zone PM10 mass concentrations were higher. –

Page 12403 line 24: Since Ca is predominantly found in coarse particles has a unimodal distribution.

We would like to thank the referee for pointing this out. The correction has been embodied in the revised ms.–

Page 12406: all these details -to- total particulate mass

The approximate percent of the analysed inorganic versus total particulate mass is already been given in Figure 2. We disagree with the referee that the details upon the way it was calculated should be omitted, as this may aid to validate comparisons in future studies. The discussion on what we believe constitutes the non-analyzed part of the particulate should also remain in the text especially since CO₃⁻ and OH⁻ are probably chemically bound, to a significant extend with the predominant Ca²⁺.–

Page 12407, line 10-20: the whole paragraph is - to- neutralizing agents. and Line 21: The formation of NH₄NO₃ is rapid compared to the formation of (NH₄)₂SO₄

Inter-ionic ratios, thermodynamic predictions and existent literature cited indicate that in our ammonium-poor environment there is insufficient ammonia to fully neutralize the available aerosol sulfate. Ammonia is, therefore, expected to be driven to the aerosol phase to be consumed forming NH₄HSO₄, (NH₄)₃H(SO₄)₂ and (NH₄)₂SO₄ which are the favoured salts in the competition between NO₃⁻ and SO₄²⁻ for the available NH₄⁺. The partial pressure of NH₃ shall therefore be very low and the concentration levels of NH₄NO₃ will, consequently, be very low as well. The above are supported by inter-ionic correlations presented. The manuscript does not state that ammonia

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

concentrations are very low but that NH_4^+ concentrations in CPM are very low. The conclusion that NH_4^+ is insufficient to completely neutralize atmospheric acidity was not based on the fact that it is mainly found in the fine fraction but on examination of its equivalent ratio with sulfate. This paragraph was not very clearly phrased, partly due to the phrase “as a result of this” (Page 12407, line 12), which is misleading. This and the following paragraph have thus changed:

“Atmospheric ammonia, in its NH_4^+ form, is found predominantly in FPM whilst the CPM is NH_4^+ poor. As has been previously stated, the ambient molar particulate NH_4^+ / SO_4^{2-} ratio has been found to be less than 1.5, which is indicative of an ammonium-poor aerosol system, where the existing NH_4^+ is insufficient to completely neutralize the available sulphuric acid. Therefore, the formation of NH_4NO_3 is not favoured (Seinfeld and Pandis, 1998 and references therein; Pathak and Chan, 2005; Trebs et al., 2005). The correlations between NH_4^+ and SO_4^{2-} (Tables 7a and b) indeed suggest that in the fine particles, NH_4^+ is an important neutralizing agent of sulphuric acid forming salts like NH_4HSO_4 , $(\text{NH}_4)_3(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{SO}_4$. In addition to this, and as expected, the respective correlations for NH_4^+ and NO_3^- are low, in agreement with the prediction that formation of NH_4NO_3 is not expected to occur to a significant extent. The relatively little NO_3^- in the fine fraction, correlates well with Mg^{2+} and relatively well with Ca^{2+} which is indicative of formation of salts like $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$. Water-soluble ionic calcium is by far the most abundant species in the CPM fraction. This taken into account, the good correlation between CPM Ca^{2+} and CPM NO_3^- and SO_4^{2-} (Tables 7a and b), suggests that calcium-containing aerosols, originating from the calcium-rich soils in the region and the quick-lime extensively used in painting facades in Greece, are probably the most important neutralizing species in the coarse fraction, on the surface of which acids like H_2SO_4 and HNO_3 react to form $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 . Lastly, strong correlations observed between Na^+ and Cl^- and Mg^{2+} and Cl^- , for both fractions, indicate the presence of NaCl and MgCl_2 salts, the biggest percentage of which is found in the coarse fraction. The above are in agreement with aforementioned studies for Greece (Tsitouridou and Samara, 1993;

Danalatos and Glavas, 1995; Eleftheriadis et al., 1998), for other locations with similar crustal composition, in the eastern Mediterranean (Graham et al., 2004; Kouyoumdjian and Saliba, 2006), as well as for other parts of the world (Davis and Jixian, 2000; Pathak et al., 2004; Xie et al., 2005). –

The Cl/Na ratio from tables 3 and 4 does not agree - to- chloride depletion occurs In fine particles

Indeed there is a difference between tables 3 and 4 and the FPM Cl-/Na+ ratio mentioned in the text, which the referee has rightfully pointed out. During the March 2004 campaign, on 3 sampling sessions, very high values of FPM Na+ and Cl- were observed. These “outliers” significantly deviated from the distribution of the rest of these species values in the FPM dataset by more than an order of the magnitude. The respective concentrations of the rest of the ionic and elemental species were not especially high, nor sampling or analytical problems were identified during these three sessions. The large quantities of these two ions in the fine fraction might be due to local meteorological effects. These samples create an “outlier’s effect” if used in the mean concentration calculations, presented in tables 3 and 4, as the resulting mean concentrations significantly increase, giving a large positive bias upon the mean concentrations. These sampling sessions were not used in the mean concentration and in the ionic balance calculations. However, they were, erroneously, used in the Cl-/Na+ calculation, which has led to a molar ratio of approximately 1, which in turn led to a distortion of our initial finding. This shall be corrected in accordance to the fact that, as a general trend chloride depletion does occur to an extend in the FPM, with the exception of some sampling sessions when, for reasons yet to be established, large quantities of Cl- and Na+ were obtained, at molar ratios well above 1. The mean chloride depletion %Cldep has been calculated according to Holland, 1984; Yao et al. (2001). In order to clarify this in the manuscript, the related part of the text will change to include a summarized version of the above discussion as follows:

“- In addition to that, the reaction of CPM CaCO_3 , with HNO_3 and H_2SO_4 predominates over the reactions of particulate NaCl with HNO_3 and H_2SO_4 , as the first set of reactions are faster than the latter. As a result of this, chloride depletion, via formation of HCl and evaporation to the gaseous phase, is negligible for the CPM fraction, where the largest percentages of particulate Cl^- and Na^+ have been observed and Ca^{2+} is by far the most predominant ion. Their ratio has been found to range between $1.6 \leq \text{Cl}^-/\text{Na}^+ \leq 2.2$ (neq/m^3) for the two sites, supporting the above conclusion. Chloride depletion was found to occur in the fine fraction, and the percentage of depleted FPM- Cl^- calculated with the method suggested by Holland (1984); Yao et al. (2001), has been found to be approximately 33% for Athinas St. and 55% for the AEDA site. However, on three sampling occasions high FPM concentrations of Cl^- and Na^+ were obtained, with a molar ratio of Cl^-/Na^+ well above 1. In the same sampling sessions, the concentrations of the rest of the species were not especially high and no sampling or analytical problems have been identified in relation to these three sessions.”

References Holland, H.D., The Chemical evolution of the Atmosphere and Oceans; NJ, 1984; p450, Yao, X., Fang, M., and Chan, C., (2001), Experimental study of the sampling artefact of chloride depletion from collected sea salt aerosols, Environmental Science and Technology, 35, 600-605–

Page 12408, line 24: the possible influence -to- not highlighted.

The related part of the manuscript has changed, in accordance to the referee’s suggestion, as follows: "For example, one could note Ca enrichment and Ga, Sr and Zr deficit. It could also be argued that S, Zn, Cu, Pb, Sn, Mo, As and Sb peaks can be attributed to fossil fuel burning and to traffic related emissions (tyres, catalysts and brakes), whilst the extensive construction activity in the centre of the city at the time has probably contributed, to a significant extend, to the aforementioned Ca enrichment, especially in Athinas St." –

Page 12408-9, line 26: The authors had previously -to- traffic has higher influence in this site.

The referee is probably referring to Page 12400, lines 22 and onwards. These lines refer to the significant increase in the CPM mass concentrations as a result of the extensive contribution by construction, traffic and overall human activity (e.g. pedestrians). As discussed in the ms, the biggest part of this increase in CPM mass concentrations has to do with crust-related elements. In the AEDA site, in the fine fraction, traffic/vehicle exhaust-related elements, like the ones mentioned in Page 12408, lines 25 and on, are reasonably found in slightly higher concentrations, due to influence of a nearby city-bus station, an important cross-road, as well as the 4-6 storey buildings surrounding the site. Summing up, the profile of the inorganic fraction in Athinas St., at 1.5 m above ground, could be described as richer in larger, dust/soil-related particles, containing high concentrations of crust-related elements, with a particularly observed significant enrichment of Ca. In return, at 25 m above ground, in AEDA, while the overall profile remains relatively similar, but with smaller overall contributions from dust/soil related species, a slightly higher influence of automotive fuel-related emissions is observed, particularly in the fine fraction. Text in Page 12408, lines 25 and on has changed, in accordance to the above.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 12389, 2006.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)