

## Authors' Responses to Reviewers' Comments

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**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  $\Theta$ , 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.

#### 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  $\theta$ ) or bigger (for low  $\theta$ ) 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  $\theta$  at a given temperature, the more efficient is the scavenging, and the magnitude of  $\Theta_w$  is expected to be close to  $\theta$ . However, it is anticipated that for hydrophilic SVOCs, which may demonstrate low or high  $\theta$ , water solubility plays an additional role in the substance wet scavenging pathways and the comparability of  $\Theta_w$  with  $\theta$ . For instance, a NMAH with high  $\theta$  in the atmosphere may demonstrate low  $\Theta_w$  due to substance dissolution in hydrometeors following particle scavenging. Conversely, a NMAH with low  $\theta$  is expected to show low  $\Theta_w$ , 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  $\theta$ ,...' – 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  $\theta$ , 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  $1 \text{ ng L}^{-1}$  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, Text S1: “*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, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT 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-O<sub>2</sub>ANT), 1,4-naphthoquinone (1,4-O<sub>2</sub>NAP), and 1,2-benzanthraquinone (1,2-O<sub>2</sub>BAA) were previously found in diesel exhaust (Choudhury, 1982; Cho et al., 2004) and biomass ..... For instance, formation of 1,4-O<sub>2</sub>NAP and 9,10-O<sub>2</sub>ANT 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, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT 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 in the current edition (formerly, Section 3.2 and 3.3):

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, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT 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<sup>-1</sup> for ΣNPAH and µg L<sup>-1</sup> for ΣOPAH, which is misleading. Unify the units all over the manuscript

### Authors' response

The units have been unified:

Page 1, L8-10: “ $\Sigma$ NPAH concentrations were 1.2-17.6 and 8.8-19.1 ng L<sup>-1</sup> at urban and rural sites, whereas  $\Sigma$ OPAHs were 269.5 – 1114.1 and 478.7 - 2384.4 ng L<sup>-1</sup> at these sites, respectively.”

11) **Reviewer’s comment**

P1L14: ‘The lowest levels of  $\Sigma$ OPAHs and  $\Sigma$ NMAHs were found at the remote site (9.2 and 390.5 ng L<sup>-1</sup>, respectively).’ – what about NPAHs? You should comment on their concentrations as well in the abstract.

**Authors’ response**

It has been revised:

Page 1, L14-15: “*The lowest levels of  $\Sigma$ N/OPAHs and  $\Sigma$ NMAHs 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 Section 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<sub>ow</sub>; 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: '(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 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: *“...(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 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, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT were found in nearly all samples...”*

Page 9, L5: *“O<sub>2</sub>ACE was the most abundant in the aqueous phase...”*

Page 9, L7: *“...BaOFLN were found less frequently with relatively low concentrations in the aqueous phase...”*

Page 9, L11: *“Overall, 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  $\pi$ -interactions. Additional NO<sub>2</sub> group on the aromatic ring increases the number of possible hydrogen bonds. However, as you conclude correctly, intramolecular H-bond between adjacent -OH and -NO<sub>2</sub> 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  $\theta$  values of 1,4-O<sub>2</sub>NAP, 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-O<sub>2</sub>NAP, 1-NNAP, 2-NNAP. The other two substances that the reviewer is referring to (5-NACE and 2-NFLU) 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  $\theta$  (Fig. 6A-B) were largely associated with precipitation particulate phase. The only exception was 9,10-O<sub>2</sub>ANT 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-O<sub>2</sub>NAP ( $\theta$ : 0.001- 0.003) and O<sub>2</sub>ACE ( $\theta$ : 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 WT

**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  $c_{\text{snow}}$  is the total analyte concentration in snow ( $\text{ng L}^{-1}$ ) and  $c_{\text{air}}$  is that ( $\text{ng m}^{-3}$ ) 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:

Page 21, Table 2, last column. In addition, we think that 2-nitro-9-fluorenone should be placed under OPAHs; no changes made.

### 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: “<sup>a</sup>: including nitrophenols, methylnitrophenols and dinitrophenols; <sup>b</sup>: including 4-NC, 3-M-5-NC and 4-M-5NC; <sup>pp</sup>: precipitation particulate phase; <sup>pa</sup>: precipitation aqueous phase; <sup>TOT</sup>: 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:

Page S3 (Table S2, second column) and S8-S10 (Table S4A and S4B, second column) 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  $>1 \text{ ng L}^{-1}$  with one decimal place and those  $<1 \text{ ng L}^{-1}$  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  $\theta$  in the footnote.

**Authors’ response**

The formula in Table S4B caption has been modified to reflect the conversion from  $\text{ng L}^{-1}$  to  $\text{ng m}^{-3}$ . The formula for calculating  $\theta$  has also been added to Table S4B caption:

Page S10, Table S4B: “... $W_T$ : total scavenging ratio (dimensionless) =  $[c_{pa+pp} (\text{ng L}^{-1}) \times 1000] / [c_g + c_p (\text{ng m}^{-3})]$  ...” “... $\theta$ : 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<sub>OM</sub> (the mixing ratio of total organic matter in PM) × 0.60 and f<sub>OM</sub>×0.40' – all spaces or no spaces between the symbol, ×, and the number

**Authors' response**

Revised:

Page 7, L29: "...corresponding to f<sub>OM</sub> (the mixing ratio of total organic matter in PM) × 0.60 and f<sub>OM</sub> × 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  $\text{ng L}^{-1}$ , 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 20, Table 1, last column (‘snowmelt volume’).

### 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  $\text{ng L}^{-1}$ ) and the sum of particle and gas phase concentrations (in  $\text{ng m}^{-3}$ ), obtained just before the snow events. This ratio seems to be derived by multiplying  $\text{ng L}^{-1}$  concentrations by a factor of 1000 and then dividing by  $\text{ng m}^{-3}$  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 ( $\text{ng L}^{-1}$ ) 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 ( $\text{ng m}^{-3}$ ), 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. Hence, 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  $\Theta$  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  $\Theta$  at 273 K (Table S4B). However, we found differences in  $W_T$  between the NMAH subgroups, namely  $W_T$  values were higher for nitrophenols ( $1.3 \times 10^4$ –  $1.6 \times 10^5$ ) and nitrosalicylic acids ( $5.7 \times 10^4$  –  $8.2 \times 10^4$ ) than nitrocatechols ( $1.1 \times 10^3$  –  $2.8 \times 10^3$ ; Table S4B), which cannot be explained by the substances’ GPP alone (compare  $\Theta$  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  $\mu\text{m}$  than for coarse PM ( $\geq 1 \mu\text{m}$ ). This parameter should 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 l13ff and p12 l6ff 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, L7, L11, L12, L16, 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<sup>-1</sup>) 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 4, L29-L33: "Snow samples were collected between winter 2015 and 2017 from three locations in Germany, i.e. Mainz (MZ15 and MZ17; urban-residential, ≈200000 inhabitants), Winterberg (WB) and Altenberg (AB; rural, >10 km from small towns), two locations in Inn Valley, Austria, i.e. Götzens (GS; urban-residential of a mid-sized city, Innsbruck, ≈140000 inhabitants) and Kolsassberg (KB; rural, 10-20 km from city and towns), two locations in the Czech Republic, i.e. Ostrava (OS; urban, conurbation with ≈700000 inhabitants) and Pustá Polom (PP1 and PP2; rural, 20..."

Page 5, L1-L2: "...km upwind from Ostrava), and one location in the Arctic, Tempelfjorden, Svalbard (TF, remote, 50-80 km from small towns). The sample site details are shown in Table 1. Fresh snow samples (all sites, except TF) were collected by..."

L7: "...which had fallen 3-2 days before, was collected at TF and stored in..."

Page 8, L27: "...for sample site in Svalbard, TF, as the snow fell 2-3 days prior..."

Page 9, L4: "...were found in nearly all samples, except at the remote site TF..."

L11: "Overall, TF and MZ17 were the least and most polluted sites..."

L19: "... (found in GS, WB, AB and KB) showed the highest concentrations..."

L20: "...9-OFLN (found in all but TF; ≤30.3 ng L<sup>-1</sup>)..."

L27: "Overall, the remote site TF and rural site KB were the least and most..."

L29: "...Snow samples OS, PP1 and PP2 were not phase-separated..."

L33: "...overall higher at the rural sites PP1 and PP2 than the urban site OS (Table S4A)."

L34: "... (i.e. aqueous + particulate) across all sites, TF and PP2 were the least..."

Page 10, L7: "...found in urban samples OS and MZ17 (Fig. 4A) ..."

L8: "...PP1, PP2, and TF (Fig. 5A). Overall in the aqueous phase, TF and MZ17 were the least and most..."

L11: "...concentrations up to 106.9 ng L<sup>-1</sup> (MZ17), followed..."

L12: "...the only NMAH found at the remote site TF."

L14: "...urban site MZ17 (Fig. 4B). Overall in the particulate phase, the remote site TF was the cleanest..."

L15: "...the urban site MZ17 was the most polluted..."

L24: "...higher than that measured for the remote sample TF"

L25: "In urban samples with the exception of OS..."

L28: "...KB and PP1, and the remote sample TF, nitrosalicylic acids..."

Page 11, L1: "...values for MZ17 and OS sampling events..."

L16: "The only exception was 9,10-O<sub>2</sub>ANT in MZ15 and MZ17 samples."

L29: "...this was more pronounced in urban and rural samples OS, PP1 and PP2."

Page 12, L8: "For the urban site OS, the analyte concentrations..."

Page 20, Table 1, column 1

Page 22-28, Figure 1-7.

- **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.

- **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 referred to as Figure 6 and 7. We have revised y-axis labels in these figures:

Page 27, Figure 6

Page 28, Figure 7

- **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 (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<sub>OM</sub> (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<sub>OM</sub>, and compared our assumptions with measured f<sub>OM</sub> 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-O<sub>2</sub>ANT), 1,4-naphthoquinone (1,4-O<sub>2</sub>NAP), and 1,2-benzanthraquinone (1,2-O<sub>2</sub>BAA) were previously found in diesel exhaust (Choudhury, 1982; Cho et al., 2004)..... formation of 1,4-O<sub>2</sub>NAP and 9,10-O<sub>2</sub>ANT 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, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT 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; 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.”

# 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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## Abstract

Nitrated and oxygenated polycyclic aromatic hydrocarbons (N/OPAHs) are emitted in combustion processes and formed in polluted air. Their environmental cycling through wet deposition has hardly been studied. Fresh snow samples at urban and rural sites in central Europe, as well as surface snow from a remote site in Svalbard were analysed for 17 NPAHs, 9 OPAHs, and 11 nitrated mono-aromatic hydrocarbons (NMAHs), of which most N/OPAHs as well as nitrocatechols, nitrosalicylic acids, and 4-nitroguaiacol are studied for the first time in precipitation. In order to better understand the scavenging mechanisms, the particulate mass fractions ( $\theta$ ) at 273K were predicted using a multiphase gas-particle partitioning model based on polyparameter linear free energy relationships.  $\sum$ NPAH concentrations were 1.2-17.6 and 8.8-19.1 ng L<sup>-1</sup> at urban and rural sites, whereas  $\sum$ OPAHs were 269.5 – 1114.1 and 478.7 - 2384.4 ng L<sup>-1</sup> at these sites, respectively. Acenaphthenequinone and 9,10-anthraquinone were predominant in snow aqueous and particulate phases, respectively. NPAHs were only found in the particulate phase with 9-nitroanthracene being predominant followed by 2-nitrofluoranthene. Among NMAHs, 4-nitrophenol showed the highest abundance in both phases. The levels found for nitrophenols were in the same range or lower than those reported in the 1980s and 1990s. The lowest levels of  $\sum$ N/OPAHs and  $\sum$ NMAHs were found at the remote site (9.2 and 390.5 ng L<sup>-1</sup>, respectively). N/OPAHs preferentially partitioned in snow particulate phase in accordance with predicted  $\theta$ , whereas NMAHs were predominant in the aqueous phase, regardless of  $\theta$ . It is concluded that the phase distribution of non-polar N/OPAHs in snow is determined by their gas-particle partitioning prior to snow scavenging, whereas that for polar particulate phase substances, i.e. NMAHs, is determined by an interplay between gas-particle partitioning in the aerosol and dissolution during in- or below-cloud scavenging.

## 1 Introduction

Nitrated and oxygenated polycyclic aromatic hydrocarbons (N/OPAHs) are formed primarily by oxidation of parent PAHs during combustion of fossil fuels as well as biomass burning, and secondarily through reactions of PAHs with atmospheric oxidants, such as O<sub>3</sub>, OH and NO<sub>x</sub> (Walgraeve et al., 2010; Bandowe and Meusel, 2017). N/OPAHs were found in emissions from gasoline, diesel and biodiesel (Pham et al., 2013; Zielinska et al., 2004; Karavalakis et al., 2010), biomass and coal burning (Ding et al., 2012; Shen et al., 2012; Vicente et al., 2016; Shen et al., 2013a; Shen et al., 2013b; Huang et al., 2014) and solid waste incineration (Watanabe and Noma, 2009). These substance groups were also suggested to play a role in light absorption properties of biomass burning particulate matter (PM) (Lin et al., 2016). Some NPAHs, e.g. 3-nitrofluoranthene (3-NFLT) and 1-nitropyrene (1-NPYR), are associated specifically with combustion sources, whereas others such as 2-nitrofluoranthene (2-NFLT) and 2-nitropyrene (2-NPYR) are produced through gas phase reaction of FLT and PYR with OH radicals and NO<sub>x</sub> (Arey et al., 1986; Bandowe and Meusel, 2017). NPAHs are also formed through reactions in the aerosol condensed phase (Keyte et al., 2013; Jariyasopit et al., 2014). Photolysis of NPAHs results in the formation of other oxygenated and nitrated species such as hydroxynitro-PAHs, quinones, and nitrated quinones (Bandowe and Meusel, 2017). Unlike NPAHs, there is no agreement on distinct formation pathways of individual OPAHs – to various extents, they originate from both primary and secondary sources (Walgraeve et al., 2010; Zhuo et al., 2017).

For instance, 9-fluorenone (9-OFLN), 9,10-anthraquinone (9,10-O<sub>2</sub>ANT), 1,4-naphthoquinone (1,4-O<sub>2</sub>NAP), and 1,2-benzanthraquinone (1,2-O<sub>2</sub>BAA) were previously found in diesel exhaust (Choudhury, 1982; Cho et al., 2004) and biomass and coal burning emission, along with acenaphthenequinone (O<sub>2</sub>ACE) (Shen et al., 2013a; Huang et al., 2014; Vicente et al., 2016), whereas in ambient PM, 9-OFLN, 9,10-O<sub>2</sub>ANT, and 1,2-O<sub>2</sub>BAA were attributed to both primary and secondary sources (Kojima et al., 2010; Souza et al., 2014; Lin et al., 2015; Zhuo et al., 2017). The contribution of primary sources is expected to be higher during the cold season with heating activities dominating the vehicular emission (Lin et al., 2015). Interestingly, benzanthrone (OBAT) does not have a stable parent PAH precursor with the same number of rings in the atmosphere (Kojima et al., 2010). This substance, together with benz(*a*)fluorenone (BaOFLN) and benz(*b*)fluorenone (BbOFLN), was associated with primary combustion sources (Albinet et al., 2007; Karavalakis et al., 2010; Shen et al., 2013b; Souza et al., 2014; Huang et al., 2014; Tomaz et al., 2016; Vicente et al., 2016). One must also note the possibility of NPAH conversion to OPAHs in the atmosphere. For instance, formation of 1,4-O<sub>2</sub>NAP and 9,10-O<sub>2</sub>ANT 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).

Many N/OPAHs are suggested to be more mutagenic than their parent species and are also classified as possible carcinogens (Finlayson-Pitts and Pitts, 2000; Lammel, 2015). Moreover, quinones, a prominent sub-class of OPAHs, are precursors of environmentally persistent free radicals (Borrowman et al., 2016) and reactive oxygen species (Chung et al., 2006; Charrier et al., 2014), inducing oxidative stress and inflammatory reactions in organisms, which may lead to cellular damage, respiratory and cardiovascular disease (Lodovici and Bigagli, 2011; Møller et al., 2014; Kelly and Fussell, 2017).

Nitrated mono-aromatic hydrocarbons (NMAHs) are composed of several chemically related compound classes such as: nitrophenols, nitroguaiacols, nitrocatechols and hydroxy-nitrobenzoic (i.e. nitrosalicylic) acids, which among

others contain nitro, hydroxyl and carboxyl functionalities (Chow et al., 2016). Nitrophenols are emitted from primary sources, particularly biomass burning but also traffic exhaust (Trempp et al., 1993), or formed in secondary processes – nitration of precursors such as phenol in the atmosphere (Harrison et al., 2005). Nitrocatechols and nitrosalicylic acids are mainly secondary oxidation products of substituted phenols (alkylphenols, methoxyphenols, hydroxybenzoic acids) emitted in primary aerosols from biomass (e.g. wood) burning (Iinuma et al., 2007; Iinuma et al., 2010; Kitanovski et al., 2012; Kahnt et al., 2013; Chow et al., 2016). Increased production of nitrocatechols in the urban environment due to anthropogenic activities, such as wood burning in winter, was suggested by previous studies (Kitanovski et al., 2012; Chow et al., 2016). Kitanovski et al., (2012) reported a high correlation between concentrations of nitrocatechols and nitrosalicylic acids ( $R^2 > 0.8$ ) in urban PM, which suggests secondary formation of nitrosalicylic acids as well as 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). NMAHs are ecotoxic (Pflieger and Kroflič, 2017) while little is known about human toxicity (Huang et al., 1995; Harrison et al., 2005; Kovacic and Somanathan, 2014). Due to nitrophenol phytotoxic potential, the research on them in precipitation was fostered during the late 1980s and early 1990s in relation with research on forest decline in central Europe (Rippen et al., 1987; Leuenberger et al., 1988; Herterich and Herrmann, 1990). Last but not least, NMAHs significantly contribute to the light absorptive properties of PM organic carbon (Mohr et al., 2013; Hinrichs et al., 2016; Bluvshstein et al., 2017; Teich et al., 2017), and can influence climate by altering Earth’s albedo. Semi-volatile organic compounds (SVOCs) in the atmosphere are subject to removal by dry particle deposition and wet scavenging. The latter consists of two processes – i.e. particle scavenging and gas scavenging. The particle scavenging is relevant for SVOCs that show higher affinity towards particulate phase (Bidleman, 1988; Shahpoury et al., 2015). This is affected by SVOC gas-particle partitioning (GPP) in the aerosol, a process controlled mainly by the substance molecular structure, PM chemical composition, and ambient temperature (Shahpoury et al., 2016). The magnitude of SVOC sorption to PM is defined by its particulate mass fraction,  $\theta$  Eq. (1):

$$\theta = c_p / (c_p + c_g) \quad (1)$$

where  $c_p$  and  $c_g$  are concentrations of SVOC ( $\text{ng m}^{-3}$ ) in the particulate and gas phases, respectively. The gas scavenging is relevant for substances which demonstrate minimum interaction with PM and therefore remain to various extents in the gas phase. Although gas scavenging is affected by GPP, the actual removal from the atmosphere is due to substance dissolution in cloud or rain droplets or sorption to snowflakes or other ice hydrometeors (Hoff et al., 1995; Bartels-Rausch et al., 2014). Following wet scavenging, SVOCs in the gas and particulate phases in the atmosphere accumulate in precipitation aqueous and particulate phases, respectively. The fraction of SVOCs removed by particle scavenging is given by  $\theta_w$  Eq. (2):

$$\theta_w = c_{pp} / (c_{pp} + c_{pa}) \quad (2)$$

where  $c_{pp}$  and  $c_{pa}$  are analyte concentrations ( $\text{ng L}^{-1}$ ) in precipitation particulate and aqueous phases, respectively. It has been shown that the magnitude of particle scavenging is generally higher than gas scavenging for hydrophobic SVOCs such as PAHs (Atlas and Giam, 1988; Bidleman, 1988; Shahpoury et al., 2015). In principle, for such substances one could apply  $\theta$  as an indicator for predicting the SVOC wet particle scavenging – i.e. the higher the  $\theta$

at a given temperature, the more efficient is the scavenging, and the magnitude of  $\Theta_w$  is expected to be close to  $\Theta$ . However, it is anticipated that for *hydrophilic* SVOCs, which may demonstrate low or high  $\Theta$ , water solubility plays an additional role in the substance wet scavenging pathways and the comparability of  $\Theta_w$  with  $\Theta$ . For instance, a NMAH with high  $\Theta$  in the atmosphere may demonstrate low  $\Theta_w$  due to substance dissolution in hydrometeors following particle scavenging. Conversely, a NMAH with low  $\Theta$  is expected to show low  $\Theta_w$ , as it undergoes gas scavenging process.

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) Eq. (3):

$$W_T = (c_{\text{snow}} \times 1000) / c_{\text{air}} \quad (3)$$

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

There is currently very limited information in the literature about the occurrence of N/OPAHs and NMAHs in precipitation, except for small number of OPAHs (Kawamura and Kaplan, 1983) and nitrophenols: 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 (Leuenberger et al., 1988; Alber et al., 1989; Herterich and Herrmann, 1990; Levsen et al., 1990; Levsen et al., 1991; Levsen et al., 1993; Schüssler and Nitschke, 2001; Bossi et al., 2002; Kohler and Heeb, 2003; Asman et al., 2005; Belloli et al., 2006; Jaber et al., 2007; Schummer et al., 2009), in North America (Ganranoo et al., 2010), and Antarctica (Vanni et al., 2001) (Table S1).

The aims of the present study were (1) to investigate the presence of N/OPAHs and NMAHs in the aqueous and particulate phases of fresh snow, (2) estimate the substance particulate mass fractions in the atmosphere using a multiphase GPP model, based on poly-parameter linear free energy relationships (ppLFER), and (3) determine the substance fractions removed by wet particle scavenging, and explore the effect of GPP vs. water solubility on target compound wet scavenging. For calculating  $\Theta$ , 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).

## 2 Experimental

### 2.1 Sampling

Snow samples were collected between winter 2015 and 2017 from three locations in Germany, i.e. Mainz (MZ15 and MZ17; urban-residential,  $\approx 200000$  inhabitants), Winterberg (WB) and Altenberg (AB; rural,  $>10$  km from small towns), two locations in Inn Valley, Austria, i.e. Götzens (GS; urban-residential of a mid-sized city, Innsbruck,  $\approx 140000$  inhabitants) and Kolsassberg (KB; rural, 10-20 km from city and towns), two locations in the Czech Republic, i.e. Ostrava (OS; urban, conurbation with  $\approx 700000$  inhabitants) and Pustá Polom (PP1 and PP2; rural, 20

km upwind from Ostrava), and one location in the Arctic, Tempelfjorden, Svalbard (TF, remote, 50-80 km from small towns). The sample site details are shown in Table 1. Fresh snow samples (all sites, except TF) were collected by placing several polypropylene trays (0.25 m<sup>2</sup> each) on the ground prior to snowfall. To this end, the snow forecast for a number of pre-selected sites was monitored on daily basis. Both collection trays and bottles were pre-cleaned prior to sample collection in the lab using detergent, tap water, deionized water, and high-purity ethanol. The snow was transferred with compaction in amber 2-L bottles and kept frozen at -18°C until analysis. Dry and light surface snow (0-5 cm deep, somewhat harder at the surface), which had fallen 3-2 days before, was collected at TF and stored in pre-cleaned amber bottles. Following this sample collection and storage procedure, we rely on exclusion of significant phase change during storage and prior to sample processing.

## 2.2 Sample processing

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. The setup consisted of a pre-assembled sterile analytical filter funnel (250 mL, graduated, Nalgene, Thermo Scientific, Waltham, MA, USA), connected to a solid-phase extraction disk (Bakerbond Speedisk, J.T. Baker, the Netherlands) using a Teflon adaptor designed in-house (Fig. S1). This was assembled on a J.T. Baker extraction station connected to a vacuum pump. A steady sample flow (10 mL min<sup>-1</sup>) was established between the filter funnel and Speedisk throughout sample processing, by occasionally applying vacuum, where needed. 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. The pH of meltwater samples was 4.5-5.

## 2.3 N/OPAH extraction and chemical analysis

0.22 µm cellulose nitrate filter in 250 mL analytical filter funnel and octadecyl (C18) Speedisk were used for N/OPAHs extraction. Speedisks were pre-conditioned with 50 mL of methanol followed by 10 mL of deionized water, and spiked with a mixture of deuterated standards, containing 75 ng of 1-nitronaphthalene-d<sub>7</sub>, 2-nitrofluorene-d<sub>9</sub>, 9-nitroanthracene-d<sub>9</sub>, 3-nitrofluoranthene-d<sub>9</sub>, 1-nitropyrene-d<sub>9</sub>, 6-nitrochrysene-d<sub>11</sub>, 9,10-anthraquinone-d<sub>8</sub>, and 9-fluorenone-d<sub>8</sub>. Filter papers containing particulate phase were spiked with the same standard mixture after sample processing prior to their extraction. After loading the samples, Speedisks were capped with aluminium foil and dried by pumping air through them for 5 min.

The filter papers containing the particulate phase were extracted following a QuEChERS method (Albinet et al., 2014). Briefly, each filter paper was placed in a glass centrifuge tube (Duran, Schott, Mainz, Germany) and added with 7 mL of dichloromethane (DCM). The centrifuge tubes were capped with screw caps containing PTFE lining. Each sample

was vortexed for 1.5 min, passed through a glass funnel plugged with a small amount of deactivated glass wool (in order to remove residual sample matrix), and concentrated to 0.5 mL using a Turbovap II (Biotage, Uppsala, Sweden). The extracts were later loaded on a pre-conditioned 500 mg SiO<sub>2</sub> cartridge (Macherey-Nagel, Weilmünster, Germany), and eluted with 9 mL of 65:35 *n*-hexane-DCM. The aqueous phase samples enriched on C18 Speedisks were eluted with 40 mL of 1:1 *n*-hexane-DCM. All extracts from particulate and aqueous phases were concentrated to 0.5 mL and the solvent was exchanged to ethyl acetate (3×5 mL). The sample volumes were further adjusted to 0.3 mL and 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. All solvents used for N/OPAH analysis were Suprasolv grade (Merck, Darmstadt, Germany).

The samples were analysed using a Trace 1310 gas chromatograph (GC, Thermo Scientific, Waltham, MA, USA) coupled to a TSQ8000 Evo triple-quadrupole mass selective detector (MS/MS, Thermo Scientific) in negative chemical ionization and selected ion monitoring (SIM) modes. The analyte separation was achieved on a J&W DB-5ms column (30 m + 10 m integrated guard, 0.25 mm ID, 0.25 µm film thickness, Santa Clara, CA, USA) with helium (99.9999%; Westfalen AG, Münster, Germany) as carrier gas at 1 mL min<sup>-1</sup> flow rate. The GC operating conditions were as follows: the GC oven was held at 60°C for 2 min, then ramped to 180°C at 15°C min<sup>-1</sup>, followed by a 5°C min<sup>-1</sup> ramp to 280°C and final hold time of 15 min. The injection port temperature was set to 250°C and operated in pulsed splitless mode (30 psi pulsed pressure for 1.5 min, and splitless time of 1.8 min). MS transfer line and ion source temperature were set to 290 and 230°C, respectively. Methane (>99.9995, Messer, Bad Soden, Germany) was used as ionization gas with 1.5 mL min<sup>-1</sup> flow rate. Emission current and electron energy were set to 100 µA and -70 eV, respectively. The samples were analysed for N/OPAHs listed in Table 2. Each target analyte was identified using its retention time and quantification ion (Table 2). The analyte quantification was done using the internal calibration method with 11-point calibration curves ranging from 0.25-1000 pg µL<sup>-1</sup>.

#### 2.4 NMAH extraction and chemical analysis

0.22-micron cellulose acetate filter in the 250 mL analytical filter funnel and divinylbenzene hydrophilic Speedisk were used for NMAH extraction. The detailed analytical method is described in a companion paper (Kitanovski and Naumoska, in preparation). Briefly, the pre-conditioned Speedisk was spiked with 100 ng of 4-nitrophenol-d<sub>4</sub>, the sample (250 mL) was acidified with 2 mL of formic acid, and passed through the disk. The elution of NMAHs from the disks was done using a mixture of acetonitrile-methanol containing 3.4 µM ethylenediaminetetraacetic acid (EDTA). The presence of EDTA in the elution solvent was necessary for complete recovery of the NMAHs from the polymeric disks. 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.

The PM retained on the cellulose acetate filters was spiked with the same quantity of 4-nitrophenol-d<sub>4</sub> and extracted using a previously published procedure (Kitanovski et al., 2012). 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  $\mu\text{M}$  EDTA. All samples were analyzed using a 1200 Series liquid chromatograph (LC; Agilent Technologies, Santa Clara, CA, USA) coupled to a 6130 single-quadrupole MS (Agilent Technologies) with an electrospray ionization (ESI) source. Separation was achieved on an Atlantis T3 column ( $150 \times 2.1$  mm ID,  $3 \mu\text{m}$ ; Waters, Milford, MA, USA), thermostated at  $30^\circ\text{C}$  during sample analysis. The NMAH elution was done using 30:15:55 methanol-tetrahydrofuran-aqueous ammonium formate buffer (5 mM, pH 3) mobile phase in isocratic mode. The deprotonated NMAHs  $[\text{M}-\text{H}]^-$  listed in Table 2 were detected in negative ion ESI and SIM modes. The analyte quantification was done using the internal calibration method in concentration range  $1\text{-}500 \text{ pg } \mu\text{L}^{-1}$ .

## 2.5 Quality control

Field blanks were prepared during sample collection by exposing the pre-cleaned sample bottles with open cap to air for 5 min at the sites. The inner wall of the bottles was rinsed with 500 mL of deionized water in the lab and processed as field blank along with the rest of samples. Limits of quantification (LOQ) for analytes were calculated based on instrument detection limits (IDL), which in turn are determined using 3 times the chromatogram baseline noise level. LOQ values were determined as mean concentration of each analyte in blanks + 3 standard deviations. For this purpose, blank values that were  $<\text{IDL}$  were replaced with IDL values. Where analyte concentrations in samples exceeded the LOQ, mean blank concentrations were subtracted from those in the corresponding samples.

## 2.6 Estimation of particulate mass fractions

The  $\theta$  for target analytes were estimated using modelled GPP constants,  $K_P$  ( $\text{m}^3\text{g}^{-1}$  at  $273.15 \text{ K}$ ), which were calculated using a multiphase ppLFR model (Shahpoury et al., 2016). The model differentiates between various organic and inorganic phases of PM, and accounts for absorption into water soluble organic matter (WSOM) and organic polymers (OP), as well as adsorption onto black carbon,  $(\text{NH}_4)_2\text{SO}_4$  and NaCl, Eq. (4):

$$K_P (\text{m}^3_{\text{air}} \text{g}_{\text{PM}}^{-1}) = \left[ (K_{\text{BC}} \times a_{\text{BC}} \times f_{\text{BC}} + K_{(\text{NH}_4)_2\text{SO}_4} \times a_{(\text{NH}_4)_2\text{SO}_4} \times f_{(\text{NH}_4)_2\text{SO}_4} + K_{\text{NaCl}} \times a_{\text{NaCl}} \times f_{\text{NaCl}}) + (K_{\text{DMSO}}/\rho_{\text{DMSO}} \times f_{\text{WSOM}} + K_{\text{PU}} \times f_{\text{OP}}) \right] \quad (4)$$

where  $K_{\text{BC}}$ ,  $K_{(\text{NH}_4)_2\text{SO}_4}$  and  $K_{\text{NaCl}}$  are the target substance partitioning coefficients ( $\text{mol m}^{-2}_{\text{surface}}/\text{mol m}^{-3}_{\text{air}}$ ) for black carbon/diesel soot,  $(\text{NH}_4)_2\text{SO}_4$  and NaCl (the last two represent the contributions of secondary inorganic aerosols and sea salt), respectively,  $a_{\text{BC}}$ ,  $a_{(\text{NH}_4)_2\text{SO}_4}$  and  $a_{\text{NaCl}}$  are the adsorbent specific surface areas ( $\text{m}^2_{\text{surface}} \text{g}^{-1}_{\text{adsorbent}}$ ), and  $f_{\text{BC}}$ ,  $f_{(\text{NH}_4)_2\text{SO}_4}$  and  $f_{\text{NaCl}}$  are their mass mixing ratios in PM ( $\text{g}_{\text{adsorbent}} \text{g}^{-1}_{\text{PM}}$ ). For  $a_{\text{BC}}$ , the geometric mean of  $18.21 \text{ m}^2 \text{g}^{-1}$  was calculated from the values reported for traffic, wood, coal, and diesel soot (Jonker and Koelmans, 2002), whereas,  $a_{(\text{NH}_4)_2\text{SO}_4}$  and  $a_{\text{NaCl}}$  of  $0.13$  and  $0.10 \text{ m}^2 \text{g}^{-1}$  were taken from Goss et al., (2003).  $K_{\text{DMSO}}$  ( $\text{m}^3_{\text{air}} \text{m}^{-3}_{\text{DMSO}}$ ) and  $K_{\text{PU}}$  ( $\text{m}^3_{\text{air}} \text{g}^{-1}_{\text{PU}}$ ) are the substance partitioning (absorption) coefficients for dimethyl sulfoxide-air and polyurethane-air partitioning systems;  $\rho_{\text{DMSO}}$  is dimethyl sulfoxide density ( $\text{g m}^{-3}$ );  $f_{\text{WSOM}}$  and  $f_{\text{OP}}$  are mass mixing ratios of absorbing phases ( $\text{g}_{\text{adsorbent}} \text{g}^{-1}_{\text{PM}}$ ), corresponding to  $f_{\text{OM}}$  (the mixing ratio of total organic matter in PM)  $\times 0.60$  and  $f_{\text{OM}} \times 0.40$ ,

respectively. The correction factors of 0.60 and 0.40 were estimated based on the data from Rogge et al., (1993). These factors were previously verified through a sensitivity study (Shahpoury et al., 2016). We assumed two scenarios for model calculations:  $f_{BC} = 0.03$  and  $f_{OM} = 0.30$ , and  $f_{BC} = 0.06$  and  $f_{OM} = 0.60$ . This resulted in  $f_{WSOM}$  and  $f_{OP}$  of 0.18 and 0.12, and 0.36 and 0.24 for the two scenarios, respectively. The contributions of inorganic salts and PM aqueous phase to the overall sorption process were neglected; we acknowledge that under high relative humidity, salts may be present in aqueous phase, and subject to liquid-liquid phase separation with PM organic matter (You et al., 2014). The individual partitioning constants used in the multi-phase model were calculated using substance-specific Abraham descriptors listed in Table S2 and ppLFER models listed in Table S3 (Abraham et al., 2010; Kamprad and Goss, 2007; Roth et al., 2005; Goss et al., 2003).

See Shahpoury et al., (2016) for more details about calculation with multiphase model and Endo and Goss (2014) for background about ppLFER concept. The predicted  $K_P$  values were converted to  $\theta$  under two scenarios with  $c_{PM}$  of 25 and 50  $\mu\text{g m}^{-3}$ , Eq. (5):

$$\theta = \frac{K_P c_{PM}}{(1+K_P c_{PM})} \quad (5)$$

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.

## 2.7 Air mass history analysis

The HYSPLIT (Draxler and Rolph, 2003) model was used to identify the air masses' three-day histories related to the snowfall events. The meteorological data ( $1^\circ \times 1^\circ$  resolution) used were from the Global Data Assimilation System (GDAS, NCEP, USA). Air mass changes were identified based on weather charts (Berliner Wetterkarte, 2015), except for sample site in Svalbard, TF, as the snow fell 2-3 days prior to sample collection. The results are presented in the Supplement, Text S1 and Fig. S2.

### 3 Results and discussion

#### 3.1 N/OPAH concentrations and distribution in snow

Snow **aqueous** and particulate phases were analysed for N/OPAHs following the method described in Sect. 2.3. **In the aqueous phase, 9-OFLN, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT were found in nearly all samples,** except at the remote site **TF**, where 9,10-O<sub>2</sub>ANT was not found (Fig. 1A and 2A). **O<sub>2</sub>ACE was the most abundant substance in the aqueous phase** ( $\leq 779.8 \text{ ng L}^{-1}$ ), followed by 9,10-O<sub>2</sub>ANT ( $\leq 89.7 \text{ ng L}^{-1}$ ) and 9-OFLN ( $\leq 45.3 \text{ ng L}^{-1}$ ). 1,2-O<sub>2</sub>BAA, 1,4-O<sub>2</sub>NAP, OBAT, and **BaOFLN were found less frequently with relatively low concentrations in the aqueous phase** (Fig. 1A and 2A). **9-OFLN, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT 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). Overall, **TF and MZ17 were the least and most polluted sites, with  $\Sigma$  OPAH aqueous concentrations of 7.3 and 834 ng L<sup>-1</sup>, respectively.** **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.**

In the particulate phase of snow, four NPAHs and seven OPAHs were detected (Fig. 1B and 2B). Among all analytes, 9,10-O<sub>2</sub>ANT (found in **GS, WB, AB** and **KB**) showed the highest concentrations of up to  $242.2 \text{ ng L}^{-1}$ , followed by 9-OFLN (found in all but **TF**;  $\leq 30.3 \text{ ng L}^{-1}$ ), BaOFLN ( $\leq 27.3 \text{ ng L}^{-1}$ ), and 1,2-O<sub>2</sub>BAA ( $\leq 23.3 \text{ ng L}^{-1}$ ). The detected NPAHs in the particulate phase, 9-NANT, 2-NFLT, 1-NNAP, and 2-nitronaphthalene (2-NNAP), showed relatively low concentrations up to 13.6, 2.6, 1.3, and  $0.32 \text{ ng L}^{-1}$ , respectively (Fig. 1B and 2B). NPAHs found in the present study are the most frequently detected congeners in the gas (1- and 2-NNAP) and particulate (2-NFLT and 9-NANT) phases (Dimashki et al., 2000; Bamford and Baker, 2003; Albinet et al., 2006; Tomaz et al., 2016; Bandowe and Meusel, 2017), with 2-NFLT being exclusively formed through reaction of FLT with oxidants in the atmosphere (Bandowe and Meusel, 2017) and the other three NPAHs being produced by both primary and secondary sources (Zhuo et al., 2017). Overall, the remote site **TF** and rural site **KB** were the least and most polluted sites in the particulate phase, with  $\Sigma$  N/OPAH concentrations of 1.9 and  $359.8 \text{ ng L}^{-1}$ , respectively (Fig. 2B).

Snow samples **OS, PP1** and **PP2** were not phase-separated for N/OPAH analysis. Out of all targeted NPAHs, only 2-NFLT ( $11.6\text{-}19.1 \text{ ng l}^{-1}$ ) was found at these sites (Fig. 3; Table S4A). Among OPAHs, OBAT, O<sub>2</sub>ACE, and 9,10-O<sub>2</sub>ANT showed the highest concentrations up to 758.1, 609.9, and  $607.7 \text{ ng L}^{-1}$ , respectively, whereas 1,2-O<sub>2</sub>BAA, BbOFLN, BaOFLN, 9-OFLN, and 1,4-O<sub>2</sub>NAP were relatively less abundant (Fig. 3; Table S4A). N/OPAH concentrations were overall higher at the rural sites **PP1** and **PP2** than the urban site **OS** (Table S4A). In terms of total N/OPAH concentrations (i.e. **aqueous** + particulate) across all sites, **TF** and **PP2** were the least and most polluted sites (Table S4A). NPAHs contributed up to 10% to the total concentrations across the samples. The predominance of OBAT, 9,10-O<sub>2</sub>ANT, O<sub>2</sub>ACE, and 9-OFLN in our study is consistent **with previous findings in the literature (Albinet et al., 2007; Souza et al., 2014; Lin et al., 2015; Tomaz et al., 2016).** 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).

### 3.2 NMAH concentrations and distribution in snow

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 up to 2155.4 ng L<sup>-1</sup>, followed by 4-NC ( $\leq 763.6$  ng L<sup>-1</sup>), 3-M-4-NP ( $\leq 547.3$  ng L<sup>-1</sup>), 2-M-4-NP ( $\leq 341.1$  ng L<sup>-1</sup>), and 5-NSA ( $\leq 313.5$  ng L<sup>-1</sup>). In this phase, 4-NG was exclusively found in urban samples OS and MZ17 (Fig. 4A), and rural and remote sites PP1, PP2, and TF (Fig. 5A). Overall in the aqueous phase, TF and MZ17 were the least and most polluted samples, with  $\sum$  NMAH concentrations of 390.5 and 4252.6 ng L<sup>-1</sup>, respectively (Fig. 4A and 5A).

The NMAHs were less abundant in the snow particulate phase (Fig. 4B and 5B). 4-NP was found in all samples, with concentrations up to 106.9 ng L<sup>-1</sup> (MZ17), followed by 2-M-4-NP ( $\leq 39.2$  ng L<sup>-1</sup>), 3-M-4-NP (21.8 ng L<sup>-1</sup>), and DNO ( $\leq 11.8$  ng L<sup>-1</sup>; Fig. 4B and 5B). Interestingly, 4-NP was the only NMAH found at the remote site TF. The rest of NMAHs were more sporadic in the particulate phase, with 3-NSA, 4-NG, and 5-NSA being found exclusively at the urban site MZ17 (Fig. 4B). Overall in the particulate phase, the remote site TF was the cleanest ( $\sum$ NMAHs: 3.5 ng L<sup>-1</sup>) and the urban site MZ17 was the most polluted ( $\sum$ NMAHs: 276.6 ng L<sup>-1</sup>) in our study.

The measured nitrophenol concentrations are in the same range as those reported previously for snow from central Europe and Antarctica (Alber et al., 1989; Vanni et al., 2001; Table S1), but lower (up to two orders of magnitude lower) than those reported in rainwater from central and northern Europe (Leuenberger et al., 1988; Herterich and Herrmann, 1990; Levsen et al., 1991; Bossi et al., 2002; Asman et al., 2005; Schummer et al., 2009; Table S1) and the USA (Ganranoo et al., 2010; Table S1). It must be noted that here we report the NMAH concentrations in both aqueous and particulate phases, which was not reported in the previous studies (Table S1). When detected, the aqueous phase concentrations of 4-NG were comparable in urban and rural samples (~ 155-285 ng L<sup>-1</sup>; Fig. 4A and 5A), indicating polluted and aged air masses with biomass burning origin (Kitanovski et al., 2014; Kroflič et al., 2015; Yang et al., 2016). These values are one order of magnitude higher than that measured for the remote sample TF (Fig. 5A). In urban samples with the exception of OS, nitrocatechols (4-NC and isomeric methyl-nitrocatechols) were the second most abundant NMAHs, following nitrophenols (Table S4A). This is in agreement with our current unpublished data and previous studies on winter PM samples (Kitanovski et al., 2012). In contrast, in rural samples KB and PP1, and the remote sample TF, 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.

### 3.3 Modelled particulate mass fractions and actual fractions removed by particle scavenging

The target compound  $\Theta$  was estimated following the method explained in Sect. 2.6. We examined three scenarios i.e., a lower, middle and upper scenario with regard to pollution: (1) with  $f_{BC}$  and  $f_{OM}$  of 0.03 and 0.30 and  $c_{PM}$  of 25  $\mu\text{g m}^{-3}$ , (2)  $f_{BC}$  and  $f_{OM}$  of 0.06 and 0.60 and  $c_{PM}$  of 25  $\mu\text{g m}^{-3}$ , and (3)  $f_{BC}$  and  $f_{OM}$  of 0.06 and 0.60 and  $c_{PM}$  of 50  $\mu\text{g m}^{-3}$ . In

fact, the 24-h mean  $c_{PM}$  values for MZ17 and OS sampling events were 25 and 27  $\mu\text{g m}^{-3}$ , respectively. No data are available from the other sites. As can be seen from Fig. 6A-C,  $\theta$  at 273 K is  $\sim 1$  (complete sorption to PM) for 70% of the target compounds, independent of the above scenarios. The calculations showed that  $<20\%$  of 1-NNAP, 2-NNAP, 1,4-O<sub>2</sub>NAP, 9-OFLN, 2,4-DNP, and DNOC, and between 20 and 80% of 5-NACE, 2-NFLN, O<sub>2</sub>ACE, 3-NSA, and 4-NG can be expected to be in the particulate phase at 273 K (Fig. 6). For these substances,  $\theta$  increases by up to two fold when increasing  $f_{BC}$ ,  $f_{OM}$ , or  $c_{PM}$ . An interesting trend was seen for 2,4-DNP and 4-NP: 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). However, our model calculations suggest the opposite pattern, i.e. complete sorption of 4-NP to PM, but  $<5\%$  sorption for 2,4-DNP. This is largely related to intramolecular H-bonding between the H-atom of the hydroxy group and the O-atom of the nitro group in ortho position. This reduces the H-bonding ability of 2,4-DNP compared to 4-NP (compare the Abraham descriptor  $A$  in Table S2).

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  $\theta$  (Fig. 6A-B) were largely associated with precipitation particulate phase. The only exception was 9,10-O<sub>2</sub>ANT 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-O<sub>2</sub>NAP ( $\theta$ : 0.001-0.003) and O<sub>2</sub>ACE ( $\theta$ : 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.

The observation for NMAHs, however, are considerably different (Fig. 7B). These substances were mainly found in the aqueous phase, including the seven analytes for which complete sorption to PM was predicted under various scenarios. Among all, 4-NP showed the highest fraction in the precipitation particulate phase and, as predicted, higher than 2,4-DNP; this was more pronounced in urban and rural samples OS, PP1 and PP2. The opposite pattern observed for NMAHs may suggest that besides GPP another process influenced the substance wet scavenging and consequently their distribution in precipitation phases. 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. We hypothesize that following both in- and below-cloud scavenging into sub-cooled droplets, particulate-phase NMAHs would dissolve into the bulk water or water layer surrounding ice hydrometeors (Hoff et al., 1995). This process is, at least partly, affected by the substance water

solubility and, therefore, is anticipated to be more efficient for highly water soluble substances such as NMAHs ( $s = 0.3\text{-}10\text{ g L}^{-1}$ ,  $\log K_{OW} = 0.64\text{-}2.54$ ; Fig. S3). This hypothesis is consistent with the results of a previous study where positive correlation was found between in-cloud scavenging efficiencies of PM-bound polar organics and the substance polarity (Limbeck and Puxbaum, 2000). This process (which potentially results in predominance of NMAHs in the aqueous phase), however, must be distinguished from the gas scavenging which was proposed by Leuenberger et al., (1985) as a dominant process for removal of volatile methylated phenols, where the predominance of these substances in the aqueous phase corresponded to their abundance in the gas phase.

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  $10^3\text{-}10^4$  and  $10^3\text{-}10^5$ , 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<sub>2</sub>NAP and 9-OFLN, the range of calculated  $W_T$  is consistent with that of modelled  $\theta$  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<sub>2</sub>ANT and OBAT (~1.1 times higher for OBAT) closely resembled that of estimated  $\theta$  at 273 K (Table S4B). However, we found differences in  $W_T$  between the NMAH subgroups, namely  $W_T$  values were higher for nitrophenols ( $1.3 \times 10^4\text{-}1.6 \times 10^5$ ) and nitrosalicylic acids ( $5.7 \times 10^4\text{-}8.2 \times 10^4$ ) than nitrocatechols ( $1.1 \times 10^3\text{-}2.8 \times 10^3$ ; Table S4B), which cannot be explained by the substances' GPP alone (compare  $\theta$  in Fig. 6C). Although based on a single precipitation event, these results are indication of additional atmospheric processes which NMAHs could undergo and which may affect their 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  $\mu\text{m}$  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.

### Final remarks

The phase-separated concentrations of nitrated and oxygenated aromatic compounds were measured in snow from several locations in central Europe and European Arctic. For the first time, we have reported the snow concentrations for several classes of nitrated and oxygenated aromatics, such as nitrocatechols, nitrosalicylic acids, nitrated and oxygenated PAHs, and 4-nitroguaiacol. Our results showed that a model-predicted particulate mass fraction,  $\theta$ , can be reliably applied in order to predict the scavenging mechanism (gas or particle scavenging) and efficiency of hydrophobic N/OPAHs and, hence, their distribution in precipitation phases i.e., aqueous and particulate. This suggests that the atmospheric lifetime of N/OPAHs in relation to removal processes follows the same pattern as that of parent PAHs (Sharma and McBean, 2002). On the contrary,  $\theta$  is not a good measure for predicting phase distribution of hydrophilic NMAHs in precipitation. Our data suggests that the phase distribution of polar particulate phase substances, such as NMAHs in snow is determined by an interplay between GPP in the aerosol and dissolution in cloud or rain droplets, or the liquid water phase on the surface of ice hydrometeors during in- or below-cloud

scavenging. This behaviour is in line with what was found for in-cloud scavenging of other polar mono- and difunctional organics, such as aliphatic alcohols, and aliphatic and monoaromatic aldehydes and carboxylic acids (Limbeck and Puxbaum, 2000), namely the polarity of these substances is a significant parameter for their scavenging when solubility is  $> 1 \text{ g L}^{-1}$ . The experimental data on GPP of NMAHs is scarce in the literature, which was also not addressed here. The contribution of gaseous polar NMAHs to the total scavenging, beyond the scope of this study, should be addressed, similar to other polar aliphatic and aromatic organics (Limbeck and Puxbaum, 2000).

### Data availability

The dataset used in this manuscript is included in the Supplement, and further information is available from the corresponding author (p.shahpoury@mpic.de).

### Competing interests

The authors declare that they have no conflict of interest.

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**Table 1. Sampling site details**

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

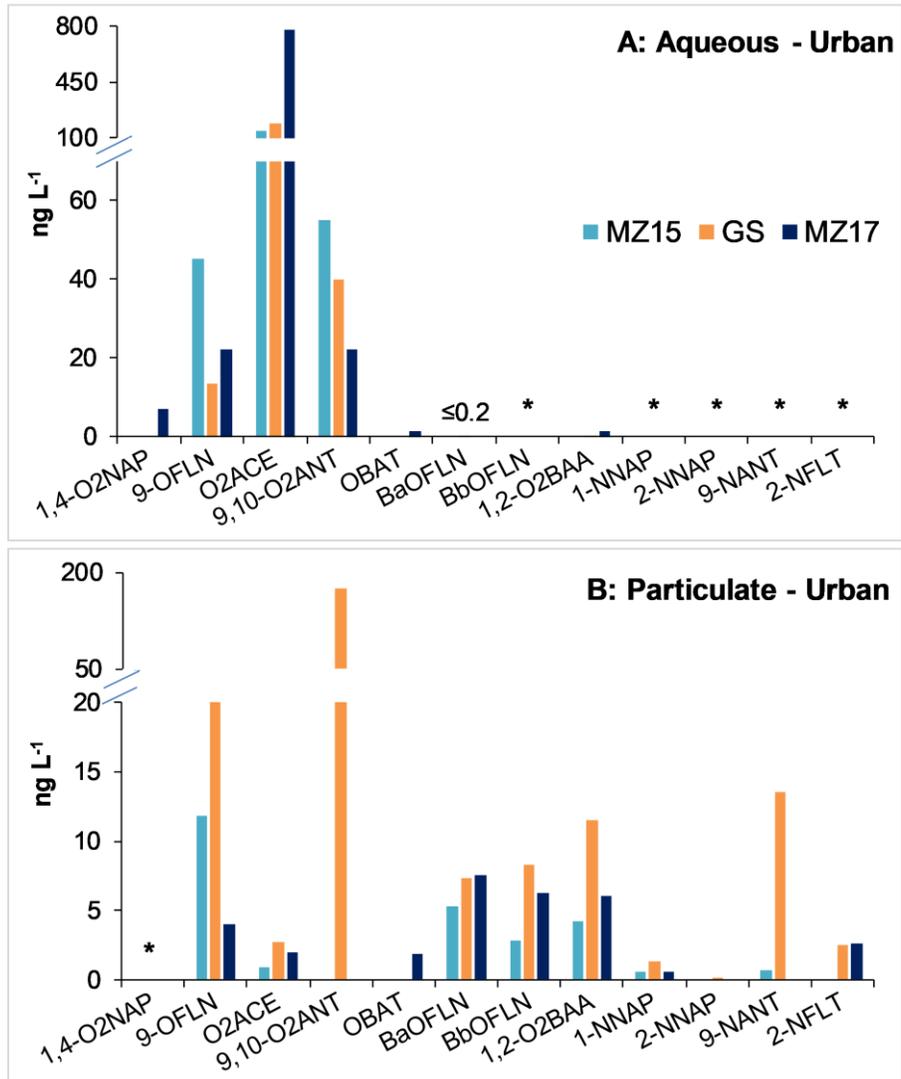
<sup>a</sup> old snow, fallen 3-2 days before sampling

**Table 2. Target compound list**

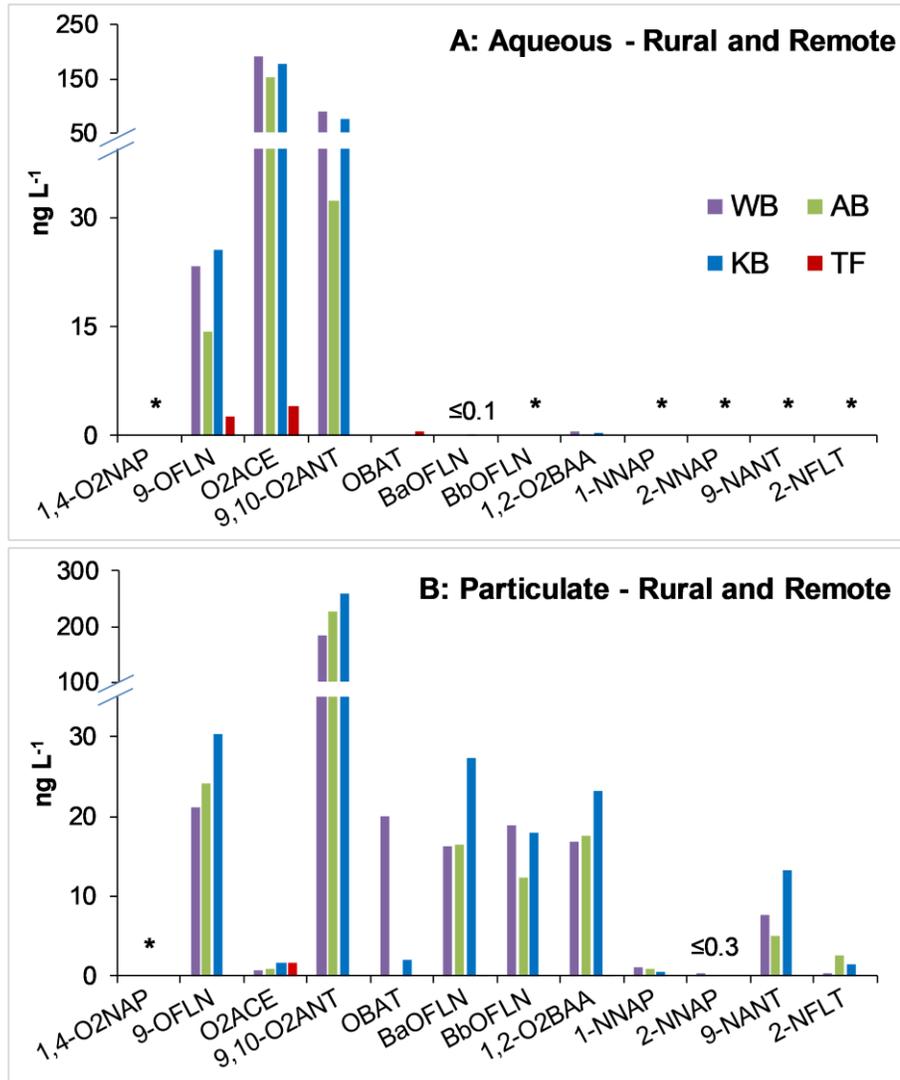
Analyte	Abbreviation	RT	Q1	Detection <sup>a</sup>
1-Nitronaphthalene	1-NNAP	12.12	173.1	P (86)
2-Nitronaphthalene	2-NNAP	12.62	173.1	P (43)
5-Nitroacenaphthene	5-NACE	17.52	199.1	n.d.
2-Nitrofluorene	2-NFLN	19.07	211.1	n.d.
9-Nitroanthracene	9-NANT	19.46	223.1	P (71)
9-Nitrophenanthrene	9-NPHE	20.64	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 <sub>2</sub> PYR	31.8	292.1	n.d.
1,6-Dinitropyrene	1,6-N <sub>2</sub> PYR	32.81	292.1	n.d.
1,8-Dinitropyrene	1,8-N <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> ANT	17.03	208.1	A (86) P (57)
Acenaphthenequinone	O <sub>2</sub> 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 <sub>2</sub> 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; <sup>a</sup> 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

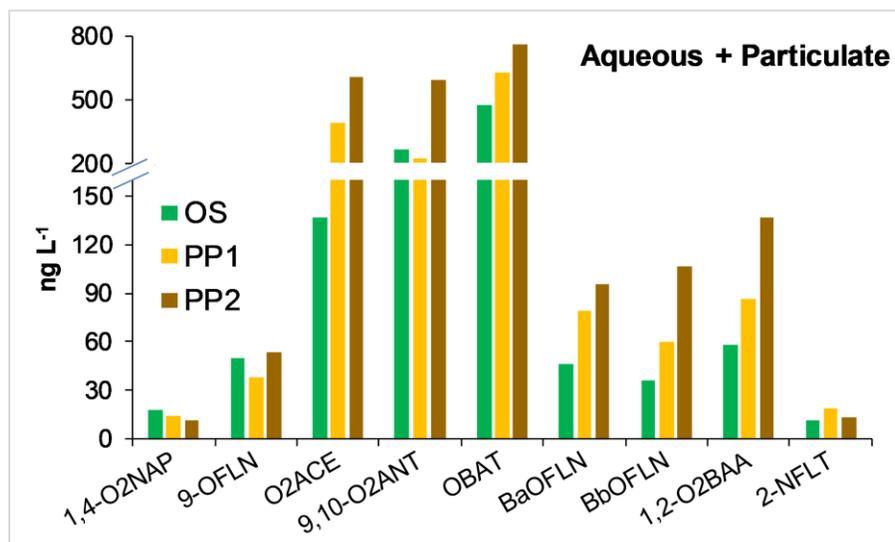
**Figure 1** N/OPAHs in urban snow samples; \* indicates values <LOQ in all samples



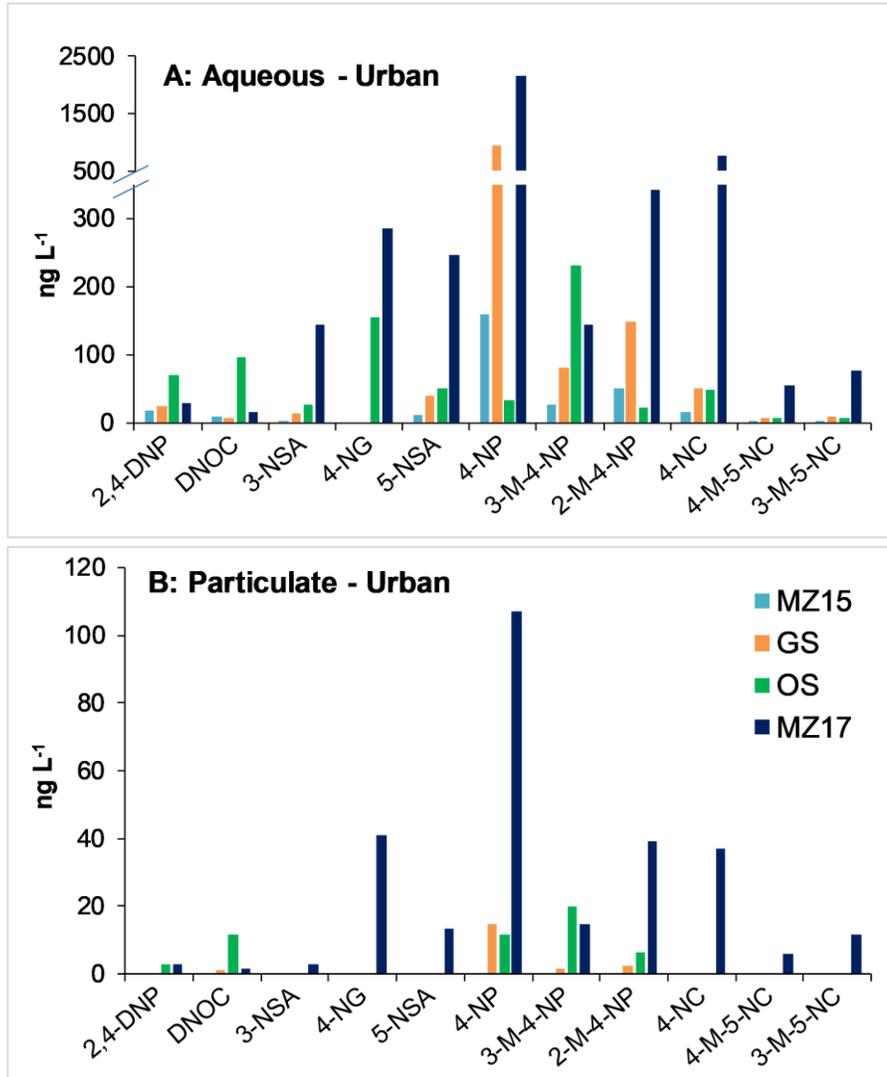
**Figure 2** N/OPAHs in rural and remote snow samples; \* indicates values <LOQ in all samples



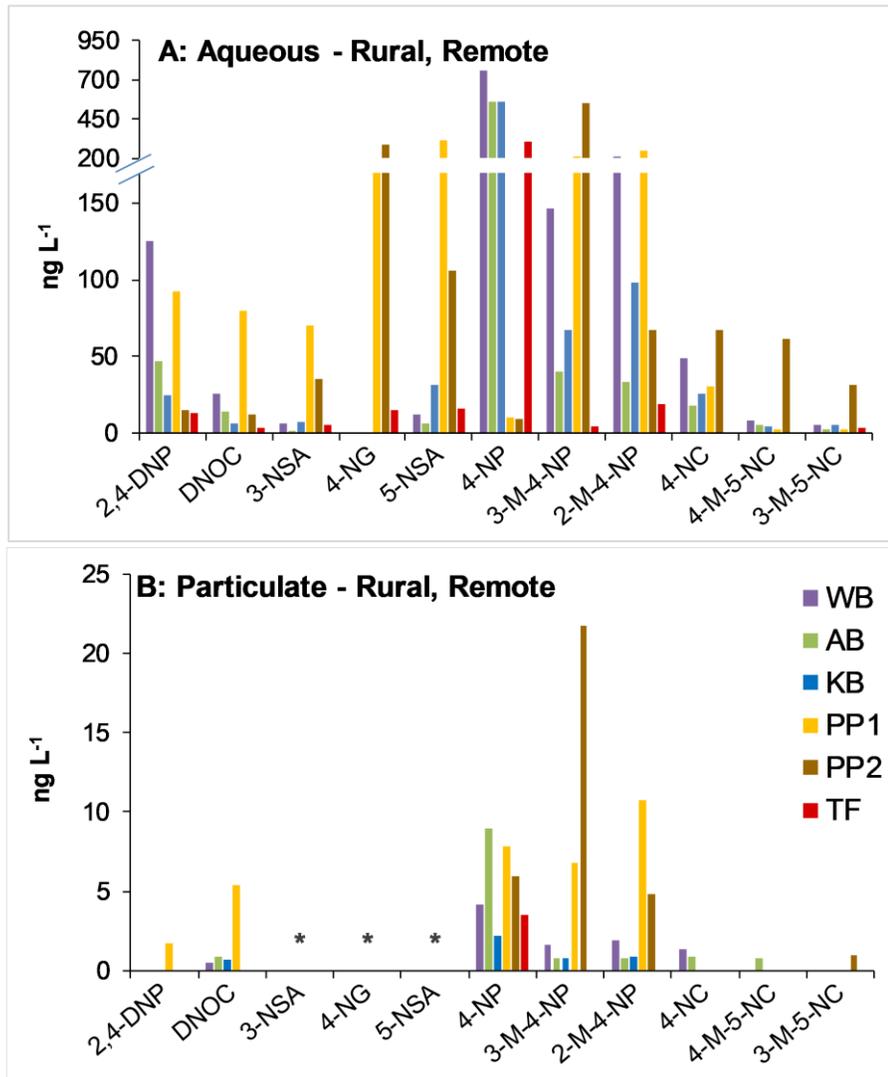
**Figure 3** NOPAHs in snow aqueous + particulate phase; urban and remote



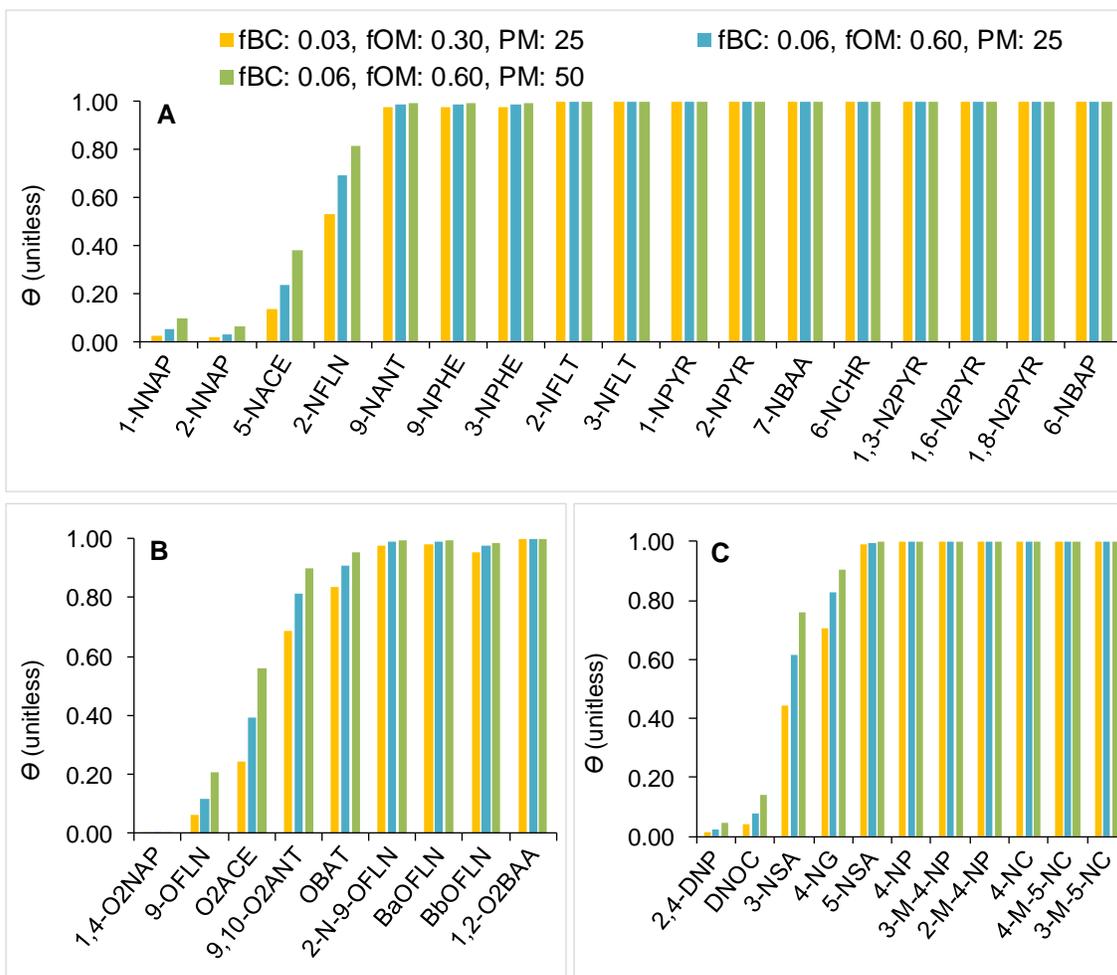
**Figure 4** NMAHs in urban snow samples



**Figure 5** NMAHs in rural and remote snow samples



**Figure 6** Particulate mass fractions  $\theta$  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 ( $\theta_w$ )

