

Authors' Responses to Reviewers' Comments

Journal: Atmospheric Chemistry and Physics

Manuscript ID: acp-2017-1242

Manuscript Title: Snow scavenging and phase partitioning of nitrated and oxygenated aromatic hydrocarbons in polluted and remote environments in central Europe and the European Arctic

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Reviewer #1 Comments

1) Reviewer's comment

The authors present a valuable dataset on the content of harmful nitro(poly)aromatic pollutants in snow precipitation. The results of field samples analyses are compared with the theoretically predicted particulate mass fractions based on substance gas-particle partitioning constants and driving forces of semi-volatile organic compounds scavenging by the atmospheric condensed phases (particulate and liquid) are discussed. Sampling, sample preparation and handling, and the subsequent analytical procedures were well-planned. I find a few shortcomings in the data analysis and/or presentation (see specific comments).

Authors' response

We appreciate the reviewer's careful consideration of our manuscript and constructive comments. We have addressed the reviewer's specific comments below.

2) Reviewer's comment

Phase partitioning is addressed at the end of the manuscript, however for the sake of clarity I would like to see its indication already in the Introduction section. When considering PM with a water layer, there are two interphases with the corresponding partitioning/equilibria that have to be taken into account – gas-liquid and solid-liquid. To avoid confusion, the experimental system needs to be defined at the beginning of the manuscript.

Authors' response

We have added a statement regarding the partitioning system that we considered for estimating the particulate mass fractions of our target substances:

Page 4, L23-26: *“For calculating Θ , our method took into account the interaction of atmospheric SVOCs with PM liquid organic and polymeric phases, as well as the interaction with PM black carbon and salts, while disregarding the partitioning into PM aqueous phase, particle-liquid interactions, and liquid-liquid phase separation within PM (Sect. 2.6).”*

3) Reviewer's comment

Overall, presentation of the data is superficial, confusing and even unclear in some parts, and this aspect of the manuscript should be substantially improved before publication (see specific comments). I also encourage the authors to edit the language of the manuscript thoroughly. I think this is a very important dataset that should be delivered to the atmospheric science community, however the presentation and discussion should be improved; I suggest a major revision of the manuscript before publication.

Authors' response

We have improved data presentation by re-making the graphs, now with better graphics and more intuitiveness. For added clarity, we replaced the sample site codes with those that reflect the site names. In addition, we have focused on describing the study's major findings and removed description of less significant results from the text. Please see below our responses to specific comments.

Please also see Fig. 1-7 in the text, and the file that is uploaded as attachment, i.e. “Updated Figures_Shahpoury et al_acp-2017-1242”.

4) Reviewer’s comment

I was confused with the introduction of particle scavenging and gas scavenging in the Introduction section. Can you correlate cp and cpp? From my point of understanding it should be the same value for low-solubility compounds (NPAH and OPAH). For water soluble compounds (NMAH), cpp+cpd value should be equal (for high θ) or bigger (for low θ) than cp. Additional explanation would help understand the investigated multiphase system.

Authors’ response

For further clarification, we have modified the statement as follows:

Page 3, L34 - Page 4, L6: “...i.e. the higher the Θ at a given temperature, the more efficient is the scavenging, and the magnitude of Θ_w is expected to be close to Θ . However, it is anticipated that for hydrophilic SVOCs, which may demonstrate low or high Θ , water solubility plays an additional role in the substance wet scavenging pathways and the comparability of Θ_w with Θ . For instance, a NMAH with high Θ in the atmosphere may demonstrate low Θ_w due to substance dissolution in hydrometeors following particle scavenging. Conversely, a NMAH with low Θ is expected to show low Θ_w , as it undergoes gas scavenging process.”

5) Reviewer’s comment

Please rephrase the sentence on P3L16-18 starting with ‘However, it is not known if this concept also applies to hydrophilic SOCs which may also demonstrate high Θ ,...’ – I would say it can be speculated or is expected that water solubility plays a role in wet scavenging rather than ‘not known’ as stated above.

Authors’ response

We have changed the sentence as follows:

Page 4, L2: “However, it is anticipated that for hydrophilic SVOCs, which may demonstrate low or high Θ , water solubility plays...”

6) Reviewer’s comment

I want to comment on the LOQ and the precision of the reported data. First of all, it seems that your LOQ was lower than the lowest concentration used for the calibration curve. This is a bad practice. Whenever one estimates LOQ from IDL, this should be verified with the calibration curve. Then, I could only calculate ambient concentrations from the sample concentrations for N/OPAH as no final sample volume is reported for NMAH. Please add it and verify the LOQ you set. Second, you don’t report on the precision of the analytical procedure/measurement. Please add the level of confidence to the data and report the concentrations accordingly (so far almost all concentrations ranging from 0.09 to thousands are reported with 2 decimal places, which is hard to believe it).

Authors’ response

- This is not correct – measured concentrations which were smaller than the lowest calibration point (IDL) were always discarded and never used. The limit of quantification (LOQ) with our method cannot possibly be lower than IDL because our LOQs are defined as the mean concentration of analytes in field blanks + 3 standard deviations, and where analyte concentrations in blanks were <IDL, we replaced them with IDL. The reviewer’s misunderstanding may be related to the sentence “...IDL values were used in cases where analyte concentrations in blanks were <IDL.” For clarification, we have revised the sentence as follows:

Page 7, L13-15: “*LOQ values were determined as mean concentration of each analyte in blanks + 3 standard deviations. For this purpose, blank values that were <IDL were replaced with IDL values. Where analyte concentrations in samples exceeded the LOQ, mean blank concentrations were subtracted from those in the corresponding samples.*”

- It is not clear to us what the reviewer implies by “*calculate ambient concentrations from the sample concentrations*”. We intended to report analyte concentrations in snowmelt and that is what we did. Back-calculating ambient concentrations was not the intention of our study. For clarification, we have now added snowmelt volumes for each sample: Page 20, Table 1 (last column)
- We don’t think it is correct to report confidence levels for our dataset because we do not report means for analysis of replicate samples; in our study $n = 1$ per site. In order to address the reviewer’s concern, we have now reported the concentrations $>1 \text{ ng L}^{-1}$ with one decimal place and those smaller than 1 ng L^{-1} with two decimal places (or more in exceptional cases in Table S4B) throughout the text and the Supplement.

7) **Reviewer’s comment**

The advantage of air mass trajectories is not clear to me. You don’t use them in the discussion of source apportionment, which is a bit superficial in general. I am aware that this was not the main scope of the study, but if you discuss possible sources of particular pollutants, you should combine the knowledge with the estimated air mass trajectories and this should bring you some conclusions. If you don’t want to go deeper here, I would shorten the source apportionment parts in the Results and discussion section (P8L15-23 and P8L31-P9L3). I also don’t know what this means: ‘The snowfalls leading to samples Ub1, Ub3, Rr1, and Rr5 followed immediately frontal passages with advection from westerly directions (Fig. S2), unlike in the other precipitation events.’ Could you add an explanation?

Authors’ response

- We have revised and moved the discussion of the air mass history analysis (previously Section 3.1) to the Supplement:

Page S5 in the Supplement: “*For all central European sites, the air masses corresponding to the snow samples had been advected mostly from westerly directions (Figure S2). They had passed over polluted areas of central and western Europe (such as in NE France/SW Germany, W and SE Germany for samples MZ15, OS, WB and AB) until the last 100-200 km before precipitation started, when they had been transported over rural areas. In conclusion, these air mass histories are quite typical for the region in the sense that the source areas of the region have contributed to pollution loading, while point sources or a single source area, such as a close city, was never determining the loading. The snowfalls leading to samples MZ15, OS, WB, and PP2 immediately followed frontal passages with advection from westerly directions (trajectories are shown in Figure S2), unlike in the other precipitation events. Snow fall in air masses following a frontal passage may have been on-going for some time prior to arrival. This could lead to somewhat lower concentrations in precipitation, as the gases and particles, to be eventually transferred into snow, may had been previously scavenged.*”

- We have added a new sentence under the current Section 3.1, i.e. “*N/OPAH concentrations and distribution in snow*”, (formerly Section 3.2) with reference to the air mass histories description in the Supplement.

Page 9, L8-11: “*9-OFLN, O₂ACE, and 9,10-O₂ANT originate from both primary (e.g. diesel exhaust, coal and biomass burning) and secondary sources, whereas OBAT and BaOFLN are associated with primary sources (see references in Sect. 1). Potential source areas for such emissions are reflected in the air mass histories of all samples (see Text S1 and Fig. S2).*”

8) *Reviewer's comment*

I would move the last paragraph of the Results and discussion to the beginning of the section (to start with less sophisticated samples). I am also not sure if there is a need to report all values here, as they are also shown in Fig. 1. The same applies to the next section (NMAH) and Fig. 2.

Authors' response

It is not clear to us what part of the results and discussion the reviewer is referring to (i.e. under which section). However, we have moved the discussion of pollution sources for OPAHs from Section 3.1 (previously 3.2) to Section 1 (Introduction) following a suggestion made by the second reviewer; however, in Section 3.1, we have made a short note about potential emission sources of OPAHs:

Page 2, L17-29: *“For instance, 9-fluorenone (9-OFLN), 9,10-anthraquinone (9,10-O₂ANT), 1,4-naphthoquinone (1,4-O₂NAP), and 1,2-benzanthraquinone (1,2-O₂BAA) were previously found in diesel exhaust (Choudhury, 1982; Cho et al., 2004) and biomass For instance, formation of 1,4-O₂NAP and 9,10-O₂ANT following photolysis of 1-nitronaphthalene (1-NNAP) and 9-nitroanthracene (9-NANT) was suggested by previous studies (Keyte et al., 2013; Bandowe and Meusel, 2017).”*

Page 9, L8-10: *“9-OFLN, O₂ACE, and 9,10-O₂ANT originate from both primary (e.g. diesel exhaust, coal and biomass burning) and secondary sources, whereas OBAT and BaOFLN are associated with primary sources (see references in Sect. 1).”*

In addition, following the suggestions by both reviewers, we have now highlighted more important findings and we removed less significant results from Section 3.1 and 3.2:

Page 9, L3 – Page 10, L2: *“Snow aqueous and particulate phases were analysed for N/OPAHs following the method described in Sect. 2.3. In the aqueous phase, 9-OFLN, O₂ACE, and 9,10-O₂ANT were found in nearly all samples, except..... High abundance of OBAT is of particular concern because this compound is precursor of the mutagenic 2- and 3-nitrobenzanthrone (Enya et al., 1997; Phousongphouang and Arey, 2003).”*

Page 10, L4-30: *“NMAHs targeted for analysis were found in all aqueous phase samples, with the exception of 4-nitroguaiacol (4-NG), which was found less frequently (Fig. 4A and 5A). 4-NP showed the highest aqueous concentrations..... nitrosalicylic acids are the second most abundant NMAH species (Table S4A), which might indicate either higher stability or higher formation of these compounds during the transport of polluted air to the rural environments and the Arctic.”*

9) *Reviewer's comment*

The acronym SOC is not intuitive for me, I would rather suggest the use of SVOC for Semi Volatile Organic Compounds.

Authors' response

SOC has been replaced with SVOC throughout the text.

Page 3, L18, L20, L21, L23, L24, L28, L29, L33, L34

Page 4, L2, L7, L23

10) **Reviewer's comment**

P1L9: You use ng L^{-1} for ΣNPAH and $\mu\text{g L}^{-1}$ for ΣOPAH , which is misleading. Unify the units all over the manuscript

Authors' response

The units have been unified:

Page 1, L8-10: " *ΣNPAH concentrations were 1.2-17.6 and 8.8-19.1 ng L^{-1} at urban and rural sites, whereas ΣOPAHs were 269.5 – 1114.1 and 478.7 - 2384.4 ng L^{-1} at these sites, respectively.*"

11) **Reviewer's comment**

P1L14: 'The lowest levels of ΣOPAHs and ΣNMAHs were found at the remote site (9.2 and 390.5 ng L^{-1} , respectively).' – what about NPAHs? You should comment on their concentrations as well in the abstract.

Authors' response

Done

Page 1, L14-15: "*The lowest levels of $\Sigma\text{N/OPAHs}$ and ΣNMAHs were found at the remote site...*"

12) **Reviewer's comment**

P1L18-19: 'interplay between gas-particle partitioning in the aerosol, particle mass size distribution, and dissolution during in- or below-cloud scavenging.' – particle mass size distribution was not clear for me, maybe 'PM size-dependent mass distribution'? The same applies to P13L3.

Authors' response

It has been revised:

Page 1, L18-19: "*...i.e. NMAHs, is determined by an interplay between gas-particle partitioning in the aerosol and dissolution during in- or below-cloud scavenging.*"

13) **Reviewer's comment**

P2L12: 'NPAHs are also formed through reactions in the aerosol condensed phase (Keyte et al., 2013; Jariyasopit et al., 2014).' – why didn't you measure them in the dissolved phase? Please comment.

Authors' response

The following statement has been added under Sect. 3.1 in order to address the reviewer's comment:

Page 9, L12-17: "*NPAHs were not found in the snow aqueous phase. Our GPP model suggests that at near-zero temperatures the targeted NPAHs would be completely sorbed to the particulate phase in the atmosphere, with the exception 1-NNAP, 2-NNAP, 5-NACE, and 2-NFLU, which would partition between gas and particulate phases. Regardless, relatively low water solubility of NPAHs, indicated by their octanol-water partitioning coefficients ($\log K_{ow}$; Fig. S3), may limit their gas scavenging from the atmosphere and subsequent presence in the snow aqueous phase.*"

14) **Reviewer's comment**

P5L10: As no other glassware was pre-baked, I wonder if there is a reason why pre-baked glass inserts were used.

Authors' response

We have revised the sentence as follows:

Page 6, L7-8: "...transferred to 2-mL vials containing pre-baked 0.4-mL glass inserts for further analysis. All other glassware used for sample analysis were washed with lab-grade detergent and deionized water, and baked at 300°C for 12hrs."

15) Reviewer's comment

P5L23: 'internal method' – do you mean internal standard method?

Authors' response

It has been revised as follows:

Page 6, L21-22: "*The analyte quantification was done using the internal calibration method with 11-point calibration curves...*"

16) Reviewer's comment

P6L23: '(NH₄)₂SO₄ and NaCl (the last two represent secondary inorganic aerosols)' – why NaCl secondary?

Authors' response

The statement has been revised as follows:

Page 7, L22-23: "...*(NH₄)₂SO₄ and NaCl (the last two represent the contributions of secondary inorganic aerosols and sea salt) ...*"

17) Reviewer's comment

P8L4-14: I suppose this paragraph reports only the values for dissolved phase. This is not clear from the sentence starting in L7 on. Please clarify.

Authors' response

We have added the phrase "aqueous" for clarification:

Page 9, L3-4: "*In the aqueous phase, 9-OFLN, O₂ACE, and 9,10-O₂ANT were found in nearly all samples...*"

Page 9, L5: "*O₂ACE was the most abundant in the aqueous phase...*"

Page 9, L7-8: "...*OBAT, and BaOFLN were found less frequently with relatively low concentrations in the aqueous phase...*"

Page 9, L11: "...*TF and MZ17 were the least and most polluted sites, with \sum OPAH aqueous concentrations...*"

18) Reviewer's comment

P9L11-12: Reference is missing

Authors' response

The related references have been added:

Page 9, L36-37: "...*with previous findings in the literature (Albinet et al., 2007; Souza et al., 2014; Lin et al., 2015; Tomaz et al., 2016).*"

19) **Reviewer's comment**

P10L8-11: in some samples 4-NG was not detected; start the sentence with 'When detected...'

Authors' response

Revised as suggested.

Page 10, L21-22: "*When detected, the aqueous phase concentrations of 4-NG were comparable in urban and rural samples*"

20) **Reviewer's comment**

P10L35-P11L1: this is not true – nitro group is strongly e-withdrawing (acceptor), therefore lower density on the aromatic ring (lower e-donor ability) and weaker π -interactions. Additional NO₂ group on the aromatic ring increases the number of possible hydrogen bonds. However, as you conclude correctly, intramolecular H-bond between adjacent -OH and -NO₂ opposes, which results in lesser interactions with the surrounding molecules for DNP in comparison to NP.

Authors' response

The reviewer is referring to pi-pi interaction which exist between neighboring electron-deficient and electron-rich aromatic rings, whereas we commented on H-bonding in the manuscript, i.e. interactions between neighboring H-donor and e-donor molecules. We have now revised the sentence for clarification:

Page 11, L6-8: "*the presence of two nitro groups on 2,4-DNP is expected to promote stronger H-bonding with PM, compared to 4-NP which has one nitro group (compare the Abraham descriptor B for the two compounds in Table S2).*"

Page 11, L11-12: "*This reduces the H-bonding ability of 2,4-DNP compared to 4-NP (compare the Abraham descriptor A in Table S2).*"

21) **Reviewer's comment**

P11L5-12: Comment also low predicted θ values of 1,4-O₂NAP, 1-NNAP, 2-NNAP, 5-NACE, 2-NFLN.

Authors' response

We have revised the entire paragraph and included explanation for phase partitioning of 1,4-O₂NAP, 1-NNAP, 2-NNAP. The other two substances that the reviewer is referring to (5-NACE and 2-NFLN) were not found in our study or were below LOQs, hence, no comments has been made about them.

Page 11, L13-25: "*For substances which demonstrate complete sorption to PM, particle scavenging is expected to be the dominant source of wet deposition and, consequently, such substances will be enriched in precipitation particulate phase. Our observations depicted in Fig. 7A support this assumption, namely, N/OPAHs with high Θ (Fig. 6A-B) were largely associated with precipitation particulate phase. The only exception was 9,10-O₂ANT in MZ15 and MZ17 samples. For substances that distribute between gas and particulate phases, both gas and particle scavenging are relevant; however, the substance water solubility is a factor that could enhance or limit the gas scavenging mechanism, regardless of the compound phase partitioning in the atmosphere. For instance, 1- and 2-NNAP are expected to be $\geq 90\%$ in the gas phase under our experimental conditions; nonetheless, they were found in the precipitation particulate phase. A similar effect was seen for 9-OFLN. This is explained by the substances' relatively low water solubility (see estimated K_{OW} in Fig. S3) which limits their dissolution in hydrometeors. On the contrary, 1,4-O₂NAP (Θ : 0.001- 0.003) and O₂ACE (Θ : 0.24- 0.56) were more enriched in the aqueous phase, which is explained by their relatively low $\log K_{OW}$ (1.95-2.13; Fig. S3). Overall, our findings support the implied assumption that phase partitioning in air is preserved in snow, provided that the substance solubility in water is not a limiting factor.*"

22) **Reviewer's comment**

P11L15: define W_T

Authors' response

We have added a new equation under Introduction, Eq. 3, and introduced the definition of W_T :

Page 4, L7-10: “*The efficiency of SVOC wet scavenging is defined by W_T (unitless) (Škrdlíková et al., 2011; Shahpoury et al., 2015) Eq. (3):*

$$W_T = (c_{\text{snow}} \times 1000) / c_{\text{air}}$$

where c_{snow} is the total analyte concentration in snow (ng L^{-1}) and c_{air} is that (ng m^{-3}) in ambient air.”

23) **Reviewer's comment**

P11L23-25: Can you definitely exclude post-sampling dissolution of water-soluble compounds in the liquid phase?

Authors' response

We rule out post-sampling dissolution of target compounds due to reasons mentioned below - we have added the following statements to the text in order to address the reviewer's concern:

Page 5, L11-15: “*Our sample processing was performed in such way to minimize the analyte phase change prior to analysis, namely the samples were thawed at room temperature in the lab and, immediately after thawing, when the samples were near freezing point, the meltwater was passed through a pre-assembled filtration-extraction setup (Fig. S1), which allowed simultaneous separation of meltwater particulate phase and extraction of aqueous phase. This made it possible to minimize the time that particles were in contact with the aqueous phase of meltwater.*”

Page 11, L31-35: “*We rule out post-sampling dissolution of NMAHs from particulate to aqueous phase for the reasons mentioned in Sect. 2.2. In addition, looking at the Czech samples, 3-M-4-NP and 2-M-4-NP, which have lower water solubility ($\log K_{OW}$: 2.27-2.43; Fig. S3) than 4-NP ($\log K_{OW}$: 1.68) and comparable pK_a values (7.15-7.33), demonstrated much higher partitioning in the aqueous phase than 4-NP did. If a post-sampling phase change had occurred, we would have observed an opposite pattern.*”

24) **Reviewer's comment**

There is a long list of measured compounds, but not so many are shown in the graphs. It took me quite some time to compare Table 2 (compound name & abbreviation), Fig. 1 (measured concentration in each fraction – denoted with abbreviations) and Table S4A (measured sum concentrations – denoted with long names). I would suggest adding a column or two in Table 2 and mark whether the compound was detected in particulate, dissolved, or both phases; or if it was not detected at all. Besides, 2-Nitro-9-fluorenone is listed among OPAHs in Table 2 – is this on purpose?

Authors' response

We have made the suggested changes in Table 2.

In addition, we think that 2-nitro-9-fluorenone should be placed under OPAHs; no changes made.

Page 22, Table 2; also provided as an attachment along with author response document.

25) **Reviewer's comment**

Table S1: In the fifth column you report ‘Total NMAHs’, but then you use superscripts TOT, P, D within the table. This should be clarified and explain the superscripts.

Authors' response

We have now added the missing legends to Table S1:

Page S2, Table S1 caption: “^a: including nitrophenols, methylnitrophenols and dinitrophenols; ^b: including 4-NC, 3-M-5-NC and 4-M-5NC; ^{pp}: precipitation particulate phase; ^{pa}: precipitation aqueous phase; ^{TOT}: total concentration in precipitation (particulate + aqueous phase concentration); N.A.: data not available; * : below limit of detection (LOD); ** : below limit of quantification (LOQ); *** : median concentration”

26) Reviewer's comment

Abbreviations should also be introduced in the SI – maybe add them to Table S2.

Authors' response

The abbreviations have been added to Table S2, S4A, S4B.

Page S3 and S8-S10 in the Supplement.

27) Reviewer's comment

Table S4A and B: add confidence intervals and report the data accordingly.

Authors' response

As previously noted in response to reviewer's comment 6, we do not think it is correct to report confidence intervals (please see our response above). However, we are now reporting values >1 ng L⁻¹ with one decimal place and those <1 ng L⁻¹ with two decimal places, or more in exceptional cases in Table S4B.

28) Reviewer's comment

Table S4B: how did you convert cpd+pp (ng l-1) into cpd+pp (ng m-3)? Explain θ in the footnote.

Authors' response

The formula in Table S4B caption has been modified to reflect the conversion from ng L⁻¹ to ng m⁻³. The formula for calculating θ has also been added to Table S4B caption:

Page S10, Table S4B: “... W_T : total scavenging ratio (dimensionless) = $[c_{pa+pp} \text{ (ng L}^{-1}) \times 1000] / [c_g + c_p \text{ (ng m}^{-3})]$...” “... θ : particulate mass fraction = $c_p / (c_g + c_p)$...”

29) Reviewer's comment

P1L3: ‘Their precipitation cycling has hardly been studied.’ – wet deposition by precipitation is a part of environmental cycling, I don't understand the meaning of precipitation cycling, please correct.

Authors' response

We have revised the sentence as follows:

Page 1, L3: “Their environmental cycling through wet deposition has hardly been studied.”

30) Reviewer's comment

P1L10: ‘snow dissolved and particulate phase’ – ‘s’ is missing in phases

Authors' response

It has been revised:

Page 1, L10-11 “*Acenaphthoquinone and 9,10-anthraquinone were predominant in snow aqueous and particulate phases, respectively.*”

31) **Reviewer’s comment**

P3L22: ‘dinitrophenols (2,4-dinitrophenol (2,4-DNP) and 2-methyl-4,6-dinitrophenol (i.e. dinitroortho-cresol, DNOC) were the most frequently measured nitrophenols...’ – end-bracket is missing after DNOC) and present perfect should be used afterwards (i.e. DNOC) have been...).

Authors’ response

The statement has been revised as follows:

Page 4, L12-15: “...*4-nitrophenol (4-NP), several methyl-nitrophenol isomers as well as dinitrophenols, 2,4-dinitrophenol (2,4-DNP) and 2-methyl-4,6-dinitrophenol (i.e. dinitro-ortho-cresol, DNOC), have been the most frequently measured nitrophenols in precipitation in urban and rural Europe...*”

32) **Reviewer’s comment**

P5L15: 30m – space is missing

Authors’ response

Revised:

Page 6, L13: “...*column (30 m + 10 m integrated guard...*”

33) **Reviewer’s comment**

P5L17: 15 °C – erase the space

Authors’ response

Revised:

Page 6, L15: “... *then ramped to 180°C at 15°C...*”

34) **Reviewer’s comment**

P7L1: ‘f_{OM} (the mixing ratio of total organic matter in PM) × 0.60 and f_{OM}×0.40’ – all spaces or no spaces between the symbol, ×, and the number

Authors’ response

Revised:

Page 7, L29: “...corresponding to *f_{OM}* (the mixing ratio of total organic matter in PM) × 0.60 and *f_{OM}* × 0.40...”

35) **Reviewer’s comment**

P7L5: use past tense in the sentence starting with ‘The individual partitioning...

Authors’ response

Revised:

Page 8, L7: “...*The individual partitioning constants used in the multi-phase model were calculated...*”

Reviewer #2 Comments

Reviewer's general comment

Shahpoury et al. present data on nitrated and oxygenated polycyclic aromatic hydrocarbons (N/OPAHs) from snow samples at different European sites. They report concentrations from particulate and liquid (melted) snow phases and estimate the fraction of N/OPAHs removed by precipitation through particle scavenging based on predicted particulate mass fractions and observed snow phase partitioning. Such data are sparse and could in principle be helpful to better understand wet removal of hydrophobic and less hydrophobic organic compounds from the atmosphere. I have, however, a number of major issues with the applied methodology and data processing which need clarification before the paper can be considered for publication. In addition, the paper lacks important details and explanations to be able to fully understand what has been done. The structure of the paper and the clarity of the results' presentations need also be improved. I recommend re-consideration after major revision.

Authors' response

We thank the reviewer for their thorough review of our manuscript and for valuable comments and suggestions. Below, we have addressed the reviewer's specific comments regarding our analytical methods as well as data processing and presentation.

1) Reviewer's comment

The authors aim at measuring the phase partitioning of N/OPAHs in snow by analyzing both the snow particulate and aqueous phases. To do so, they pass the melted snow samples through a filtration-extraction system. My concern is that the observed distributions between snow particulates (retained on a filter) and snow water (extracted on a sorbent) might be strongly biased for compounds with some water solubility, which upon sample thawing will dissolve from the particulates into the melt water. This potential artefact needs to be thoroughly addressed as it might render many of the presented results useless. One of the main findings of the study is the unexpected behavior of highly water soluble NMAHs (p11 129-30). Considering the potential experimental bias, I wonder if this finding really holds.

Authors' response

We have addressed this concern in our response to [comment no. 23](#) from reviewer 1, since she/he raised the same concern. Please see above our response to that comment for details. Briefly, we have added additional statements to the text, regarding our well-planned analytical method which aimed to minimize sample processing artifacts, as well as evidence from our target compounds dissolution patterns compared to their estimated water solubility. We have ruled out post-sampling dissolution artifacts.

2) Reviewer's comment

Snow particulate concentrations are given in ng L^{-1} , which will strongly depend of the final volume during sample extraction. As this final volume is an arbitrary choice of the authors (and not even reported), it is not clear to me how these concentrations can be used in any reasonable way beyond comparing between different samples. Even the comparison with snow aqueous phase concentrations seems difficult to me. Adding them up to a total snow concentration, as done in Fig. 1 and Table S4A seems hard to justify as well to me.

Authors' response

This is a misunderstanding perhaps arising from not reporting the meltwater volumes. The analyte concentrations in each snow phase (aqueous or particulate) were calculated using the volume of melted snow which we measured carefully. Hence, the concentrations in the particulate and aqueous phases can be compared, and can be added together to report total analyte concentrations in snow.

For clarification, we have now added the volumes for melted snow samples to Table 1, and made a note under Section 2.2 (sample processing).

Page 5, Line 20-22: “The volume of meltwater for each sample was determined during filtration using the graduated filter funnel (Fig. S1), and used for calculating the final analyte concentrations in aqueous and particulate phases.”

Page 21, Table 1, last column (snowmelt volume); the table is also provided as an attachment along with author response document.

3) Reviewer’s comment

To make my confusion complete, in Table S4B the authors calculate dimensionless total scavenging ratios from the sum of snow particulate and aqueous phase (in ng L^{-1}) and the sum of particle and gas phase concentrations (in ng m^{-3}), obtained just before the snow events. This ratio seems to be derived by multiplying ng L^{-1} concentrations by a factor of 1000 and then dividing by ng m^{-3} concentrations, ignoring that the denominator in the unit is referring to solvent volume in one case and air volume in the other. This seems very odd to me and needs explanation.

Authors’ response

The method that we applied for calculating scavenging ratios is a standard method that is well documented in the literature. The multiplication of analyte concentration in snowmelt (ng L^{-1}) by a factor of 1000 is done in order to have the same units in the numerator ($\text{ng L}^{-1} \times 1000$) and denominator (ng m^{-3}), as scavenging ratio is a dimensionless value. To support our approach, we have now cited previous papers that used this method.

Page 4, L7-8: “The efficiency of SVOC wet scavenging is defined by W_T (unitless) (Bidleman, 1988; Poster and Baker, 1996; Škrdlíková et al., 2011; Shahpoury et al., 2015)”

4) Reviewer’s comment

The conclusion that the phase partitioning of NMAHs is determined by an interplay between GPP, particle mass size distribution, and dissolution during in- or below-cloud scavenging (abstract 117-19 and p12 113-19) is weak and not convincing. Even assuming the applied methodology was artefact-free and the calculation of the total scavenging ratio can be justified (see above), I cannot follow the authors’ reasoning why the observations would indicate an importance of particle mass size distribution and dissolution. This needs to be much better laid out in the discussion and all data in support need to be shown (p12 114-15). Much of this conclusion seems to originate from one single sample, where additional measurements have been made. The poor robustness of results that would follow from this needs to be addressed as well.

Authors’ response

We agree that results from a single precipitation event cannot be used to draw a strong conclusion; however, the results that the reviewer is referring to are *indication* of an atmospheric process that should not be overlooked. We have revised the entire paragraph and the related statement in the abstract:

Page12, L8-23: “For the urban site OS, the analyte concentrations in the gas and particulate phases of the air have been determined (sample collected over 24h preceding snowfall onset; Table S4B) in addition to concentrations in precipitation. The scavenging ratios W_T calculated for the target N/OPAHs and NMAHs (see Eq. 3) were 10^3 - 10^4 and 10^3 - 10^5 , respectively (Table S4B), which fall within the range suggested for removal of polyaromatic compounds through wet particle scavenging (Shahpoury et al., 2015). With the exception of 1,4- O_2 NAP and 9-OFLN, the range of calculated W_T is consistent with that of modelled Θ at 273 K (Table S4B), meaning that the particle scavenging was the dominant removal mechanism. The difference in W_T between 3- and 5-NSA (~1.4 times higher for 5-NSA) and between 9,10- O_2 ANT and OBAT (~1.1 times higher for OBAT) closely resembled that of estimated Θ at 273 K (Table S4B). However, we found differences in W_T between the NMAH subgroups, namely W_T values were higher for nitrophenols (1.3×10^4 – 1.6×10^5) and nitrosalicylic acids (5.7×10^4 – 8.2×10^4) than nitrocatechols (1.1×10^3 – 2.8×10^3 ; Table S4B), which cannot be explained by the substances’ GPP alone (compare Θ in Fig. 6C). Although based on a single precipitation event, these results are indication

of additional atmospheric processes that NMAHs could undergo, and which may affect the substance wet scavenging. For instance, PM size-dependent mass distribution is a parameter which was suggested to influence the snow scavenging efficiencies (Zhang et al., 2013) – i.e. lower efficiency in the PM size range 0.01-1 μm than for coarse PM ($\geq 1 \mu\text{m}$). This parameter should to be taken into account in future studies, and more precipitation episodes need to be considered in order to draw a full picture.”

Page 1, L18-19: “i.e. NMAHs, is determined by an interplay between gas-particle partitioning in the aerosol and dissolution during in- or below-cloud scavenging.”

5) Reviewer’s comment

On p7 113ff and p12 16ff the authors discuss acid dissociation in particles in relation to pH. However, they seem to not be aware of sample pH being a different thing than particle pH, i.e. pH of particle liquid water. With a melted snow sample being highly diluted in comparison to aerosol particles, the measured sample pH cannot be used to describe acid dissociation in particle liquid water. This needs to be corrected appropriately.

Authors’ response

We agree with the reviewer’s point of view. We have revised the entire paragraph and removed the statement that the reviewer is referring to. However, under Section 2.6, we do mention the general effect that pKa and pH could have on gas-particle partitioning predictions with our model:

Page 8, L13-22: “One must note that the ppLFER model used here predicts K_P of a substance in neutral form. In particulate phase, depending on pH of the PM aqueous phase and pK_a of the target substance, NMAHs may partly or completely deprotonate, resulting in enhanced solubility of the substance in the aqueous phase (Ahrens et al., 2012). This implies that the actual partitioning could be under-predicted for such substances. The effect is expected to be relevant for 5-nitrosalicylic acid (5-NSA; see Table 2 for compound abbreviations), pK_a : 1.95 at 298 K (Aydin et al., 1997), 3-nitrosalicylic acid (3-NSA; we expect similar pK_a as that of 5-NSA), 2,4-DNP, pK_a : 4.07 at 298 K (Lide, 2010), and DNOC, pK_a : 4.48 at 293 K (WHO, 2000). The rest of NMAHs have noticeably higher pK_a values – 4-NP: 7.15, 2-methyl-4-nitrophenol (2-M-4-NP): 7.33, 3-methyl-4-nitrophenol (3-M-4-NP): 7.33, 4-nitrocatechol (4-NC): 6.93 at 298 K; we expect pK_a values for 4-methyl-5-nitrocatechol (4-M-5-NC) and 3-methyl-5-nitrocatechol (3-M-5-NC) to be close to that for 4-NC.”

6) Reviewer’s comment

A “dissolved” phase is not a thing. There are particulate, aqueous, or gas phases, for example, but a dissolved phase does not exist and the term needs to be replaced throughout all the manuscript.

Authors’ response

We have changed the phrase “dissolved” to “aqueous” throughout the text:

Page 1, L11, L16;
Page 3, L29, L31;
Page 4, L19, L25;
Page 5, L14, L15, L22;
Page 6, L4, L5;
Page 8 L4, L6, L14, L15;
Page 9, L3, L4, L5, L8, L11, L12, L17, L34;
Page 10, L4, L5, L8, L21;
Page 11, L23, L27, L31, L34;
Page 12, L5, L7, L30.

7) *Reviewer's comment*

The experimental section lacks many details, e.g. flow rate during extraction (p4 123), volume of ethyl acetate (p5 18-9), volume of buffer (p5, 132-33), concentration of EDTA (p5, 133), duration of ultrasonication (p6 11), volume of buffer (p6 11-2), etc. Please make sure any reader would be able to fully repeat your experiments with the information given.

Authors' response

We have added the details mentioned in the reviewer's comment.

Page 5, L19: "*A steady sample flow (10 mL min⁻¹) was established...*"

Page 6, L6: "*...the solvent was exchanged to ethyl acetate (3×5 mL).*"

Page 6, L30-31: "*The SPE extracts were further concentrated to near dryness using TurboVap II and later dissolved in 1 mL mixture of methanol and 7.15 mM ammonium formate buffer pH 3 (3:7, v/v) containing 400 μM EDTA.*"

Page 6, L33 – Page 7, L1: "*Briefly, the particles were extracted using methanol containing 3.4 μM EDTA with agitation (3×5 min) in an ultrasonic bath. The final extracts were concentrated to near dryness, and dissolved in 1 mL mixture of methanol and 7.15 mM ammonium formate buffer pH 3 (3/7, v/v), containing 400 μM EDTA.*"

8) *Reviewer's comment*

Data presentation could be improved. All the abbreviations for the different sites are impossible to remember. I suggest removing them completely from the discussion text and referring to the name of the sites instead.

Authors' response

It is not possible for us to use the actual names due to their length because they limit the visibility of data in the bar charts. In order to address the reviewer's concern, we have replaced the original abbreviations, which represented the site types, with those that represent the actual site names. These changes have been highlighted throughout the text.

Page 22-28, Figure 1-7; also provided as attachment along with Author Response document.

• *Reviewer's comment*

Other abbreviations are used without explanation, e.g. the indices WSOM and OP (p6, 129).

Authors' response

The abbreviation WSOM and OP were actually defined in the text:

Page 7, L19-20: "*... for absorption into water soluble organic matter (WSOM) and organic polymers (OP)...*"

• *Reviewer's comment*

Different panels in the Figures are sometimes difficult to compare, because the order of compounds changes.

Authors' response

We have remade all the graphs and ordered the substance names in a consistent way:

Page 22-28, Figure 1-7; also provided as an attachment together with author response document.

- **Reviewer's comment**

Figure 3 contains empty brackets in the y-axis label, Figure 4 even contains only empty brackets as y-axis label.

Authors' response

Empty brackets indicate dimensionless parameters. Since we have remade all figures, Figure 3 and 4 are now labeled as Figure 6 and 7. We have revised y-axis labels in these figures:

Page 27, Figure 6

Page 28, Figure 7

Both figures are provided in an attachment together with the author response document.

- **Reviewer's comment**

The discussion of air mass back trajectories in 3.1 is odd, as it is nowhere else in the manuscript referred to. If still important, it should be substantiated.

Authors' response

We have moved the discussion of air mass history analysis to the Supplement (currently Page S5, Text S1), and made a reference in the text:

Page 9, L10-11: "*Potential source areas for such emissions are reflected in the air mass histories of all samples (see Text S1 and Fig. S2).*"

9) Reviewer's comment

Correction factors for f_{OM} (p7 11-2) are taken from a study in the 1980s done in Los Angeles, USA. I wonder if this is really the best reference for the sites sampled by the authors. Also, these factors are likely to differ substantially both between sites but also between different meteorological situations. A note on the sensitivity of the results on such highly uncertain parameters would be helpful.

Authors' response

Studies reporting comprehensive chemical composition of aerosol organic matter are extremely rare and the reference we used, Rogge et al., 1993, is amongst a few available in the literature, which reflect empirical data across sites. In a previous publication, we conducted a sensitivity study regarding the allocation of f_{OM}, and compared our assumptions with measured f_{OM} sub-fractions from a central European site. We have now added a statement in the text and cited the publication containing the sensitivity analysis:

Page 8, L1-2: "*These factors were previously verified through a sensitivity study (Shahpoury et al., 2016).*"

10) Reviewer's comment

Sections 3.2 and 3.3 are tedious to read with all the abbreviations and very detailed concentrations. I suggest discussing the main observations in these measurements in a more compact way and leaving much of the numbers to the corresponding Figures and Tables. Also, some paragraphs might be moved to the Introduction (e.g. p8 114-22). The space gained here should be used to discuss main findings of the paper in a more substantiated way (see comment above).

Authors' response

We agree with the reviewer and, as suggested, “p8 114-22” has been moved to Introduction section. The same has been done for NMAHs:

Page 2, L17-29: *“For instance, 9-fluorenone (9-OFLN), 9,10-anthraquinone (9,10-O₂ANT), 1,4-naphthoquinone (1,4-O₂NAP), and 1,2-benzanthraquinone (1,2-O₂BAA) were previously found in diesel exhaust (Choudhury, 1982; Cho et al., 2004)..... formation of 1,4-O₂NAP and 9,10-O₂ANT following photolysis of 1-NNAP and 9-NANT was suggested by previous studies (Keyte et al., 2013; Bandowe and Meusel, 2017).”*

Page 3, L6-11: *“Increased production of nitrocatechols in the urban environment due to.....biomass burning as the major emission source, similar to the previous reports on nitrocatechols (Iinuma et al., 2010; Kitanovski et al., 2012; Kahnt et al., 2013; Chow et al., 2016; Caumo et al., 2016).”*

In addition, we removed the discussion of less significant results and highlighted our major findings under Section 3.1 and 3.2:

Page 9, L3 - Page 10, L2: *“Snow aqueous and particulate phases were analysed for N/OPAHs following the method described in Sect. 2.3. In the aqueous phase, 9-OFLN, O₂ACE, and 9,10-O₂ANT were found in nearly all samples High abundance of OBAT is of particular concern because this compound is precursor of the mutagenic 2- and 3-nitrobenzanthrone (Enya et al., 1997; Phouongphouang and Arey, 2003).”*

Page 10, L4-30: *“NMAHs targeted for analysis were found in all aqueous phase samples, with the exception of 4-nitroguaiacol (4-NG), which was found less frequently (Fig. 4A and 5A). 4-NP showed the highest aqueous concentrations nitrosalicylic acids are the second most abundant NMAH species (Table S4A), which might indicate either higher stability or higher formation of these compounds during the transport of polluted air to the rural environments and the Arctic.”*

Table 1. Sampling site details

	Coordinates	Sampling date	Snowfall started	Sample collected	Snowmelt volume (L)
Urban					
MZ15, Mainz	49.99° N, 8.23° E	23 Feb 2015	8:00	12:45	0.4
GS, Götzens	47.23° N, 11.31° E	25 Feb 2015	Overnight	9:00	0.45
OS, Ostrava	49.86° N, 18.26° E	19 Feb 2016	14:00	19:00	0.5
MZ17, Mainz	49.99° N, 8.23° E	10 Jan 2017	9:00	15:00	1
Rural					
WB, Winterberg	51.18° N, 8.49° E	03 Mar 2015	15:00	18:30	0.5
AB, Altenberg	50.78° N, 13.69° E	05 Mar 2015	Overnight	8:00	0.5
KB, Kolsassberg	47.28° N, 11.65° E	25 Feb 2015	Overnight	10:00	0.5
PP1, Pustá Polom 1	49.86° N, 17.98° E	19 Feb 2016	9:30	23:00	0.5
PP2, Pustá Polom 2	49.86° N, 17.98° E	23 Feb 2016	14:00	23:00	0.5
Remote					
TF, Tempelfjorden	78.45° N 17.32° E	4 Mar 2015	1 Mar 2015	after snowfall ^a	1.65

^a old snow, which had fallen 3-2 days before sampling

Table 2. Target compound list

Analyte	Abbreviation	RT	Q1	Detection ^a
1-Nitronaphthalene	1-NNAP	12.12	173.1	P (86)
2-Nitronaphthalene	2-NNAP	12.62	173.1	P (43)
5-Nitroacenaphthene	5-NACE	17.52	199.1	n.d.
2-Nitrofluorene	2-NFLN	19.07	211.1	n.d.
9-Nitroanthracene	9-NANT	19.46	223.1	P (71)
9-Nitrophenanthrene	9-NPHE	20.64	223.1	n.d.
3-Nitrophenanthrene	3-NPHE	21.4	223.1	n.d.
2-Nitrofluoranthene	2-NFLT	25.75	247.1	P (71)
3-Nitrofluoranthene	3-NFLT	25.80	247.1	n.d.
1-Nitropyrene	1-NPYR	26.63	247.1	n.d.
2-Nitropyrene	2-NPYR	26.95	247.1	n.d.
7-Nitrobenz(a)anthracene	7-NBAA	29.41	273.1	n.d.
6-Nitrochrysene	6-NCHR	30.66	273.1	n.d.
1,3-Dinitropyrene	1,3-N ₂ PYR	31.8	292.1	n.d.
1,6-Dinitropyrene	1,6-N ₂ PYR	32.81	292.1	n.d.
1,8-Dinitropyrene	1,8-N ₂ PYR	33.54	292.1	n.d.
6-Nitrobenz(a)pyrene	6-NBAP	36.73	297.1	n.d.
1,4-Naphthoquinone	1,4-O ₂ NAP	10.18	158.1	A (14)
9-Fluorenone	9-OFLN	13.78	180.1	A (100) P (86)
9,10-Anthraquinone	9,10-O ₂ ANT	17.03	208.1	A (86) P (57)
Acenaphthoquinone	O ₂ ACE	17.82	198.1	A (100) P (100)
2-Nitro-9-fluorenone	2-N-9-OFLN	20.54	225.1	n.d.
Benz(a)fluorenone	BaOFLN	22.88	230.1	A (29) P (100)
Benz(b)fluorenone	BbOFLN	23.82	230.1	P (86)
Benzanthrone	OBAT	25.07	230.1	A (29) B (43)
1,2-Benzanthraquinone	1,2-O ₂ BAA	26.46	258.1	A (71) B (100)
3-Nitrosalicylic acid	3-NSA	3.60	182	A (100) P (11)
5-Nitrosalicylic acid	5-NSA	5.07	182	A (100) P (11)
4-Nitrocatechol	4-NC	7.76	154	A (90) P (33)
4-nitroguaiacol	4-NG	8.29	168	A (50) P (22)
4-Methyl-5-nitrocatechol	4-M-5-NC	9.47	168	A (90) P (22)
4-Nitrophenol	4-NP	10.00	138	A (100) P (100)
2,4-Dinitrophenol	2,4-DNP	10.92	183	A (100) P (33)
3-Methyl-4-nitrophenol	3-M-4-NP	13.19	152	A (100) P (89)
3-Methyl-5-nitrocatechol	3-M-5-NC	14.01	168	A (100) P (22)
2-Methyl-4-nitrophenol	2-M-4-NP	16.72	152	A (100) P (89)
Dinitro-ortho-cresol	DNOC	17.05	197	A (100) P (78)

Abbreviations, retention times (RT), and quantification ions (Q1) of target analytes; ^a analyte detection in aqueous (A) or particulate (P) phase; numbers in brackets indicate percentage of detection across the samples in each phase; n.d.: not detected

Figure 1 N/OPAHs in urban snow samples; * indicates values <LOQ in all samples

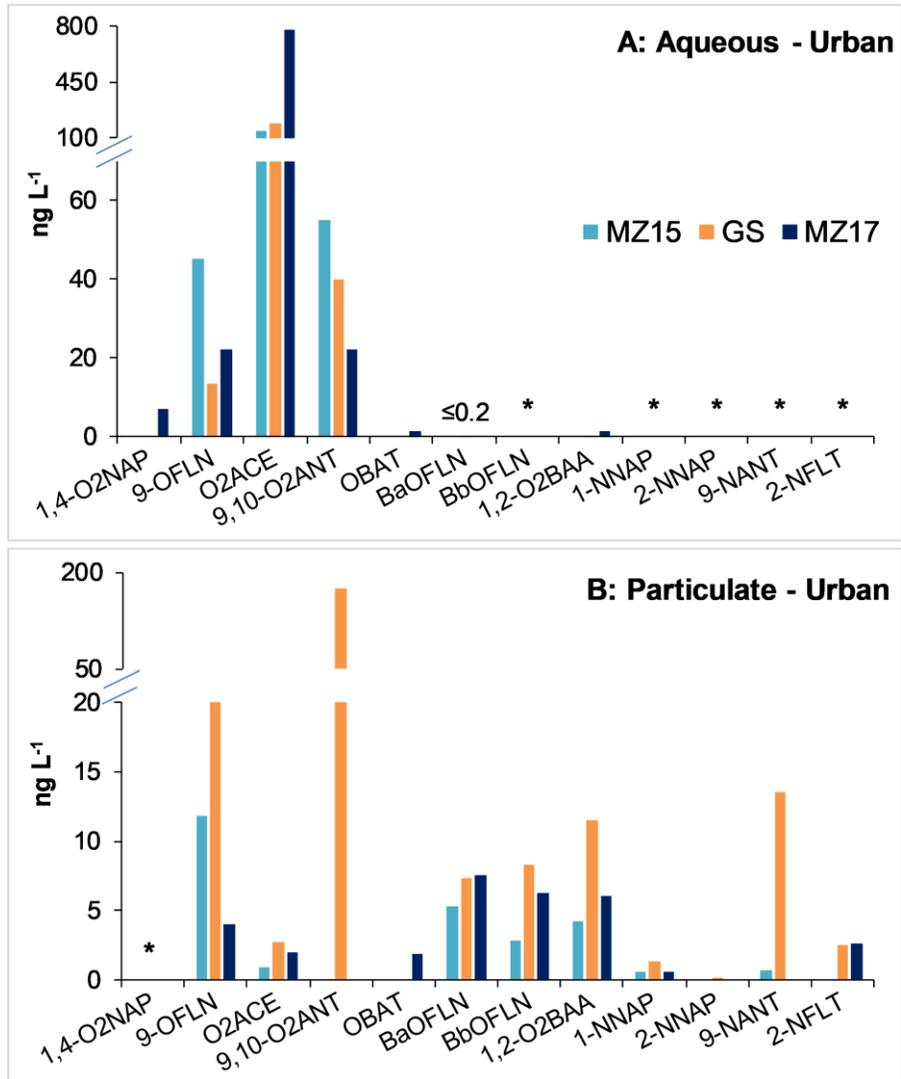


Figure 2 N/OPAHs in rural and remote snow samples; * indicates values <LOQ in all samples

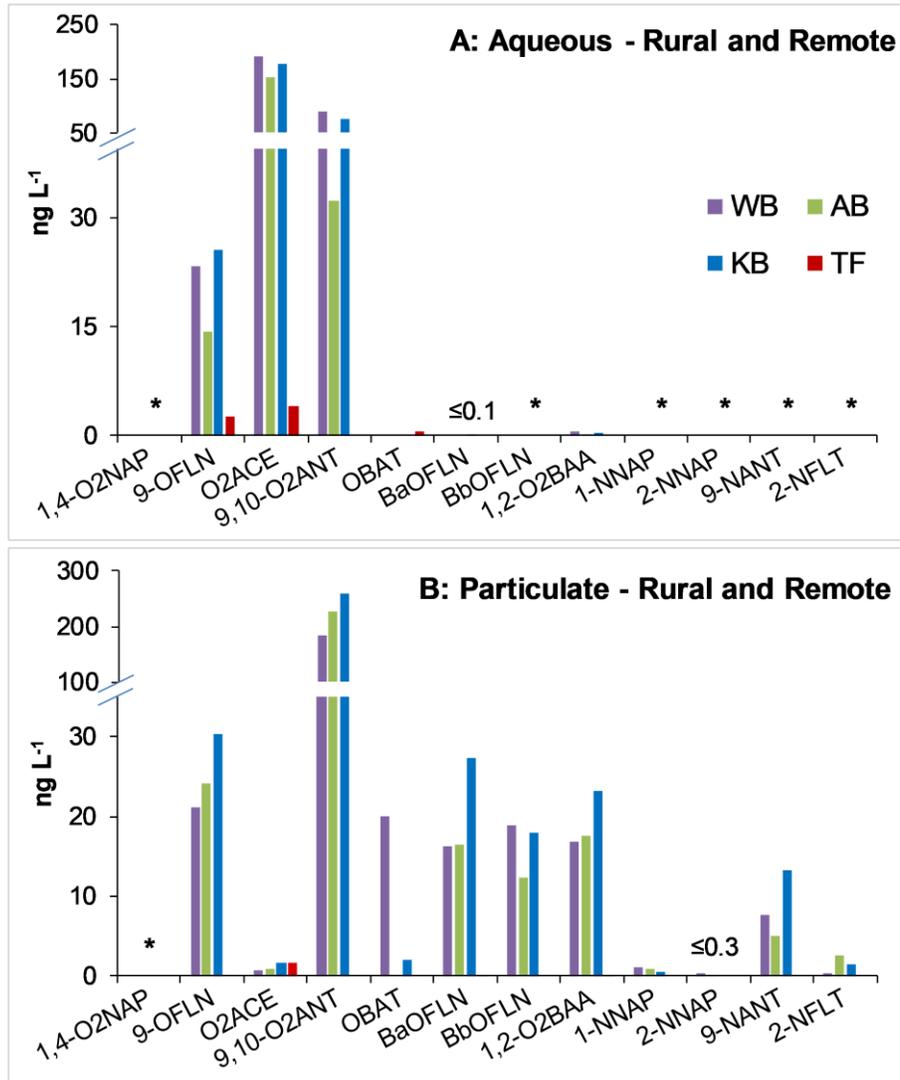


Figure 3 NOPAHs in snow aqueous + particulate phase; urban and remote

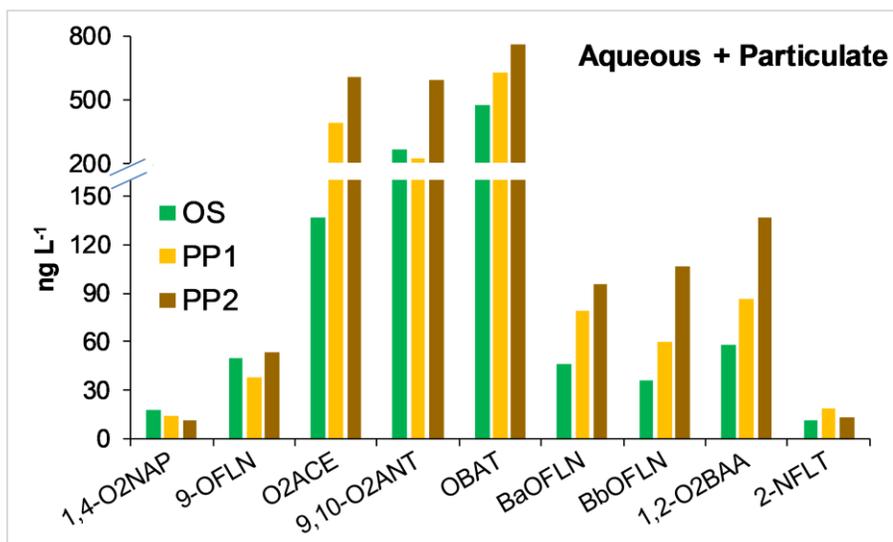


Figure 4 NMAHs in urban snow samples

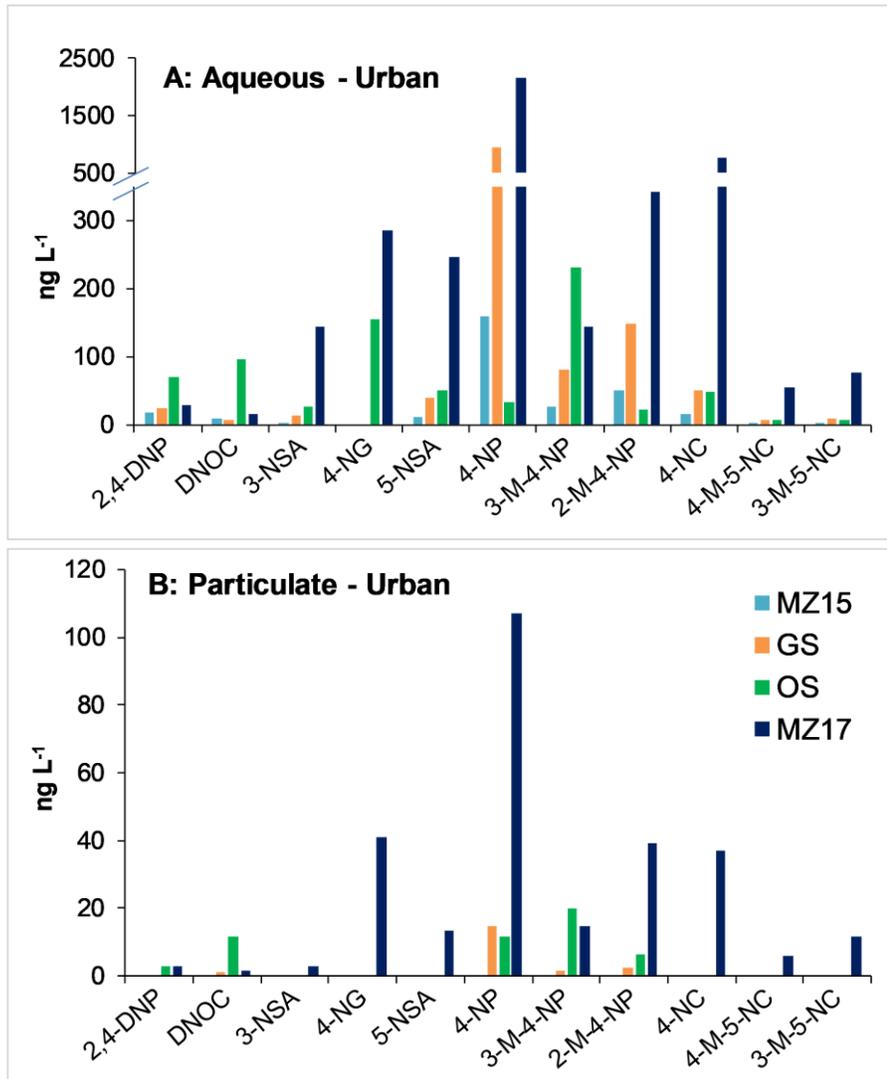


Figure 5 NMAHs in rural and remote snow samples

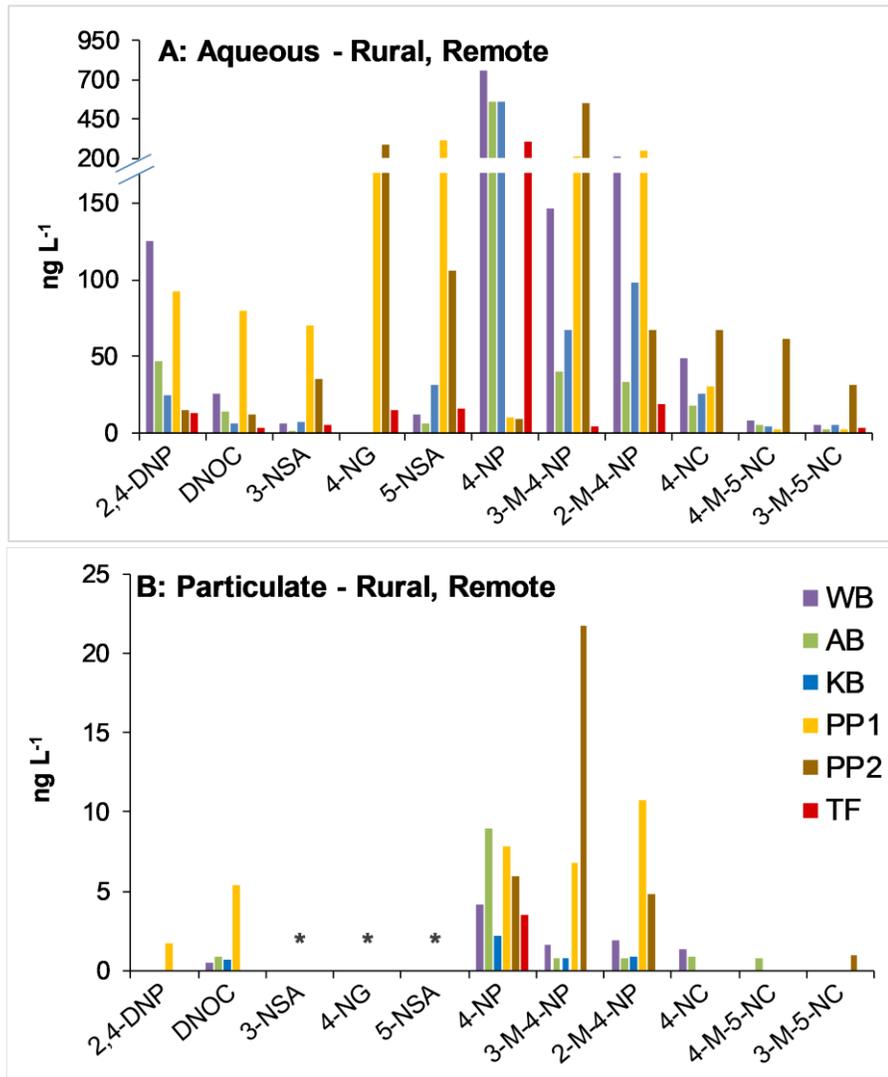


Figure 6 Particulate mass fractions θ estimated at 273 K using multiphase gas-particle partitioning model for NPAHs (A), OPAHs (B), and NMAHs (C)

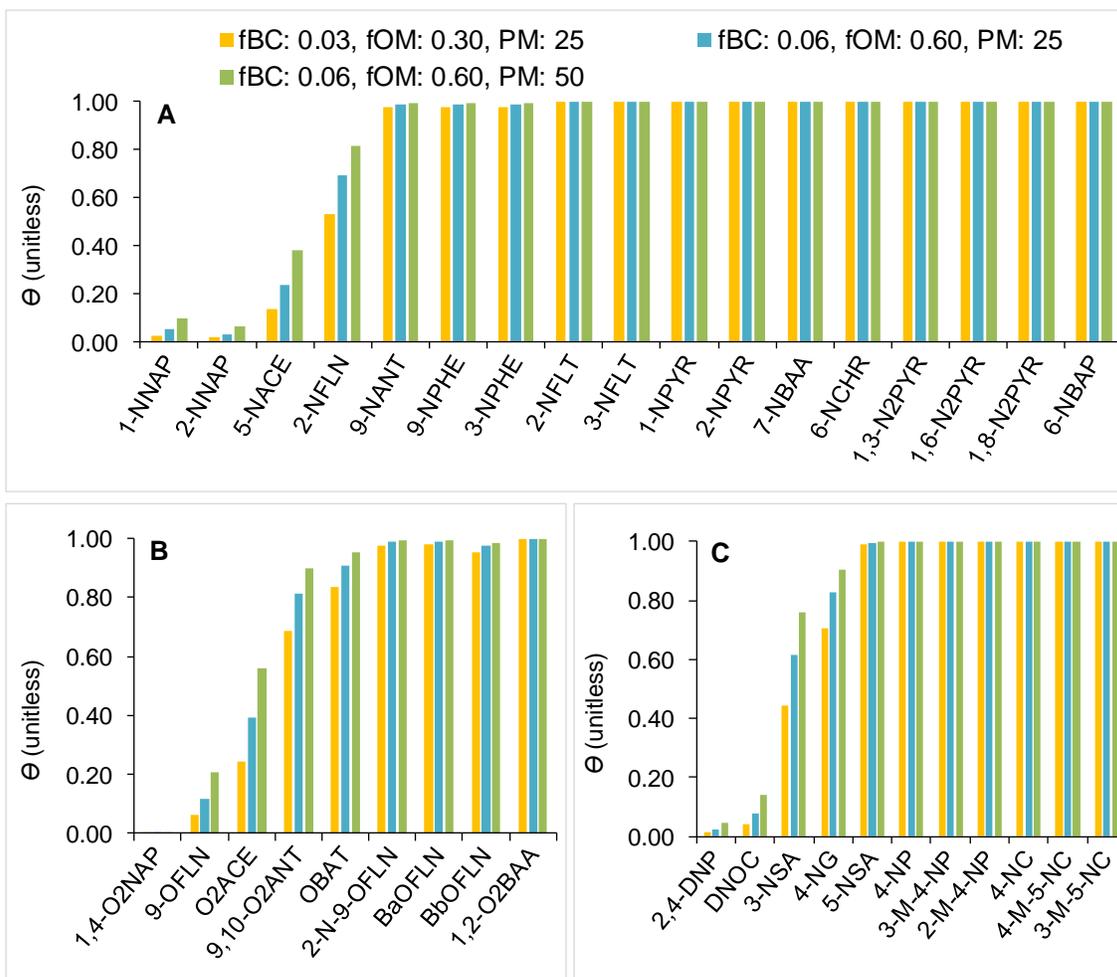


Figure 7 Fraction of N/OPAHs (A) and NMAHs (B) removed by particle scavenging (θ_w)

