

## ***Interactive comment on “Anthropogenic and natural constituents in particulate matter in the Netherlands” by E. P. Weijers et al.***

**E. P. Weijers et al.**

weijers@ecn.nl

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Dear editor, colleagues,

Below we address the reviewer issues/questions raised during the open discussion of the paper “Anthropogenic and natural constituents in particulate matter in the Netherlands” by E. P. Weijers et al.. We like to thank the reviewers for their comments. We think that the readability, clarity and content of the paper has improved considerably as a consequence of the comments.

Anonymous Referee #1 Received and published: 17 December 2010

Apart from some textual suggestions containing improvements, clarifications and reductions (part A), which were all followed, the major issues raised by reviewer 1 were

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the use of a factor of 1.3 for TC (B), presence of mineral dust at the Rotterdam site (C) and the estimation of the natural contribution (D). The points are addressed in this order below:

A

Page 26516, line 4: it would be advisable to use a different acronym for CBM, to avoid confusion with the Chemical Mass Balance receptor model. Please insert “pragmatic” after “the so-called”.

As it was not used further in the text, the acronym CBM was skipped. The word “pragmatic” has been inserted.

Page 16517, line 12: what is DCMR?

We clarified the meaning of DCMR.

Page 26517, line 19: were mineral matter components (Ca, Al, Mg, K, Fe,...) analysed?

The mineral matter components were analysed together with a number of other element. An enumeration of all elements analysed is inserted on page 26519 as suggested below.

Page 26518, line 3: were both types of filters intercompared in terms of mass?

No, only the quartz filters were. The comparison for mass on both filter types was part of another (internal) study. It showed that the mass measurements with quartz were, on average, 2  $\mu\text{g}/\text{m}^3$  higher than those with teflon. Page 26518, line 5: how was the soluble fraction extracted from the filters? Please describe the methodology used. The extraction procedure has been explained now.

Page 26519, line 8: please list the elements determined by ICP-MS. Same for the elements summed up to form “total metals”. Figure 3 shows a rather large NA mass which is probably mineral matter given that the major tracers (Al, Ca, ...) were not determined. Is this correct? Otherwise please describe how these constituents were

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analysed.

This observation is not correct. In Figure three the mineral dust tracers are part of the total metals fraction and are separated out in the mass closure procedure. We have now given all elements that were analysed by ICP-MS in this study. It includes the major tracers like Al, Si, Ca, etc.. We have further clarified the analytical methodology. We have further indicated what is meant by 'total metals'.

Page 26523, line25: The levels of SS in PM10 in Cabauw are surprisingly low, especially in comparison with those at Hellendoorn and Vredepeel (located farther away from the coastline). How do the authors interpret this?

In the winter period 7-10 days were missing at Cabauw (compared to the other stations) likely to explain the lower sea salt level at Cabauw. A remark of this kind is added in section 3.1 in reference of table 2.

Page 26526, section 4.2: this section should be summarised, the role of water uptake by aerosols in the mass closure is already well known.

The section has been shortened considerably.

B

Page 26523, line 5: it would be useful for the authors to briefly discuss the limitations of applying a constant factor of 1.3 to TC, instead of converting OC to OM, based on their results. They obtain the "maximum change" at the kerbside site, despite the fact that at this site TC is made up of a larger proportion of EC than OC due to the fresh vehicular emissions, and therefore the increase in the mass due to heteroatoms should be lower than at a rural site where the proportion of OC is higher. Table 4: please provide values also as % of mass, this would greatly aid the reader.

We agree with the referee that there might be some overestimation at a kerbside site. However, the conversion from OC to organic material (OM) is quite uncertain even in the US where many more monitoring data of OC are available than in Europe. This

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is the reason to take a minimalistic approach for a conversion factor via the parameter TC. The use of total carbon in turn is due to the uncertain OC-EC split in the various chemical analysis approaches in use in Europe (ten Brink et al., 2004). These analysis procedures correspond well for total carbon, but yield very different EC/OC ratios. We follow here the approach of US-EPA (Frank, 2006) who compared total mass with summed contributions of the chemical components analysed for a very large number of filters. Frank obtained an optimal mass closure with total carbonaceous matter (TCM) defined as 1.3 times the amount of total carbon (TC). This is derived from measurements in the Speciation Trends Network which contains by definition urban background stations. Therefore, an average factor of 1.3 seems a good compromise in the present study with three types of stations (rural, urban background and kerbside). Remarks of this kind have been added to the text. Table 4 now also includes values as percentage of mass.

C

Page 26525, line 5: the absence of an increase in mineral matter seems unusual, given that the authors do detect an increase in the metal content. The metals are deposited on the traffic ways and therefore should be resuspended simultaneously with mineral dust from the pavement. If no increase in the metal content had been detected, it could have been argued that due to the frequent rain and humidity road dust resuspension is not a significant source in Rotterdam. However, given that metals were detected, it seems unlikely that they would be dissociated from mineral matter originating from the pavement. How do the authors explain this? Would they expect to find the same results in other major cities, e.g., Amsterdam?

As was already indicated in the original text, we share the reviewer's surprise (page 26525, line 3). It seems plausible that a rise in both metals and mineral dust deposited on the street should occur at a traffic site. Their respective magnitude and increase may well be different as the sources of mineral dust (earth crust material from further away) and metals (nearby traffic) are obviously different. A lower rise in mineral dust

than elsewhere may not seem unlogica due to the low area of bare soils or sparsely vegetated areas as well as humid conditions in the Netherlands. The fact that the station is situated not far from a busy crossing with traffic lights resulting in relatively low vehicle speeds may further affect levels of mineral dust. Little is known on the strength of mineral dust resuspension as function of local conditions (traffic intensity, road type, distance to junctions, etc) and meteorology. We have rephrased line 4-5 on page 26525 including the remark that this remains a topic to be investigated.

Page 26532, line 10: it was stated in previous sections that road dust resuspension in Rotterdam is not linked with mineral dust, which is a contradiction with what is stated here.

The statement that resuspension appeared not to be linked with mineral dust in Rotterdam was made earlier with some surprise and the need for further study. We added the word “usually” into the text on page 26532, line 9.

D

Page 26530, line 17: based on the authors’ reasoning, the contribution of natural sulphate should be 5%, not 5-10%.

It is stated that 5% of the primary sulphate is of marine origin. There are some additional sources of natural sulphate indicating that the natural part of sulfate is between 5 and 10% with 10% as an upper limit. In table 5 we did use the 5%. We slightly changed the text to stress that we used the conservative estimate.

In addition, considering the vast contribution of total nitrate to PM levels in the Netherlands, 5% seems like a rather large % for natural nitrate contributions. The authors’ reasonings in this entire section are perfectly valid from a theoretical point of view, but it would be interesting to read reviewers’ comments if a study originating in Southern Europe ever tried to justify sulphate and nitrate as being natural... Regarding OC, as stated by the authors the debate on the natural vs anthropogenic sources of OM is

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currently large and inconclusive. I would therefore recommend a more conservative approach and to remove OC from the calculation of the natural PM fraction.

The 5% for nitrate was mentioned as an absolute upper percentage (see lines 5-6). To meet the reviewer's criticism we now apply the range 0-5% in the approximation. The suggestion to remove OC from the approximation is not followed. We extensively discuss the limitations here. However, although there is much debate, it is agreed upon that a substantial part is of natural origin. We want to point out that in the evaluation of the  $^{14}\text{C}$  determination in Dutch PM samples a percentage of some 70% was obtained for the biogenic contribution (including agricultural activities and biomass burning). With this in mind, a range of 25-50% seems defensible. In addition, we want to have an estimate for all constituents to obtain a complete picture here.

Page 26532, line 26: 20% of mineral dust as natural in NL is not a very conservative Approach

As a more conservative estimate we now apply a central value of 10% (which by the way change the estimation with  $0.5 \mu\text{g}/\text{m}^3$ ).

Page 26533, line 15: in general, the assumptions described in section 4.4 regarding the natural fraction of PM seem to provide a rather high estimation (25% of  $\text{PM}_{10}$ ). The approach is correct, but more conservative assumptions would probably yield a more realistic estimate.

See remarks above where more conservative assumptions have been made. Note that the contributions of sea salt and the carbonaceous particles dominate the natural contributions. Small adjustments in the assumptions concerning SIA and mineral dust do not impact the estimates to a large extent.

Anonymous Referee #2

Below we address the reviewer issues/questions raised during the open discussion of the paper "Anthropogenic and natural constituents in particulate matter in the Nether-

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lands” by E. P. Weijers et al.. We like to thank the reviewer for his comments and text suggestions.

Specific comments In the following comments sometimes revised phrasings are proposed. This appeared the best way of highlighting the points that were difficult to understand at first reading. Of course different presentation may be chosen if the desired level of transparency is reached.

p26515 line 4: replace “balance” by “closure”, as used by Harrison et al.

Done.

P 26518 line 10 to 16: IC is a standard technique, could be compressed

This text has been reduced.

P 26519 Line 7 which filter type was used for elements, , in case of silicon: digestion method?

Information on filter type and digestion method has been given.

Lines 19-20. present overview (at least range) on sample numbers

This information has been given.

P 26520 Line 10/table 2: In the table average values are presented with indicators of variability (not explained, presumably standard deviations). For such data showing variation over time which is driven by meteorology there might be few high values being very influential on the average values. Use of the more robust medians is recommended, as well as use of min/max or 10/90percentiles instead of standard deviations.

Indeed, table 2 provides the means and standard deviations. We have adjusted the table caption to clarify the use of standard deviations. We feel along with the reviewer’s comment that medians may be more robust. However, for the application in a mass closure exercise we prefer the use of averages for the following reason. The different

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species in PM show different variability with meteorological conditions. For example, sodium peaks with westerlies whereas sulphate peaks at easterlies and nitrate is much more enhanced in slow wind speed conditions than sulphate is. Hence, when medians are used the median concentrations for every component represent various air masses / conditions. Hence, these introduce additional uncertainties in the mass closure compared to the use of averages. Considering that we have about 30 filters per station with complete chemical analysis this might be of particular importance. To test the robustness of the averages at days with complete chemical analysis we have compared the concentrations of the components to the averages of the full time series and these were in good agreement showing that the averages given here are representative.

P26521 Lines 1-5: Did you make an ion balance (equivalent concentrations)? Any conclusion from this? Does the observation apply also to median concentrations? Lines 24 and following: A table showing the assumed oxides would be helpful.

Yes, an ion balance was made. It proved that the majority of the nitrate is in the form of ammonium nitrate and present in the fine mode at Cabauw. These findings were confirmed by MARGA and MARGA-sizer observations that were partially performed simultaneously. These data are reported by ten Brink et al. (2009) and Schaap et al. (2010). The observation made here is also valid for the median concentrations as well as for the averages over all available samples. A table of the oxides is presented in Schaap et al. (2010a) and we have added the reference.

P 26522: Lines 4 and following: This section is not entirely clear. First of all, the note given in brackets in line 7 may lead to confusion, because the chosen factor of 3.26 actually does include chloride (based on seawater composition). So the note "contribution of Cl is then neglected" only makes sense if this refers to the measured chloride concentrations. If this understanding is correct, please replace the note by "contribution of actually measured Cl is then neglected". For clarity it should be added that measured Na and Cl concentrations are eliminated from the mass closure total after the SS constituent has been calculated.



This is correct and inserted/changed in the text.

Secondly, the statement in line 9 “change in the not-analysed part. . .” is not expressed sufficiently clear. Proposal for change: (according to the reviewer’s understanding): “The estimated SS contribution (using the given Na<sup>+</sup> concentration and the factor of 3.26) will differ from the actually measured sum of Na and Cl concentrations. Hence, the difference between this sum and the estimated SS contribution has to be discounted from the NA fraction.” With regard to the neglected Mg and other seawater compounds it should be noted that the calculation described results in double counting of these compounds as long as they are part of the “metals” fraction. Of course this is of minor importance for the balance. Similarly, it should be stated more clearly that double counting of sulphate has been taken into account by subtraction of SS sulphate from SIA sulphate.

These remarks clarify the procedure and the texts have been rephrased according to the reviewer’s suggestions.

P 26523 Line 4-5: the statement of maximum change (+1.4 µg/m<sup>3</sup>) is confusing because in table 3 an average increase by 1.5 µg/m<sup>3</sup> is reported for PM<sub>10</sub> at urban sites. Presumably the statement refers to PM<sub>2.5</sub> only. If so, this should be made clear.

This was indeed the case and made clear in the text

P26529 Lines 4-11: Again, the issue is not expressed in a way that it can be understood easily. Provided the reviewer did understand correctly what is meant, the problem could be addressed as e.g. “From this formation pathway the problem arises how to correctly assign the coarse mode nitrate to the PM constituents SIA and SS, respectively. In the chemical... (. . .). Hence, when one would put both the sea salt estimate and the full coarse mode nitrate into the SS constituent, the sea salt.. (. . .)” Lines 12-29: This section is not very transparent, some proposals for improvement follow: Line 12, 2nd sentence should more clearly show which calculations are presumed to have been made according to the reviewer’s understanding: “The first is to replace (on a

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molar basis) a part or all of the estimated chloride concentration in the SS constituent by the measured coarse nitrate concentration. In case the coarse nitrate exceeds the estimated chloride the remaining part of nitrate is kept in the SIA constituent". Line 14: "The second option is to keep the estimated SS constituent as it is and to discount from the SIA constituent the coarse nitrate fraction that potentially may replace the sea salt chloride" Line 15: the statement given is not completely valid, as the actual measured chloride has been omitted in the mass balance. A more appropriate statement could be: "The first option reflects the substitution processes taking place on sea salt particles"

The reviewer understood the meaning correctly and we have followed the suggestions of the reviewer to clarify the text.

P 26530 Line 17: should be 5-6% according to the arguments given This issue has already been addressed in the answer to the first reviewer (see above)

P 26531 Line 5: Following the argumentation that there is 4% of NO emissions assignable to soils, of which 2/3 are agricultural and 1/3 is from forests (which also are agricultural to a large part!) and all other processes contributing by 1% at most the given estimate of 5% natural NO<sub>x</sub> appears much too high.

We have addressed this point in the answer to the first reviewer and applied a range of 0-5% for the natural contribution to nitrate .

Line 11: Ammonia is a compound with a complex atmospheric chemistry, and having particularly high dry and wet deposition rates. Hence, the assumption that all naturally emitted ammonia ends up in the PM phase appears to be an exaggeration.

We assume that both natural and anthropogenic ammonia have the same lifetime as both are emitted from low sources. As ammonia is in thermodynamic equilibrium with ammonium in aerosols and is constantly exchanging between gas and aerosol phase, especially with a lot of ammonium nitrate, we feel that the natural to anthropogenic

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ratio is the same in both the gas and aerosol phase. For a more detailed assessment including all processes a model study is required. We have added the first assumption to the text.

P26533 Line 7: In this calculation the estimated SS, which assumes no Cl losses, is taken as the actual natural contribution. A comment on validity and limitations of this approach should be given.

We have referred back to the discussion in section 4.3 by adding the following comment: “Note, that this fraction represents the source attribution and therewith fresh sea salt as discussed in section 4.3 and would be lower when one reflects the chloride loss in this calculation”

Technical comments P26514 line 16: replace “mass not account for” by “unaccounted mass” for better readability line 17: “equal of were lower”: typo, replace “of” by “or”  
done

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C13419/2011/acpd-10-C13419-2011-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26513, 2010.

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