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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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General comments The paper reports data on PM composition from a comprehensive measurement program carried out in the Netherlands The results and their implications are of substantial interest, both scientifically and for the clean air policy in the North-West European region. However, I agree with reviewer 1 concerning the potential exaggeration of the natural PM fraction. The method to infer natural PM contributions from (estimated) shares of natural emissions is questionable. As the dataset comprise chemical compositions from various sites of different location and type the paper cannot be short. However, some parts could be well compressed. On the other side, some more clear explanations would considerably improve the readabiklity and transparancy. Some important comments on this are already given by reviewer #1 which I also support.

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. P 26518 line 10 to 16: IC is a standard technique, could be compressed P 26519 Line 7 which filter type was used for elements, , in case of silicon: digestion method? Lines 19-20. present overview (at least range) on sample numbers 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. 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 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.

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+ 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. P 26523 Line 4-5: the statement of maximum change (+1.4 μg/m^3) is confusing because in table 3 an average increase by 1.5 μg/m^3 is reported for PM10 at urban sites. Presumably the statement refers to PM2.5 only. If so, this should be made clear.

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 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”

P 26530 Line 17: should be 5-6% according to the arguments given

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 NOx appears much too high.

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.

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.

Technical comments

P26514 line16: replace “mass not account for” by “unaccounted mass” for better readability line 17: “equal of were lower”: typo, replace “of” by “or”

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