Response to reviewers' comments

Journal: ACP
Title: Nitropolyaromatic hydrocarbons - gas-particle partitioning, mass size distribution, and formation along transport in marine and continental background air
Author(s): Gerhard Lammel et al.
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We would like to thank the reviewers for their thoughtful reading, comments and questions, which considerably helped to improve this manuscript. We have addressed all comments below and have indicated the corresponding modifications in the revised version of the manuscript which is attached to this response (changes highlighted).

Colour coding below:
(1) comments from Referees,
(2) author's response,
(3) author's changes

Anonymous Referee #1

This manuscript provides a study of nitro-PAHs in 2 background locations. The study includes results about their atmospheric concentrations, gas/particle partitioning measurements and modeling, particle size distribution and substance patterns together with an evaluation of the urban influence of the samples using a Lagragian particle dispersion model. Overall, the manuscript results are scientifically relevant and well presented. The modeling approach used to track the air mass history and to understand the nitro-PAHs sources and processes is very interesting and inovative. Thus, I recommend the publication of this paper in ACP after some minor revisions listed below.

Line 46: OK to cite review papers but you should also cite some key papers.
Early key papers will be added. Sentence will be re-ordered.

Line 47: mutagenicity yes. Toxicity, no: What about metals, PAHs, other POPs. . ..?
True. Will be corrected

Line 55: recent paper about that: (Keyte et al., 2016) -
This paper is cited (line 55). No change will be made.

Line 59-60: OK for 2-NFlt. Instead of 3-NFlt, better to give as an example for primary source, 1-nitropyrene.
Both 3NFLT and 1NPYR are dominated by the primary sources, i.e. diesel and gasoline (Ciccioli et al., 1989; IARC, 1989) vehicles for 3NFLT, and diesel and gasoline vehicles (Ciccioli et al., 1989; IARC, 1989), coal-fired power plants, Al smelters, carbon blacks (IARC, 1989), and coal stoves (Tang et al., 2005) for 1NPYR. But, based on smog-chamber studies; also heterogeneous oxidation by OH radicals was indicated as a (secondary) source for 1NPYR (Jariyasopit et al., 2014b, mentioned in the text, lines 397-398). No change will be made.

References:

Ciccioli P., Cecinato A, Brancaleoni E, Draisci R, Liberti A: Evaluation of nitrated polycyclic aromatic hydrocarbons in anthropogenic emission and air samples: A possible means of detecting reactions of carbonaceous particles in the atmosphere. Aerosol Sci. Technol. 1989, 10, 296-310.

IARC: Diesel and gasoline engine exhausts and some nitroarenes. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Vol. 46, International Agency for Research on Cancer, Lyon. 1989, URL: http://monographs.iarc.fr/ENG/Monographs/vol46/volume46.pdf.
Tang N, Hattori T, Taga R, Igarashi K, Yang XY, Tamura K, Kakimoto H, Mishukov VF, Toriba A, Kizu R, Hayakawa K: Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan–Japan Sea countries. Atmos. Environ. 2005, 39, 5817-5826.

Line 68: 2007 instead of 2006
Will be corrected

Line 72: an altitude (remote) site in the French Alps has been also investigated in (Albinet et al., 2008).
Will be corrected i.e., added to list of studies in remote environments

Line 174: PM10 determined by gravimetry using dedicated filters? Using automatic measurement instrumentation? Precise method and references.
Will be specified

Lines 261-266: These results refer to the particulate phase. What about the gaseous phase? You should discuss both phases or the total. Heterogenous photolysis is true for PAHs too. You could also have an enhanced formation of nitro-PAHs during night-time. Is the pattern the same for all PAHs and all nitro-PAHs or did you notice some differences for specific compounds? The time trend of some compounds should be shown somewhere as an example.
This is a misunderstanding: These results refer to the total, gas + particulate phases.
Will be specified

Line 286, Table 3: what about the altitude (remote) site in the Alps? The concentrations seemed very low.
Thanks. Results at high altitude site in the Alps will be added to Table 3 and discussed.

Line 289: ïA˛s´ should be defined before. This refers to the particulate phase, right? -
Particulate mass fraction θ. The parameter will be introduced

Lines 293-300: this paragraph should be moved in the “Mass size distributions” section.
Thanks, yes, we agree. Will be moved.

Line 344, Figure 3: There is a problem with the x-axis, it should be the opposite or the size distribution shown is wrong. PAH and nitro-PAHs are mainly associated to the finest aerosol particles. You should also show the standard deviation of the particle size distribution for each size range. As it is shown on this figure, you should remove these data from the Table 1.
Thanks, yes, the x-axes were inverted erroneously. Plots will be corrected. Standard deviation of the mean will be shown together with (absolute) mass size distributions.

Lines 374-377: To evaluate the influence of primary or secondary sources of nitro-PAHs, it is better to focus on the 2-NFlt/1-NPyr ratio.
Indeed, this ratio had been used in the literature to this end, and is applied in this study (lines 431-439). However, nowadays, this appears inappropriate, as heterogeneous oxidation by OH radicals was indicated to be a possible secondary source for 1NPYR (Jariyasopit et al., 2014b, mentioned in the text, lines 397-398).

Lines 378-388: What about the day/night variations? Did you notice anything specific showing a predominance of day-time or night-time processes at the continental site? This is then useful to support the findings of the following paragraph (Lines 389-396).
The day/night variation of the ratio 2NFLT/1NPYR, the concentration of a secondarily formed over a primary emitted NPAH, reflects the combination of the diurnal variations of 1NPYR emissions, 2NFLT formation rate, and photochemical sinks of both substances, all unknown in quantitative terms. The day/night variation was 2NFLT/1NPYR ≈12/≈16 for day/night, which, therefore, is considered insignificant. No immediate conclusion could be drawn.

References:

Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., 2007. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. Sci. Total Environ. 384, 280-292.
Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezo, J.L., 2008. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys. Part 1: Concentrations, sources and gas/particle partitioning.
Atmos. Environ. 42, 43-54.
Keyte, I.J., Albinet, A., Harrison, R.M., 2016. On-road traffic emissions of polycyclic aromatic hydrocarbons and their oxy- and nitro- derivative compounds measured in road tunnel environments. Sci. Total Environ.

Anonymous Referee #2
The Lammel et al. manuscript reports on measurements, partitioning calculations, and back-trajectory modeling of PAHs and nitro-PAHs at two European sites. The sites were chosen to study the transport of PAHs and nitro-PAHs from urban locations. Samples were collected using high-volume samplers, and particles were collected onto quartz fiber filters and gases using polyurethane foam plugs. Samples were extracted using dichloromethane and extracts were analyzed by gas chromatography-mass spectrometry. Partitioning calculations were performed using a recent poly-parameter linear free energy relationship. Particle trajectories were modeling using HYSPLIT and FLEXPART. There are a lot of high quality data and analyses presented in the manuscript, and the work should prove to be a valuable contribution to the field. There are no concerns with the methodology employed. The primary concern is with the quality of the representation-the technical writing and organization. There are a lot of grammatical errors and undefined symbols and acronyms. It is hard to follow the results as they are presented, particularly with regard to the discussions and conclusions being presented.
I recommend significant attention to the quality and clarity of the presentation, and perhaps another round of reviews following revision. Several specific suggestions and recommendations are provided below regarding grammar/symbols/abbreviations through the abstract and introduction. The intent here is to provide examples of the types of changes that need to be made throughout the manuscript; all such needed changes are not noted beyond the introduction.

Abstract: Why are the fractional doses not reported for the background site? Or is that being used to characterize the fraction at the marine site? This is not clear in the abstract as written.
The reason is that advection to the continental background site was influenced by a too homogeneous source distribution in central Europe (during the campaign). This explanation was given in lines 245-247 of the main text (no change).

On line 25, it is suggested to replace “were received” with “were calculated”.

Will be corrected
Line 22-23: For easier reading, recommend to move “with 2-nitrofluranthene . . . most abundant” out of the parenthesis and to the end of the sentence, and then start a new sentence with “While the concentration. . .”
Will be corrected

Line 31: NPYR is not defined or otherwise discussed
True. Acronym will be introduced

Line 36-37: Seems out of place. Recommend to remove or better integrate with rest of paragraph.
True. Will be integrated into rest of paragraph.

Line 49-50: Add comma after “more than one third”. On line 50, ambient what? Aerosols?
Yes. Will be specified.

Line 55: Insert “a” between “only” and “few”
Will be corrected

Line 60: Suggest to change “indicative for” to “indicative of” or “indicators for”
Yes, thanks. Will be corrected

Line 63: SVOCs is not defined
True. Acronym will be introduced

Line 69: Suggest removing “However . . . studied”. It has already been established (lines 66-67) that most NPAH observations are in urban areas. Could then use something like ”Though there are a few studies in unpolluted environments: studies were conducted by. . .”.
Will be phrased as suggested.

Also suggest to change all the “were” to “have been” (lines 70-75) as measurements may be ongoing or planned.
Will be phrased as suggested.

Line 66-67: Suggest to change “suspect to” to “expect to”
True. Will be phrased as suggested.

Line 79-80: Suggest to change “lack of data. . .obvious” to “However, there is limited NPAH data from remote atmospheric environments. . .”
Will be phrased as suggested.

Line 80: Revise “aim of study to study”
Thanks. ‘…to study’ will be replaced by ‘…to characterise’

Line 112-113: What was the collection period of for the QFF samples at K-puszta?
The collection period at the continental site will be specified in the sentence (previously in lines 111-113).

Line 116: Ni is undefined
Yes, thanks. Will be specified.

The comments/suggestions below address the clarity of the manuscript and analyses/conclusions presented. There are some technical questions here, but I think that more of the questions/comments arise from organizational structure and imprecise wording.

Conceptually, the urban fractional dose is clear; but how exactly were they calculated? I think much more time needs to be spend on the discussion of the calculated doses, sensitivities, and uncertainties to support the first paragraph of the conclusions section.
The calculation of the fractional dose was explained in the Supplementary material, S2.1.2. This text (S2.1.2) will be shifted to the main text (new Section 2.5), including all equations used for calculation of the dose. Uncertainties will be addressed. The new text will read:
"2.5 Quantification of urban influence on samples
The potential urban influence for individual samples collected at the marine site was based on the fraction of released Lagrangian particles which travelled through an urban boundary layer. A backward run from the sampling site was performed with Lagrangian particles (i.e. air parcels) being released during the entire sampling period. Three urban areas were considered, i.e. Izmir (≈300 km direct distance, 38.2-38.8°N/26.2-27.3°E), Athens (≈300 km, 37.8-38.1°N/23.5-23.8°E) and Istanbul (≈500 km away, 40.8-41.1°N/28.6-29.5°E).
The urban fractional dose, $D_{u\ i}$, an air mass collected in sample i had received for a given simulation period Δt can be derived as:
(4) $D_{u\ i} = \Sigma_t N_{blua}(t) \times \Delta t_{Rblua} / (N_{tot}(t) \times \Delta t_i)$
with $N_{blua}(t)$ = number of virtual particles within the urban boundary layer during the specific time step, model output time resolution Δt_{Rblua} = 0.5 h, and $N_{tot}(t)$ = number of virtual particles present during the specific time step. Under the given flow conditions in the region, a 2-day time horizon is considered her. Hence, the simulation period is given as:
(5) $\Delta t_i = \Delta t_{sample} + 48h$
with Δt_{sample} being the sampling time. $D_{u\ i}$ takes values between 0 and 1, corresponding to none or all, respectively, of the entire sample air having crossed the urban boundary layer. The D_u time series with allocation to 3 urban areas is shown in the SM, Fig. S3.
The comparison of urban influence in samples of various sample volume, V, requires normalisation to V, a relative dose (equ. (5), with n = total number of samples collected). Values of $D_{ru\ i}$ may exceed 1.
(6) $D_{ru\ i} = [\Sigma_n V_n/(nV_i)] \times D_{u\ i}$
The urban fractional dose, $D_{u\ i}$, accuracy is limited by the meteorological input data (here 0.125°×0.125° resolution, hourly) and boundary layer depth calculation. In the FLEXPART model, the latter is done according to Vogelezang and Holtslag, 1996."

Line 209-213: The discussion of the two OM phases is confusing as written. Is one phase low molecular mass/water soluble OM and the other phase high molecular mass/organic soluble OM?
This text will be rephrased. The new text will read: "OM is assumed to be constituted of two separate phases, low to mid molecular mass, both organic soluble and water soluble OM. For these, ppLFER equations for dimethyl sulfoxide-air (representing the low molecular mass range) and for polyurethane ether-air (representing the high molecular mass OM) are used, respectively (Shahpoury et al., 2016)."

Line 229: What is meant by "the substance patterns are similar"? Diurnal patterns? Monomer ratios? Monomer fractions? (also Line 254)
Composition of NPAH mixture. Will be specified.

Line 241: Assume "this" data set refers to the marine data set? Language throughout could be more specific and precise (see also comment above).
Yes. Will be specified

Line 256: What is the evidence for the secondary emissions of 4rPAHs? Are the cited studies part of the same campaign? Or is this an inference based on a prior study? Or using measured monomers or ratios using a method in the cited study?
Yes, the cited studies focussed on the atmosphere-surface exchange during the campaigns. This will be clarified to avoid confusion. The revised sentence (lines 256-259) will read: "The investigation of the diffusive air-surface exchange processes during the measurements presented here showed that 4rPAHs were in fact influenced by secondary emissions, namely throughout day and night from the soil at the continental site (by average 16.3 and 9.3 pg m^{-2} h^{-1} for FLT and PYR, respectively; Degrendele et al., 2016) or occasionally from surface seawater at the marine site (during at least 1 day-time interval out of in total 3 of this data subset; Lammel et al., 2016)."

Line 262-267: Is the day/night ratio of PAHs to n-PAHs sufficiently explained by photochemistry? Or may there be measurement-based explanations as well? For example, do the citations referenced support that the photolysis rates of n-PAHs are faster than those of PAHs? If so, this should be explicitly stated. Is the much higher day/night ratio of PAHs surprising given reported oxidation timescales of hours? What exactly is meant by "the same could be reflected" in line 267? Emission rates are governing ratios (based on line 271)? Or that n-PAHs are photochemically degraded faster than precursors (based on line 275)?
Are the lowest reported remote concentrations due to changing urban emissions? Changing photochemistry? Or improvements of in analytical techniques? Some combination? Further discussion on this point is warranted.
Further elaboration on NPAH sources and sinks is impossible, as not enough is known about NPAH atmospheric fate. In fact, this was a major motivation for this study. While the atmospheric lifetimes of 4rPAHs are limited by homogeneous reactions, no such statement is possible for NPAHs. Their lifetimes are eventually limited by heterogeneous photolysis or heterogeneous thermal reactions, but cannot be quantified, as these rate coefficients depend on PM composition and have almost not studied at all (with the exception of wood smoke particles; Fan et al., 1996). Therefore, it is unknown, whether NPAHs are photochemically degraded faster than their precursors. The day/night ratio of PAHs could not be explained by the sinks (stronger during day-time), but is in agreement with the finding of secondary emissions (stronger during day-time) at the site (discussed in lines 262-263).
Also, NPAH field studies are scarce, such that little data exist for comparison (Table 3) and no conclusions can be drawn from existing data with regard to temporal trends.
In order to put day/night ratios into better context, the sentences discussed here (lines 262-271) will be rephrased; "NPAH lifetimes may be limited by heterogeneous photolysis, but available kinetic data are scarce and limited to few aerosol types" (specification in line 265-266). Furthermore, limited knowledge of NPAH atmospheric fate will be highlighted by adding "…but their atmospheric lifetimes are still unknown." To a sentence in the introduction (namely: "These substances have been suggested as tracers for air pollution on the time scales of hours to days" in lines 61-62); The sentence ".More studies into NPAH atmospheric fate, both field observations and kinetic data, are needed in order to assess and quantify spatial and temporal trends, the long-range transport potential and persistence.." (will be added to the conclusions, after line 457).

Line 289-290: Particle phase distributions? What does the symbol theta represent?
Thanks. Will be introduced at first mentioning (line 190)

Was the pp-LFER also used for the PAHs? Discussion focused on n-PAHs.

In this study gas-particle partitioning of parent PAHs was not studied. However, the ppLFER model used had been applied previously on parent PAHs, which showed good prediction power across three urban and rural sites in Europe and the Mediterranean (Shahpoury et al., 2016).

How sensitive are the partitioning results to the assumptions in the pp-LFER? What are the uncertainty bounds on the phase predictions? Are they significant enough to influence any conclusions presented regarding phase partitioning?

More discussion on the shallow slopes observed for the marine n-PAHs would be valuable. The model does not seem to be capturing any of the observed variance.

In lack of experimental data, the ppLFER model for most NPAHs is based on estimated solute-specific Abraham solvation parameters for the various types of molecular interactions. The estimation is based on a group contribution method (ACD, 2015). Experimentally based descriptors used for one NPAH, i.e. 9-nitroanthracene, lead to better predictions (RMSE = 0.33, log K_p units) than the estimated descriptors (RMSE = 0.75). The sensitivity of assumptions on PM phase composition, made in the model had been tested and it was found that the mixing ratios of the WSOSOM and organic polymers' phases, as well as the soot surface area do not contribute significantly to the discrepancy (<< 1, log K_p units).

The predicted variation of K_p is significantly less than the observed for four NPAHs at the marine and one at the continental site (discussed in lines 335-349). The reason is unknown. Apart from PM properties it might be related to sampling or sample handling, although a number of such issues can be excluded, as same sampler, same temperature range, same sampling protocols applied across sites with both satisfactory and deficient agreement between predicted and observed K_p.

Satisfactory and deficient agreement between predicted and observed K_p across sites will be discussed accordingly.

Sentences to be added: "While the sensitivity of assumptions regarding PM phase composition, made in the model do not contribute significantly to the deviations (<< 1, log K_p units), a significant part can be attributed to the usage of estimated solute-specific Abraham solvation parameters (taken from ACD, 2015), in lack of experimentally based descriptors. E.g., for an urban site (Tomaz et al., 2016) it was found that experimentally based descriptors used for 9NPAH lead to better predictions than the estimated descriptors i.e., RMSEs differed by 0.43 log units (…) The reason is unknown. Moreover, sampling or sample handling artefacts cannot be excluded, even so same temperature range, sampler and sampling protocols applied across sites with both satisfactory and deficient agreement between predicted and observed K_p."

Is there a distinction between observed yield and potential yield? Or are these terms being used interchangeably?

All observed yields are conservatively considered to be potential yields. This will be better specified by replacing "c_{PAH} (total concentrations) and reflects an upper estimate, as other PAH photochemical sinks, such as formation of oxy-PAHs, are neglected" by "…c_{PAH} (total concentrations). This yield is called 'potential' as it reflects an upper estimate , as other PAH photochemical sinks, such as formation of oxy-PAHs, are neglected".

Line 436-437: What is meant by "hardly limited by"?

Will be rephrased: "The mass size distribution is determined by the particle size upon emission (primary NPAHs) and condensation and redistribution in the aerosol along transport, hence, does not include the short-lived coarse mass fraction. This indicates a high long-range transport potential."

Line 446-447: “Levels” of what?
NPAH levels. Will be specified.

Further correction:
In Table 1 (in the line: ‘marine gas’) and Table 2 (in the column ‘marine θ‘) minor mistakes (which do not impact on the conclusions) were found and will be corrected.

Nitro-polycyclic aromatic hydrocarbons - gas-particle partitioning, mass size distribution, and formation along transport in marine and continental background air

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Abstract

Nitro-polycyclic aromatic hydrocarbons (NPAH) are ubiquitous in polluted air but little is known about their abundance in background air. NPAHs were studied at one marine and one continental background site i.e., a coastal site in the southern Aegean Sea (summer 2012) and a site in the central Great Hungarian Plain (summer 2013), together with the parent compounds, PAHs. A Lagrangian particle dispersion model was used to track air mass history. Based on Lagrangian particle statistics, the urban influence on samples was quantified for the first time as a fractional dose to which the collected volume of air had been exposed to.

At the remote marine site, the 3-4 ring N~~nitro-~~PAH (sum of 11 targeted species) concentration was 23.7 pg m^{-3} while the concentration of 4-ring PAHs (6 species) was 426 pg m^{-3}. 2-nitrofluoranthene (2NFLT) and 3-nitrophenanthrene were the most abundant NPAHs. Urban fractional doses in the range <0.002–5.4% were calculat~~receiv~~ed. At the continental site, the Σ_{11} 3-4rNPAH and Σ_6 4rPAH were 58 and 663 pg m^{-3}, respectively, with 9-nitroanthracene and 2NFLT being highest concentrated amongst the targeted NPAHs. The NPAH levels observed in the marine background are the lowest ever reported and remarkably lower, by more than one order of magnitude, than one decade before. Day-night variation of NPAHs at the continental site reflected shorter lifetime during the day, possibly because of photolysis of some NPAHs. The yields of formation of 2NFLT and 2-nitropyrene (2NPYR) in marine air seem to be close to the yields for OH-initiated photochemistry observed in laboratory experiments under high NO_x conditions. Good agreement is found for prediction of NPAH gas-particle partitioning using a multi-phase poly-parameter linear free energy relationship. Sorption to soot is found less significant for gas-particle partitioning of NPAHs than for PAHs.

The NPAH levels determined in the southeastern outflow of Europe confirm intercontinental transport potential.

Keywords: long-range transport potential, semi-volatile organic compounds, PAH photochemistry,

1. Introduction

PAHs may undergo chemical transformations in the gaseous and in the particulate phase (Finlayson-Pitts and Pitts, 2000; Keyte et al., 2013). Nitro-PAHs (NPAHs)~~, earlier predicted based on smog-chamber experiments (Atkinson and Arey, 1994), and later~~ observed in urban and rural areas (Nielsen et al., 1984; Feilberg et al., 2001; Finlayson-Pitts and Pitts, 2000; Keyte et al., 2013) and predicted based on smog-chamber experiments (Atkinson and Arey, 1994), seem to be most significant derivatives: Mutagenicity ~~and toxicity~~ of atmospheric aerosols in general is mostly related to NPAHs (Grosjean et al., 1983; Garner et al., 1986; Finlayson-Pitts and Pitts, 2000; Claxton et al., 2004; Hayakawa, 2016). A large part, more than one third, of the mutagen potential of ambient aerosols may be attributable to NPAHs (Schuetzle, 1983).

Secondary formation of NPAH from PAHs is thought to occur on short time scales (hours). This has been observed for PAHs collected on filters (Ringuet et al., 2012a; Zimmermann et al., 2013; Jaryasopit et al., 2014a, 2014b), and also in in urban plumes (Bamford and Baker, 2003; Arey et al., 1989; Reisen and Arey, 2005). Although many NPAHs are emitted from road traffic, only a few are abundant in this source type (Arey, 1998; Keyte et al., 2013 and 2016; Inomata et al., 2015; Alves et al., 2016). The occurrence of various isomers of nitrofluoranthene (NFLT) and nitropyrene (NPYR) can be used to study PAH sources, PAH chemical transformations and the role of the photo-oxidants hydroxyl radical (OH) and nitrate radical (NO_3) (Ciccioli et al., 1996; Finlayson-Pitts and Pitts 2000). E.g., 3- and 2-nitrofluoranthene (3-, 2NFLT) are indicative of~~or~~ primary and secondary sources, respectively. These substances have been suggested as tracers for air pollution on the time scales of hours to days (Ciccioli et al., 1996; Finlayson-Pitts and Pitts 2000; Keyte et al. 2013), but t~~. ~~heir atmospheric lifetimes are still unknown.

Like their precursors, NPAHs are semivolatile organic compounds (SVOCs), partitioning between the phases of the atmospheric aerosol. Similar to other SVOCs, the NPAHs' phase distribution was found to depend on temperature (summer and winter campaigns in the Alps; Albinet et al., 2008b) and results from both absorptive as well as adsorptive contributions (Tomaz et al., 2016). NPAHs have primarily been observed in polluted areas (e.g. Pitts et al., 1985; Ramdahl et al., 1986; Garner et al., 1986; Albinet et al., 2007~~6~~ and 2008a; Ringuet et al., 2012a and 2012b; Zimmermann et al., 2012; Barrado et al., 2013; Li et al., 2016). ~~However, NPAHs have hardly been studied in the unpolluted environment: ~~Though there are a f~~F~~ew studies ~~were conducted~~ in~~ the~~ rural environments i.e., in Germany (Ciccioli et al., 1996), in the French Alps (100-1000 pg m^{-3} range for the sum of 10 NPAHs; Albinet et al., 2008a) and in northern China (Li et al., 2016). Very few measurements have been~~were~~ performed in the remote atmospheric environment i.e., in the Mediterranean (Tsapakis and Stephanou, 2007), high altitude sites in the Himalayas (single data; Ciccioli et al. 1996) and French Alps (Albinet et al., 2008a), and in the Arctic (with so-called Arctic haze; Masclet et al. 1988; Halsall et al. 2001). With regard to the long-range transport potential, the state of the knowledge is that at least some NPAHs are expected~~suspect~~ to go into intercontinental transport (Lafontaine et al., 2015) and might be ubiquitous in the global atmosphere (Ciccioli et al., 1996).

However, there is limited~~a lack of~~ NPAH data from remote atmospheric environments is obvious and little is known about their long-range transport potential. The aim of this study was to characterise~~study~~ the long-range transport potential of NPAHs by measurements at remote sites of Europe, addressing the continental background and the outflow of the continent.

2. Methodology

2.1 Sampling

High-volume air sampling was conducted at a marine background site, Finokalia (35.3°N/25.7°E, 250 m a.s.l.), in the context of a coordinated field experiment 2-13 July 2012

(Lammel et al., 2015) and at a continental background site in central Europe, K-puszta (46º58'N/19º33'E, 125 m a.s.l.; Degrendele et al., 2016), 5-16 August 2013. The Finokalia site is located on a cliff at the northern coast of Crete, some 70 km east of major significant anthropogenic emissions (Iraklion, a city of 100000 inhabitants with airport and industries; Mihalopoulos et al., 1997; Kouvarakis et al., 2000). The K-puszta site is located on a clearing, characterised by uncultivated grassland, in a mostly coniferous forest in the Hungarian (Pannonian) Great Plain, ca. 70 km and 270 km southeast of Budapest and Vienna, respectively (≈2 mn inhabitants each). The background site character of both observatories had been demonstrated (Borbély-Kiss et al., 1988; Kouvarakis et al., 2000; Vrekoussis et al., 2005). Meteorological and trace gas measurements are covered by both observatories, which are stations of the EMEP network (EMEP, 2015).

High volume air samples were collected using a HV-100P (Baghirra, Prague, Czech Republic), equipped with a multi-stage cascade impactor (Andersen Instruments Inc., Fultonville, New York, USA, series 230, model 235) with five impactor stages, corresponding to 10–7.2, 7.2–3, 3–1.5, 1.5–0.95 and 0.95–0.49 µm of aerodynamic particle size, D, (spaced roughly equal ΔlogD), a backup filter collecting particles < 0.49 µm and, downstream, two polyurethane foam plugs (PUFs, Molitan, Břeclav, Czech Republic, density 0.030 g cm^{-3}, placed in a glass cartridge), together 10 cm high. Particles were sampled on slotted QFF substrates (TE-230-QZ, Tisch Environmental Inc., Cleves, USA, 14.3 × 13.7 cm) and glass fibre filters (Whatman, 20.3 × 25.4 cm). The filters had been cleaned prior to use by heating 108 (330°C). PUFs were cleaned (8 hour-extraction in acetone and 8 hours in dichloromethane (DCM)), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to deployment. The sampler was operated at constant flow rate of 68 m3 h^{-1}. Day/night sampling (changing at sunset and sunrise) of gaseous samples (PUF) was performed at both sites (V = 600-1000 m^3), while at the marine site the impactor filter (QFF) samples were collected over 24 h (5) or 48 h (3).

PUFs were cleaned (8 hour-extraction in acetone and 8 hours in dichloromethane (DCM)), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to deployment. The sampler was operated at constant flow rate of 68 m^3 h^{-1}. Day/night sampling of gaseous samples (PUF) was performed at both sites (12 h, V ≈ 700 m^3), while at the marine site the impactor filter (QFF) samples were collected over 12 h (n = 1), 24 h (4) or 48 h (3).

Particle number concentration, N, was determined by an optical particle counter (Grimm model 107, Ainring, 31 channels between 0.25 and 32 mm of aerodynamic particle diameter, D). Aerosol surface concentration, S (cm^{-1}), was derived as $S = \pi \Sigma_i N_i D_i^2$ assuming sphericity. Hereby, true S will be underestimated, in particular if particles of irregular form were abundant (e.g. Jaenicke, 1988). Comparisons with absolute methods (e.g. Pandis, et al. 1991) suggest that the discrepancy may reach up to a factor of 2-3. The mass median diameter (D_m, µm), was derived as $\log D_m = \Sigma_i m_i \log D_i / \Sigma_i m_i$ with m_i denoting the mass in size class i, D_i being the geometric mean diameter collected on stage i of the cascade impactor.

2.2 Chemical analysis

All air samples were extracted with DCM using an automatic warm Soxhlet extractor (Büchi B-811, Switzerland). Deuterated PAHs (D8-naphthalene, D10-phenanthrene, D12-perylene; Wellington Laboratories, Canada) were used as surrogate standards for both PAHs and NPAHs. Deuterated PAHs proved to be suitable surrogate standards for NPAHs. These were spiked on each PUF prior to extraction. The extract was split in two parts, 1/9 for PAHs and Nitro-PAHs analysis, 9/10 for PBDEs, PCBs and OCPs. The PAHs and Nitro-PAHs aliquot was a subject to open column chromatography clean-up. Glass column (1 cm i.d.) was filled with 5 g activated silica (150°C for 12 h), sample was loaded and eluted with 10 mL *n*-hexane, followed by 40 mL DCM. The cleaned sample was evaporated under a stream of nitrogen in a TurboVap II apparatus (Biotage, Sweden), transferred into a conical GC vial and spiked with recovery standard, terphenyl, the volume was reduced to 100 µL.

GC-MS analysis of 4-ring PAHs (fluoranthene (FLT), pyrene (PYR), benzo(b)fluorene (BBN), benzo(a)anthracene (BAA), triphenylene (TPH) and chrysene (CHR)) and 2-4 ring NPAHs (1- and 2-nitronaphthalin (1-, 2NNAP), 3- and 5-nitroacenaphthene (3-, 5NACE), 2-nitrofluorene (2NFLN), 9-nitroanthracen (9NANT), 3- and 9-nitrophenanthren (3-, 9NPHE), 2- and 3-nitrofluoranthene (2-, 3NFLT), 1- and 2-nitropyrene (1-, 2NPYR), 7-nitrobenz(a)anthracene (7NBAA), 6-nitrochrysene (6NCHR) was performed using a gas chromatograph atmospheric pressure chemical ionization tandem mass spectrometer (GC-APCI-MS/MS) instrument, Agilent 7890A GC (Agilent, USA), equipped with a 60m × 0.25mm × 0.25um DB-5MSUI column (Agilent, J&W, USA), coupled to Waters Xevo TQ-S (Waters, UK). Injection was 1 µL splitless at 280°C, with He as carrier gas at constant flow 1.5 mL min^{-1}. The GC oven temperature program was as follows: 90°C (1 min), 40°C/min to150°C, 5°C/min to 250°C (5 min) and 10°C/min to 320°C (5 min). APCI was used in charge transfer conditions. The isomers 2- and 3NFLT were not separated by the GC method, but co-eluted and are reported as sum.

Recovery of native analytes varied 72-102% for PAHs and deuterated PAHs, 70-110% for NPAHs (details see supplementary material (SM), Table S1a). The results were not recovery corrected. The mean of field blank values was subtracted from the sample values. Values below the mean + 3 standard deviations of the field blank values were considered to be <LOQ. Field blank values of some analytes in air samples were below the instrument limit of quantification (ILOQ), which corresponded to 0.004-0.069 pg m^{-3} for NPAHs (except for 1NNAP for which it ranged 0.60-0.87 pg m^{-3}) and 0.010-0.126 pg m^{-3} for 4-ring PAHs (except for FLT and PYR for which it ranged 0.17-0.59 pg m^{-3}) (Table S1).

Higher LOQs were determined for some of the NPAHs and for all 4-ring PAHs in gaseous air samples (PUFs), namely 0.006-0.009 ng (corresponding to 3.5-8.0 pg m^{-3}) for 3NACE and 2NPYR, 0.028-0.097 (corresponding to 16-86 pg m^{-3}) for 2NNAP, 2NFLT and 1NPYR, and 0.10-0.27 ng (corresponding to ≈60-240 pg m^{-3}) for 4-ring PAHs (except for FLT and PYR for which it was 1.71 and 1.05 ng, respectively, corresponding to ≈600-1500 pg m^{-3}). In particulate phase samples, where separate field blanks for the 2 different QFFs were determined (on the impactor stages on one hand side and the backup filter on the other hand side), higher LOQs were determined for some of the NPAHs and for all 4-ring PAHs, namely 0.008-0.089 ng (corresponding to 4.6-79 pg m^{-3}) for 2NNAP, 2NFLT, 1NPYR and 2NPYR, 0.26-0.31 ng (corresponding to 150-274 pg m^{-3}) for 9NANT, and 0.05-0.22 ng (corresponding to ≈30-200 pg m^{-3}) for 4-ring PAHs (except for FLT and PYR for which it was 0.79 and 0.36 ng, respectively, corresponding to ≈200-700 pg m^{-3}).

The breakthrough in PUF samples was estimated (Pankow, 1989; ACD, 2015; Melymuk et al., 2016), and as a consequence, 2-3 ring PAHs and 2-ring NPAHs results were excluded from this study as their sampling may have been incomplete. We, therefore, report $\Sigma_6$4rPAH and Σ_{11}3-4rNPAH.

Particulate matter mass (PM_{10}) was determined by gravimetry (microbalance, filters accommodated to stable temperature and humidity, 3 replicate weighings), and organic matter (OM) and elemental carbon (EC) contents of PM by a thermal-optical method (Sunset Lab., USA; EUSAAR protocol).

2.3 Gas-particle partitioning

Gas-particle partitioning was studied by applying a multiphase ppLFER model, which was recently introduced (Shahpoury et al., 2016). In brief, partitioning of semivolatile compounds in air can be described (Yamasaki et al., 1982), by

$$(1) \qquad K_p = c_{ip} / (c_{ig} \times c_{PM})$$

where K_p (m^3air (g PM)$^{-1}$) is the temperature dependent partitioning coefficient, c_{PM} (g m^{-3}) is the concentration of particulate matter in air, c_{ip} and c_{ig} are the analyte (i) concentrations (ng m^{-3}) in the particulate and gas phase, respectively. K_p can be predicted using models based on single- and poly-parameter linear free energy relationships (spLFER, ppLFER). spLFER's relate the partitioning coefficient to one physic-chemical property i.e., assume one process to determine the sorption process, while ppLFER's in principle account for all types of molecular interactions between solute and matrix (Goss and Schwarzenbach, 2001). The observed particulate mass fraction~~,~~ data, $\theta = c_p / (c_g + c_p)$ (Table 2), were tested with both a spLFER and a ppLFER model. The spLFER chosen is the widely used K_{oa} model of Finizio et al., 1997 (results presented in the Supplementary material (SM), S2.3). The ppLFER is a multi-phase model recently presented (Shahpoury et al., 2016) and applied for NPAHs (Tomaz et al., 2016). It is based on linear solvation energy relationships (Abraham, 1993; Goss, 2005):

$$(2) \qquad \log K_p = eE + sS + aA + bB + lL + c$$

$$(3) \qquad \log K_p = sS + aA + bB + vV + lL + c$$

where capital letters E, S, A, B, L, and V are solute-specific Abraham solvation parameters for excess molar refraction (describes interactions between π- and lone (n-) electron pairs), polarizability/ dipolarity, solute H-bond acidity, solute H-bond basicity, logarithm of solute hexadecane-air partitioning coefficient (unitless), and McGowan molar volume (cm^3 mol^{-1})/100, respectively (Endo and Goss, 2014). The corresponding parameters e, s, a, b, l, and v reflect matrix-specific solute-independent contribution to K_p. In lack of experimental data, the solute descriptors for NPAHs were taken from M.H. Abraham (personal communication). The multi-phase ppLFER considers adsorption onto soot, $(NH_4)_2SO_4$, and NH_4Cl, and absorption into particulate organic matter (OM). OM is assumed to be constituted of two separate phases, low to mid~~high~~ molecular mass, both organic soluble and water soluble OM. For these, ~~represented by a~~ ppLFER equations for dimethyl sulfoxide-air (representing the low molecular mass range)~~on one hand side, and high molecular mass OM, represented by a ppLFER equation~~ and for polyurethane ether-air (representing the high molecular mass OM) are used, respectively (Shahpoury et al., 2016).

A conventional single-parameter LFER (K_{oa}) model is applied, too.

2.4 Air mass history analysis

The HYSPLIT (Draxler and Rolph, 2003) and FLEXPART (Stohl et al., 1998, 2005) models were used to identify air mass histories over 10 and 2 days, respectively. The possible influence of polluted air on samples was quantified using a novel method of applying Lagrangian particle statistics (FLEXPART, see SM, S2.2). To this end, for the entire sampling period, one particle per second was released. The model output is generated at 0.062° (≈7 km), every 30 minutes and expressed as 'residence time' i.e., a measure of the time particles resided in grid cells. ECMWF meteorological data (0.125°×0.125° resolution, hourly) were used as input.

2.5 Quantification of urban influence on samples

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The potential urban influence for individual samples collected at the marine site was based on the fraction of released Lagrangian particles which travelled through an urban boundary layer. A backward run from the sampling site was performed with Lagrangian particles (i.e. air parcels) being released during the entire sampling period. Three urban areas were considered, i.e. Izmir (≈300 km direct distance, 38.2-38.8°N/26.2-27.3°E), Athens (≈300 km, 37.8-38.1°N/23.5-23.8°E) and Istanbul (≈500 km away, 40.8-41.1°N/28.6-29.5°E).

The urban fractional dose, $D_{u\ i}$, an air mass collected in sample i had received for a given simulation period Δt can be derived as:

$$(4) \qquad D_{u\ i} = \Sigma_t\, N_{blua}(t) \times \Delta t_{Rblua} / (N_{tot}(t) \times \Delta t_i)$$

with $N_{blua}(t)$ = number of virtual particles within the urban boundary layer during the specific time step, model output time resolution Δt_{Rblua} = 0.5 h, and $N_{tot}(t)$ = number of virtual particles present during the specific time step. Under the given flow conditions in the region, a 2-day time horizon is considered her. Hence, the simulation period is given as:

$$(5) \quad \Delta t_i = \Delta t_{sample} + 48h$$

with Δt_{sample} being the sampling time. $D_{u\ i}$ takes values between 0 and 1, corresponding to none or all, respectively, of the entire sample air having crossed the urban boundary layer. The D_u time series with allocation to 3 urban areas is shown in the SM, Fig. S3.

The comparison of urban influence in samples of various sample volume, V, requires normalisation to V, a relative dose (equ. (5), with n = total number of samples collected). Values of $D_{ru\ i}$ may exceed 1.

$$(6) \quad D_{ru\ i} = [\Sigma_n V_n/(nV_i)] \times D_{u\ i}$$

The urban fractional dose, $D_{u\ i}$, accuracy is limited by the meteorological input data (here 0.125°×0.125° resolution, hourly) and boundary layer depth calculation. In the FLEXPART model, the latter is done according to Vogelezang and Holtslag, 1996.

3. Results and discussion

The NPAH levels are distinctly lower at the marine than at the continental site, $\Sigma_{11\ 3\text{-}4r}$NPAH = 22.5 and 58.5 pg m^{-3}, respectively (Table 1). The NPAHs showing the highest concentrations were 2NFLT and 3NPHE at the marine (Fig. 1b) and 9NANT and 2NFLT at the continental site (Fig. 1d, Table 2). The substance patterns (composition of NPAH mixture) at both sites are similar, though ($R^2 = 0.76$, $P > 0.99$, t-test). At the marine site, advection was northerly, with air masses originating (time horizon 10 days) in eastern and central Europe and, towards the end of the campaign, in the western Mediterranean. The site was placed into the southeastern outflow of Europe. NO_x (0.2-0.6 ppbv), EC (0.2-0.8 µg m^{-3}) and PM_{10} (18.3-39.3 µg m^{-3}) reflect background conditions. Air mass history analysis suggests that the somewhat elevated concentration in the first sample collected at the marine site (Fig. 1a) is related to long-range transport influenced by passage over the urban areas of Izmir and Istanbul (urban fractional dose D_u = 5.0%, in contrast to the mean which was 1.6%; Fig. S3). Overall, urban fractional dose in the range <0.002–5.4% was received at the marine site. Across all samples at the marine site, D_u is found to be significantly correlated with the pollutant sum concentrations $\Sigma_{6\ 4r}$PAH and $\Sigma_{11\ 3\text{-}4r}$NPAH (R^2 = 0.61 and 0.69, respectively, both $P > 0.99$).

From the marine site~~is~~ data set, subsets of each two samples are formed, representing minimum (i.e., almost no influence from industrialised area 48 hours prior to arrival (hereforth called ‘marine background’, urban fractional dose D_u = 0.4%) and maximum observed influence (hereforth called ‘background with urban influence’, D_u = 3.1%; SM Table S2, Figure S3). The results for these subsets are listed in Tables 1-3. Such classification was not deemed meaningful for the samples collected at the continental site, as the relevant source distribution in central Europe was too homogeneous during this episode. Advection was mostly from northwest and partly from easterly directions, with air mass origin (time horizon of 10 days) mostly in central Europe and, to a lesser extent in eastern Europe and the western Balkans. The NO_2 (1.2-2.6 ppbv), total carbon (3-6 µg m^{-3}) and PM_{10} (10.7-46.3 µg m^{-3}) levels during the campaign reflect continental background conditions.

The 4-ring PAH concentrations in samples from the continental site on the one hand, and in background air with urban influence collected at the marine site (urban areas 300-500 km away) on the other hand, are similar (Table 2). Also, the substance patterns are more similar than when relating all samples at the marine site i.e., R^2 = 0.88 ($P > 0.999$, t-test) instead of R^2 = 0.76. The investigation of the diffusive air-surface exchange processes during the measurements presented here showed that~~At both sites,~~ 4rPAHs were in fact influenced by secondary emissions, namely throughout day and night from the soil at the continental site (by average 16.3 and 9.3 pg m^{-2} h^{-1} for FLT and PYR, respectively; Degrendele et al., 2016) or occasionally from surface seawater at the marine site (during at least 1 day-time interval out of in total 3 of this data subset; Lammel et al., 2016). In the data set from the continental site, we study day/night (D/N) effects (subsets listed in Tables 1-3, too): PAH concentrations (c_{tot}) were ≈60% higher during the day than during the night, while c_{tot} of NPAH~~ concentrations~~ were by average ≈5% lower during the day (Table 2). NPAHs are subject to photolysis, while PAHs are not. At the site, the PAH concentrations were driven by re-volatilisation from soil, determined by temperature variation (Degrendele et al., 2016). For NPAHs (partly primary emitted) this indicates that the higher emissions during the day (due to re-volatilisation and road traffic) were compensated by short~~low~~er lifetime. NPAH lifetimes may be limited by ~~(because of~~ heterogeneous photolysis, but available kinetic data are scarce and limited to few aerosol types (~~;~~ Fan et al., 1996; Feilberg and Nielsen, 2000, 2001; García-Berríos et al., 2017). Also, ~~The same could be reflected in~~ different NPAH/PAH ratios (the potential NPAH yields), which were 5.6% and 8.9% at the marine and continental sites, respectively, reflect the combination of emission sources and photochemical sinks. The NPAH/PAH ratios at the two sites~~se~~ were influenced by similar substance patterns upon emission, similar irradiation (summer, no or almost no clouds) and deposition velocities (θ in the range 0.05-0.20 for Σ_{11} 3-4rNPAH and Σ_{6} 4rPAH, no precipitation), but different re-volatilisation fluxes and different characteristic transport times elapsed. Distance to major urban source areas was 300- >1000 km at the marine and 100-500 km at the continental site. The NPAH/PAH ratios being lower at the more distant receptor site, the marine site, may suggest that photochemical degradation of NPAHs along transport was on average faster than degradation of the precursors. xxx

The NPAH levels observed in marine background air are the lowest ever reported. Remarkably, the concentrations are much lower, by more than one order of magnitude, than one decade before at the same site during the same season (Tsapakis and Stephanou, 2007). The concentrations observed now are a factor of 4-10 lower than in a forest site in Amazonia two decades before (which might have been influenced by biomass burning emissions), ~~and also~~ a factor of 3 lower (for 2NPYR) than observed at an extremely remote site in the Himalayas two decades before (Ciccioli et al., 1996), and comparable to a high altitude site in the Alps (with the exception of 2NPYR which was observed one order of magnitude higher there in winter; Albinet et al., 2008a; Table 3). The NPAH levels observed at the marine site with influence of pollution and at the continental site are comparable, but also at the lower end of the range spanned by previous observations at rural and remote sites (Table 3).

Gas-particle partitioning

The time-weighted mean NPAH phase distributions (Σ_{11}3-4rNPAH) differ, corresponding to θ = 0.05 and 0.17 at the marine and continental sites, respectively, – despite similar temperatures (Table 1). In contrast and despite of similar temperature ranges, the 4-ring PAHs' (Σ_{6}4rPAH) particulate mass fraction was higher at the marine than at the continental site (θ = 0.42 and 0.20, respectively). ~~The NPAH mass size distribution had its maximum in the <0.49 μm size range at both sites. The 4-ring PAHs mass size distribution had 2 maxima, <0.49 μm and between 0.95 and 1.5 μm, at the marine site, but one at <0.49 μm at the~~

~~continental site (Table 1). This is probably related to the presence of aged aerosol at the marine site vs. a larger contribution of fresh aerosols at the continental site. This is, furthermore, supported by the analysis of air mass origins that shows significant influence of urban areas for only few samples at the marine and for all samples at the continental site (SM S2).~~

Both 4-ring PAHs and 3-4 ring NPAHs were more associated with PM in polluted air than in clean air. This trend is weak for PAHs with θ = 0.02 for $\Sigma_6$4rPAH in marine background but 0.07 in background with urban influence (and θ = 0.09 and 0.20 for CHR; Table 2), but is obviously strong for NPAHs, namely θ = 0.19 for 2NPYR in marine background but 0.69 in background with urban influence, ≈0.93 in polluted continental air, and θ = 0.01 for Σ_{11}3-4rNPAH in marine background but 0.22 in background with urban influence (Table 2). The urban influenced air at the marine site is also reflected in a much higher OC (a factor of 3 higher than the all-campaign mean) and elevated EC, (less prominent, ≈50% above mean). This confirms the understanding that gas-particle partitioning of both PAHs (Lohmann and Lammel, 2004; Shahpoury et al., 2016) and NPAHs (Tomaz et al., 2016) is mostly determined by absorption in POM and adsorption to soot. When comparing polluted air at the continental site and background with urban influence at the marine site, a strong shift of $\Sigma_6$4rPAH towards the particulate phase, θ ≈0.21 vs. 0.07, respectively, is found, while for Σ_{11}3-4rNPAH θ are similar i.e., ≈0.16 vs. 0.22, respectively. This phase partitioning trend of the 4rPAHs could be explained by sorption to EC, which is a factor of ≈2 higher, but not by OC (only ≈20% higher). In conclusion, these observations consistently indicate that sorption to soot is less significant for gas-particle partitioning of NPAHs than for PAHs.

While NPAHs were significantly phase-shifted (θ = 0.24 during day-time but θ = 0.58 during night-time), this was not the case for 4rPAHs (θ = 0.18 during day-time and θ = 0.23 during night-time). This is in line with the perception that the temperature sensitivity of phase change is stronger for the substance class with stronger molecular interactions in the condensed phase, NPAHs. E.g., the enthalpies of phase change between air and OC of FLT and NFLT are -98 and -75 kJ mol^{-1}, respectively (OC represented by DMSO; ACD, 2015).

Good agreement is found for the prediction of NPAH partitioning using the multi-phase (3-phase) ppLFER with most values predicted within one order of magnitude of the observed values (Fig. 2; quantification of deviations in S2.3.1). While the sensitivity of assumptions regarding PM phase composition, made in the model do not contribute significantly to the deviations (<< 1, log Kp units), a significant part can be attributed to the usage of estimated solute-specific Abraham solvation parameters (taken from ACD, 2015), in lack of experimentally based descriptors. E.g., for an urban site (Tomaz et al., 2016) it was found that experimentally based descriptors used for 9NPAH lead to better predictions than the estimated descriptors i.e., RMSEs differed by 0.43 log units. The agreement of the ppLFER prediction is better than assuming absorption (into OM) to be the only relevant process (K_{oa} model; see S2.3.2, Fig. S5). The same was found when studying gas-particle partitioning of NPAHs in urban air (Tomaz et al., 2016). This supports the perception that gas-particle partitioning of NPAHs is governed by various molecular interactions with OM, with its polarity being well represented by DMSO, better than by octanol. Earlier, it had been found for eight 3-4rNPAHs at urban and rural sites (Li et al., 2016) that the dual model, assuming adsorption (to soot) and absorption (into OM) predicts better than single adsorption (to the total aerosol surface i.e., Junge-Pankow) or single absorption (K_{oa}) models do.

The interactions with the aerosol matrix of 9NPHE (continental site) and 5NACE, 2NFLN, 2NFLT and 1NPYR (marine site) are less well represented than other NPAHs by the model as suggested by low slopes of their log $K_{p\ \mathrm{experimental}}$/log $K_{p\ \mathrm{predicted}}$ relationships. The reason is unknown. Moreover, sampling or sample handling artefacts cannot be excluded, even so same temperature range, sampler and sampling protocols applied across sites with both satisfactory and deficient agreement between predicted and observed K_p. Further conclusions are not supported by the limited amount of data and uncertainties on both the model (estimated ppLFER parameters) and experimental (concentrations close to LOQ) sides.

Mass size distribution

The NPAH mass size distribution had its maximum in the <0.49 µm size range at both sites. The 4-ring PAHs mass size distribution had 2 maxima, <0.49 µm and between 0.95 and 1.5 µm, at the marine site, but one at <0.49 µm at the continental site (Table 1). This is probably related to the presence of aged aerosol at the marine site vs. a larger contribution of fresh aerosols at the continental site. This is, furthermore, supported by the analysis of air mass origins that shows significant influence of urban areas for only few samples at the marine and for all samples at the continental site (SM S2).

Sums of NPAHs' and PAHs' mass size distributions are found unimodal with the maximum in particles <0.49µm, except PAHs at the marine site, which shows a second maximum between 1.5 and 3.0 µm (Fig. 3). At the marine site, 50 and 69% of 1NPYR and 2NFLT, respectively, were found associated with particles <0.45µm and 68 and 86%, respectively, with particles <0.95 µm, and even more, 83% and 100%, respectively, with particles <0.45µm at the continental site.

$\Sigma_6$4rPAH mass size distributions are shifted to larger particles in background with urban influence as compared to marine background air (both collected at the marine site) i.e., MMD = 0.19 and 0.28, respectively. However, such a trend is not apparent for NPAHs (Table 2). The size shift of PAHs is not corresponding to the PM_{10} mass size distribution: The MMD of PM_{10} for all samples collected at the marine site was 0.58 µm, while it was 1.13 and 0.62 µm in the marine background and background with urban influence data subsets, respectively. The PM_{10} as well as the OC mass size distributions were bimodal with maxima corresponding to < 0.49 µm and 3.0-7.2 µm particles (MMDs listed in Table 2), while the EC mass size distribution was unimodal, with the maximum concentration in the finest fraction. At the continental site, the Σ_{11}3-4rNPAH mass size distribution was bimodal with maxima corresponding to < 0.49 µm and 7.2-10 µm particles, while the $\Sigma_6$4rPAH mass size distribution was unimodal, with the maximum concentration in the finest fraction (for all samples as well as for day and night data subsets; Table 1).

The formation of a second maximum, at larger particles than emitted, reflects the redistribution of semivolatile organics in an aged aerosol, hence, is expected at receptor sites such as the marine site. This was also observed in polluted air, at rural and suburban sites, but not at traffic sites or in winter at a rural site, when primary emissions dominated (unimodal; Albinet et al., 2008b; Ringuet et al., 2012b).

Substance patterns and NPAH formation during long-range atmospheric transport

Among the targeted NPAHs and apart from NNAPs, which were highest concentrated, 2NFLT and 3NPHE prevailed at the marine site (accounting together for ≈60% of the NPAH mass, excluding the NNAPs), while at the continental site 9NANT and 2NFLT prevailed (accounting for ≈65% together) (Fig. 1, summarised in Fig. S4). The analytical method did not separate the isomers 2NFLT and 3NFLT, but at receptor sites, far from diesel emissions it appears justified to assume $c_{2NFLT} >> c_{3NFLT}$ (Finlayson-Pitts and Pitts, 2000; Zimmermann et al., 2012). The ratio 1NPYR/2NPYR is higher, ≈1, at the continental site than at the marine site (≈0.25), which reflects the significance of primary sources for polluted air (Atkinson and Arey, 1994; Finlayson-Pitts and Pitts, 2000; Zimmermann et al., 2012). This ratio was found similarly high or even higher at urban sites (Ringuet et al., 2012c; Tomaz et al., 2016). Similarly, the ratio 2NFLT/1NPYR, the concentration of a secondarily formed over a primary emitted NPAH, has been used as indicator for fresh emissions (if < 5) vs. photochemically aged air mass (Keyte et al., 2013). These values were >> 5 in 21 out of 22 and 7 out of 8 samples at the marine and continental sites, respectively. The only sample collected at the continental site with elevated primary NPAH (2NFLT/1NPYR = 4.3) was possibly influenced by emissions from Budapest, which was passed by the advected air within the last hours before arrival. The only sample collected at the marine site with elevated primary NPAH (2NFLT/1NPYR = 5.9) was indeed directly influenced by emissions into the boundary layer above the Izmir and Istanbul metropolitan areas (urban fractional dose D_u = 5.0% for samples no. 1 and 2 in Fig. S3). In conclusion, these results from receptor / background sites confirm the existing knowledge about primary emitted and secondarily formed NPAHs.

The ratio of two secondarily formed NPAHs, 2NFLT/2NPYR, indicative for day- vs. night-time formation paths (Atkinson and Arey, 1994; Ciccioli et al., 1996), is found ≈2 at the marine and ≈8 at the continental site (normalised to the precursor ratio i.e., 2NFLT/2NPYR/(FLT/PYR); Table 4). Such low values point to day-time (OH initiated) formation, while night-time (NO_3 initiated) formation was negligible, practically excluded at the marine site. This is in line with the perception that NO_3 must have been very low in this remote environment. (NO_x levels at the marine site were in the range 0.2-0.6 ppbv). A similar conclusion had been drawn in a semi-rural environment (Feilberg et al., 2001).

For 2NFLT and 2NPYR (secondary sources only) and for 1NPYR, which has mostly primary sources (Finlayson-Pitts and Pitts, 2000; Ringuet et al., 2012a; Jariyasopit et al., 2014a, 2014b) we infer the potential yields (Table 4). Here, yield is defined as c_{NPAH}/c_{PAH} (total concentrations). This yield is called 'potential' as it ~~and~~ reflects an upper estimate, as other PAH photochemical sinks, such as formation of oxy-PAHs, are neglected. The yield of 2NFLT in polluted air exceeds the one in background air only slightly, while the yield of 2NPYR in polluted air exceeds the one in background air much more (a factor of 3 higher).

As expected, the highest potential yield of 1NPYR is found in polluted air (both sites), reflecting the dominance of primary emissions of 1NPYR. Similarly, higher yields of secondary NPAHs are found for marine background air compared to background air with urban influence (marine site), reflecting the longer reaction times elapsed since PAH emission. The yield for 2NFLT, c_{2NFLT}/c_{FLT}, ≈ 2-4% at both sites ranges higher than the one for 2NPYR, c_{2NPYR}/c_{PYR}, which is found ≈ 0.5-2%. Note that because of the co-elution of

2NFLT and 3NFLT, and neglect of 3NFLT, the so derived values of c_{2NFLT}/c_{FLT} represent actually upper estimates. Apart from sites which were immediately influenced by PAH sources (road traffic, power plant, biomass burning), only very few studies reported NPAH together with precursor data in both phases of ambient air. c_{2NPYR}/c_{PYR} = 1.0%, similar to our finding at remote sites, but a very high c_{2NFLT}/c_{FLT} = 12.9% were reported from a suburban site in France in summer during day-time (corresponding values for night-time were 2.0 and 9.4%, respectively; Ringuet et al., 2012c). 2NFLT was not separated from 3NFLT (similar to our data set). A suburban site will be influenced by direct 3NFLT emissions, such that c_{2NFLT}/c_{FLT} is an upper estimate. Much lower ratios, c_{2NFLT}/c_{FLT} = 0.20% and c_{2NPYR}/c_{PYR} = 0.08% were reported as the median values for 90 sites of various categories, rural and urban, in northern China in summer (Lin et al., 2015). These yields are somewhat higher for the subset of the rural sites. The potential yields found at the marine site in our study are close to the yields for OH-initiated photochemistry observed in laboratory experiments under high NO_x conditions i.e., 3% for c_{2NFLT}/c_{FLT} and 0.5% for c_{2NPYR}/c_{PYR} (Atkinson and Arey, 1994).

4. Conclusions

For the first time pollution contained in individual background air samples was quantified, by means of a fractional dose. The fractional dose indicated how much the collected volume of air had been exposed to an urban boundary layer within a given time horizon. This is found suitable to discriminate among samples and discuss results, clearly beyond qualitative reasoning on back trajectories alone. The concept could be applied to any type of georeferenced origin and might be useful to track the influence of land use of various kind, or ship and aircraft routes.

Our measurements confirmed occurrence of mutagenic NPAHs, earlier reported from polluted atmospheric environments of America, Europe and Asia, also for the European background atmosphere and the outflow of Europe. These substances obviously go into intercontinental transport and might be indeed ubiquitous. The ~~long-range transport potential is hardly limited by the~~ mass size distribution~~, which~~ is determined by the particle size upon emission (primary NPAHs) and condensation and redistribution in the aerosol along transport, hence, does not include the short-lived coarse mass fraction. This indicates a high long-range transport potential. However, the observation of 3.8 and 0.92 pg m^{-3} of 2NFLT and 2NPYR, respectively, measured at the southeastern outflow of Europe (the lowest ever reported concentrations; Table 3), may indicate that their abundance in the remote global environment could be less than anticipated. Earlier, this was based on a single measurement of 2NPYR, 3 pg m^{-3}, at an extremely remote site in central Asia two decades before (Ciccioli et al., 1996). Moreover, this air, classified as marine background, was not completely clean, but had been exposed to a non-zero fractional urban pollution dose (0.4% of the total, time horizon of 2 days). More measurements at remote sites should verify NPAH levels globally. PAHs have been abated significantly in Europe during the last decades (EEA, 2014), which should also be reflected in long-term trends of their derivatives. However, a temporal trend for the Aegean or the southeastern outflow of Europe in summer cannot be inferred based on the current and the earlier (2002; Tsapakis and Stephanou, 2007) campaign data. NPAHs should be included in monitoring programmes to better assess the exposure of human health hazards of atmospheric pollution, even in remote areas.

Understanding of NPAH formation in ambient air is still rudimentary. Although our observations of a potential NPAH yield are in agreement with laboratory studies of OH-initiated photochemistry, the kinetics of NPAHs, both formation from parent PAHs and photolysis remains to be quantitatively studied under relevant conditions for the background atmosphere i.e., low NO_x and on various aerosol matrices including sea salt, respectively. More studies into NPAH atmospheric fate, both field observations and kinetic data, are needed in order to assess and quantify spatial and temporal trends, the long-range transport potential and persistence.

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Table 1. Overview time weighted mean concentrations in the particulate and gas phases, and ambient temperature. Data subsets (B = background, P = polluted, D = day mean, N = night mean) and mass size distribution (<0.45/0.45-0.95/0.95-1.5/1.5-3.0/3.0-7.2/7.2-10 µm aerodynamic equivalent diameter) in brackets.

Site	Phase	Σ_{11} 3-4rNPAH (pg m^{-3})	Σ_6 4rPAH (pg m^{-3})
Marine	particulate (n = 8)	4.1 (3.5/0.6/0.2/0.03/0.03/0.00) (B: 0.2/P: 8.7)	43 (28/8.1/1.2/6.2/4.3/1.7) (B: 7.9/P: 42.4)
	gas (n = 21)	18.4 (B: 13.2/P:31.1)	403 (B:321/P:580)
	T(°C)	25.6 (B: 27.1/P: 22.0)	
Continental	particulate (n = 22)	24.3 (20.5/2.9/0.7/0.04/0.06/0.15) (D:13.9/N:34.6)	129 (87/28/12/0.6/0.0/0.0) (D:146/N:116)
	gas (n = 22)	34.2 (D:42.9/N:25.5)	517 (D:649/N:384)
	T(°C)	23.1 (D:28.8/N:17.5)	

Table 3. Comparison of total (g + p) concentrations in air, c_{tot} (pg/m^3), with other measurements at remote and rural sites

	1NPYR (pg/m^3)	2NFLT (pg/m^3)	2NPYR (pg/m^3)	References
background CEu summer 2013	1.1	15 [a]	1.3	this work (continental)
E Mediterranean summer 2012	0.74	8.6 [a]	2.5	this work (marine)
E Mediterranean clean summer 2012	0.21	3.8 [a]	0.92	this work (marine background [b])
E Mediterranean clean summer 2002	-	29	21	Tsapakis and Stephanou, 2007
Ross Sea coast, Antarctica	<0.02 [c]	<0.03 [c]		Vincenti et al., 2001
Himalayas, Nepal 1991	-	-	3	Ciccioli et al., 1996
Forest Amazonia 1993	2	15	8	
Rural Northern Germany 1991	-	-	3	
Rural Denmark winter-spring 1982	9±5 [c]	-	-	Nielsen et al., 1984
Semi-rural Denmark all year 1998-99	40	97	6.3	Feilberg et al., 2001
Remote Alps 2002	2.2	-	-	Schauer et al., 2004
Rural Alps 2002	6.6	-	-	
Rural Alps [d] winter 2002-03	21	96 [a]	81	Albinet et al., 2008a
Rural Alps [d] summer 2003	4.2	28 [a]	5.7	
Remote Alps [e] winter 2002-03	2.4	1.3 [a]	14.8	
Remote Alps [e] summer 2003	0.6	1.8 [a]	0.7	
Rural Southern France 2004	0.6	2.6 [a]	1.6	Albinet et al., 2007

[a] co-eluted with 3NFLT, assuming $c_{3NFLT} = 0$

[b] samples No. 9, 10, 19 and 22 in Fig. S3

[c] particulate phase concentration only

[d] Val de Maurienne sites (Albinet et al., 2008a)

[e] Plan de l'Aiguille site (Albinet et al., 2008a)

Table 4: Selected 4-ring PAHs and primary and secondary 3-4 ring NPAH total (g + p) time-weighted mean concentrations ±σ (pg m^{-3}). Potential yields, c_{NPAH}/c_{PAH}, in brackets. σ given for n > 2.

Site		Marine			Continental
	Data subset	all (n = 8[a])	marine background (n = 2[b])	background with urban influence (n = 2[c])	all (n = 22)
Primary	FLT	213±161	161	259	342±215
	PYR	146±130	103	188	226±131
Primary and secondary (potential yield)	2NFLN [d]	0.038±0.12	<0.18	0.15	0.034±0.044
	1NPYR	0.62±1.1 (0.4±0.2%)	0.21 (0.2%)	1.4 (0.7%)	1.1±0.6 (0.6±0.3%)
Secondary (yield)	2NFLT [e]	7.7±8.5 (3.6±2.0%)	1.68 (1.0%)	11.0 (4.2%)	15±10 (6.5±7.5%)
	2NPYR	2.2±2.6 (1.5±0.7%)	0.92 (0.9%)	3.3 (1.8%)	1.3±1.7 (0.74±1.09%)

[a] 8 filter and 21 PUF samples

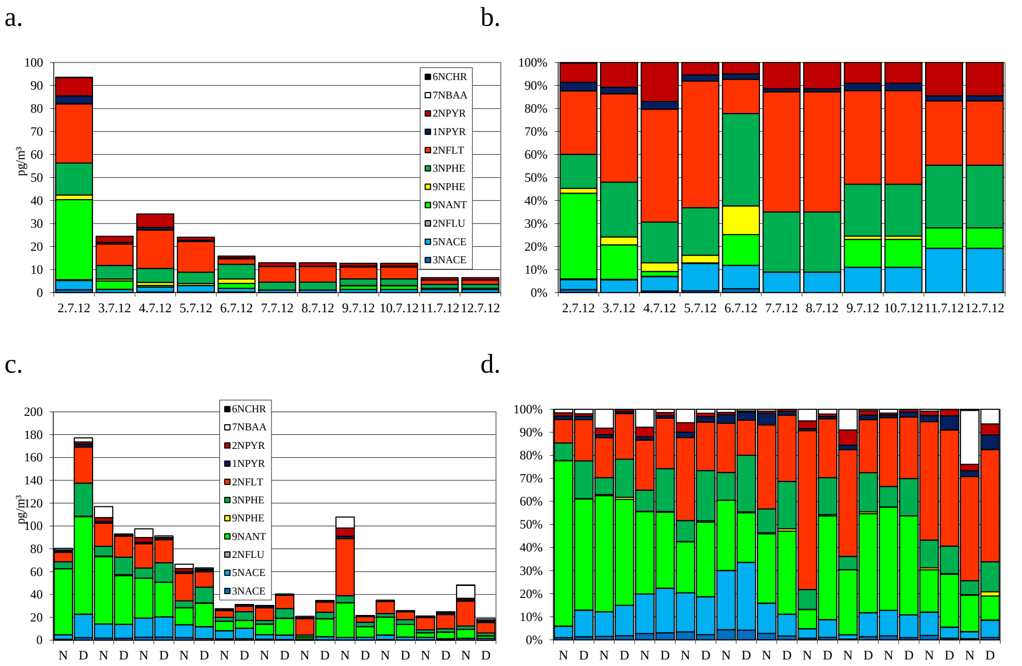
[b] 2 filter and 6 PUF samples i.e., No. 9-10 and 19-22 in Fig. S3 (urban fractional dose D_u = 0.4%)

[c] 2 filter and 5 PUF sample i.e., No. 1-2 and 15-18 in Fig. S3 (D_u = 3.1%)

[d] no yield given as c_{FLN} not quantified

[e] co-eluted with 3NFLT, assuming $c_{3NFLT} = 0$

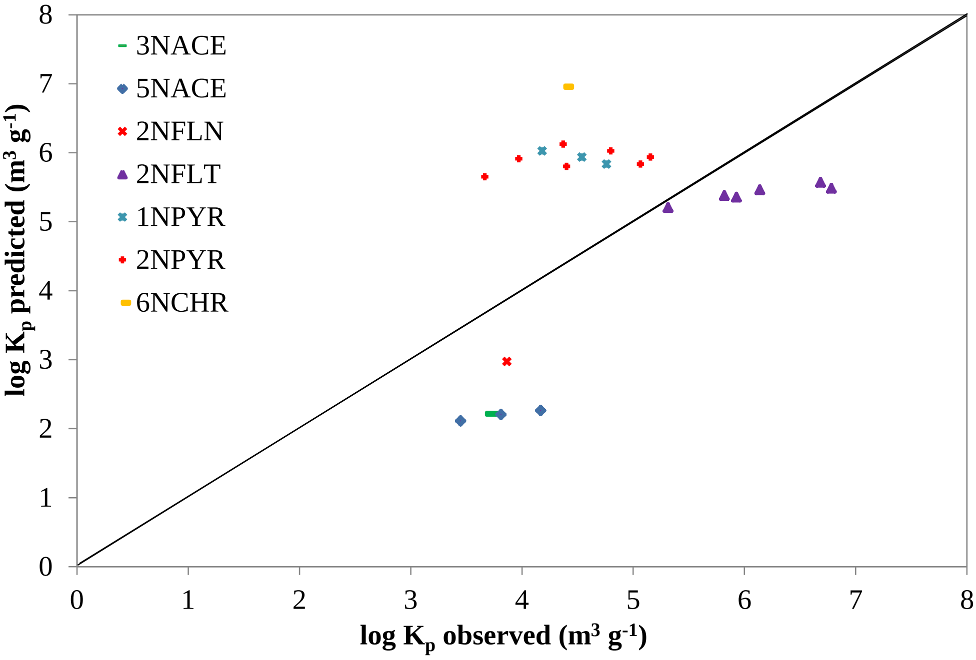
Fig. 1: Time series of absolute (a, c; pg m^{-3}) and relative (b, d) total (gas + particulate) NPAH concentrations at the (a, b) marine (24 h means shown [a]) and (c, d) continental site (day / night means)



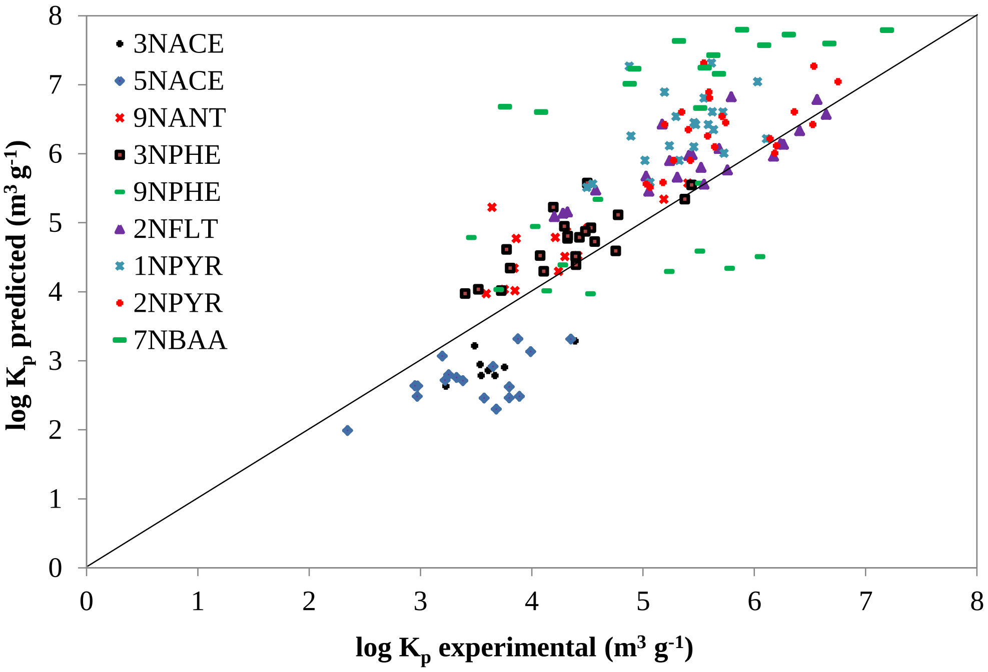
[a] gas-phase (PUF) sampled day / night, particulate phase (filter) sampled 1-4 subsequent days / nights, 4 during the period 7.-12.7.12

Fig. 2: Predicted versus experimental log K_p (m^3 air g^{-1} PM) for NPAHs using the multi-phase ppLFER model at the (a) marine and (b) continental site

a.



b.



3NACE
5NACE
9NANT
3NPHE
9NPHE
2NFLT
1NPYR
2NPYR
7NBAA
log K_p predicted ($m^3 g^{-1}$)
log K_p experimental ($m^3 g^{-1}$)
0
1
2
3
4
5
6
7
8

Fig. 3. Time-weighted mean $\Sigma_6$4rPAH and Σ_{11}3-4rNPAH mass size distributions (pg m^{-3}) at the marine and continental sites. ~~Upper cut-off of impactor stage given in µm of aerodynamic particle size.~~ The error bars show the standard deviation from the campaign mean.

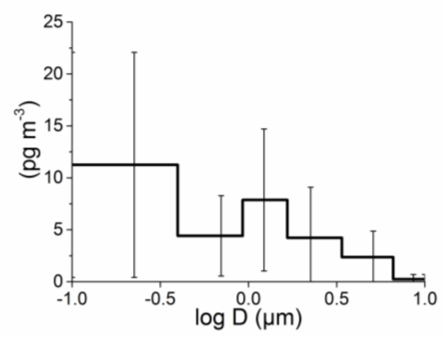
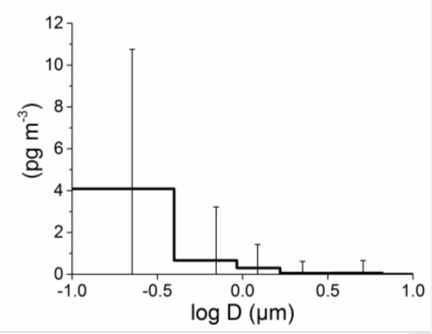
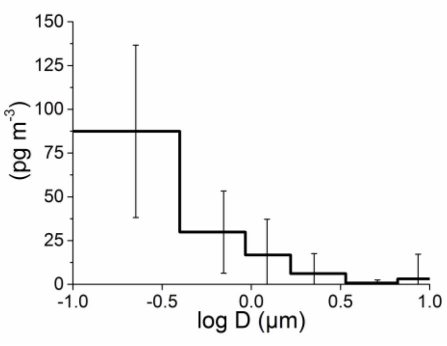
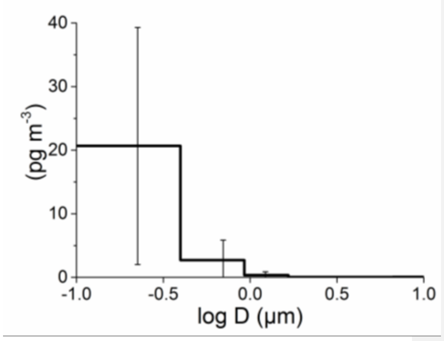
Site	PAH	NPAH
Marine		
Continental		

Table 2. Total (g + p) time-weighted concentrations, c_{tot} (pg m^{-3}), particulate mass fraction, $\theta = c_p / c_{tot}$, and mass median diameter (MMD, µm), of of 2-4-ring NPAHs and 4-ring PAHs at the marine (as ‘mean (background mean/ urban influence mean)’, n = $8(2^a/2^b)$) and continental (as ‘mean (day mean/ night mean)’, n = 22(11/11)) sites, together with temperature and supporting aerosol parameters (PM_{10} and carbonaceous mass fractions). LOQ = limit of quantification, nd = no data.

	Marine			Continental		
	c_{tot} (pg m^{-3})	Θ	MMD (µm)	c_{tot} (pg m^{-3})	Θ	MMD (µm)
FLT	226 (161/259)	0.07 (0.03/0.07)	0.58 (0.43/0.52)	342 (432/251)	0.11 (0.11/0.12)	0.062 (0.101/0.034)
PYR	158 (103/188)	0.04 (0.01/0.05)	0.21 (0.022/0.22)	226 (276/176)	0.18 (0.18/0.19)	0.075 (0.105/0.055)
BBN	4.1 (2.0/5.5)	0.01 (nd/0.05)	0.022 (nd/0.022)	15 (16/13)	0.61 (0.58/0.65)	0.079 (0.127/0.053)
BAA	2.8 (<LOQ/3.4)	0.28 (nd/0.29)	0.022 (nd/0.022)	16 (14/18)	0.91 (0.90/0.92)	0.070 (0.090/0.060)
TPH	12 (8.5/14)	0.02 (nd/0.05)	0.022 (nd/0.022)	23 (26/21)	0.51 (0.41/0.63)	0.070 (0.090/0.057)
CHR	23 (10/29)	0.22 (0.09/0.20)	0.15 (0.022/0.15)	41 (44/38)	0.75 (0.71/0.80)	0.074 (0.105/0.055)
Σ_6 4rPAH	426 (284/499)	0.07 (0.02/0.07)	0.31 (0.19/0.28)	663 (808/517)	0.21 (0.19/0.25)	0.071 (0.10/0.051)
3NACE	0.21 (0.17/0.39)	0.05 (0.00/0.14)	0.022 (nd/0.022)	1.0(1.0/1.0)	0.05 (0.01/0.11)	0.022 (nd/0.022)
5NACE	1.8 (1.5/2.0)	0.07 (0.00/0.00)	0.022 (nd/nd)	6.8 (7.6/6.0)	0.03 (0.01/0.05)	0.022 (0.022/0.022)
2NFLN	0.01 (<LOQ/0.15)	0.02 (nd/0.00)	1.19 (nd/nd)	0.035 (0.035/0.034)	0.00 (0.00/0.00)	nd
9NPHE	0.73 (0.84/0.55)	0.00 (0.00/0.00)	nd	0.21 (0.28/0.13)	0.36 (0.43/0.20)	0.022 (0.022/nd)

3NPHE	4.8 (3.4/5.0)	0.00 (nd/nd)	nd	7.4 (10.0/4.8)	0.24 (0.15/0.44)	0.109 (0.067/0.116)
9NANT	4.2 (1.1/8.2)	0.00 (0.00/0.00)	nd	22 (22/22)	0.23 (0.14/0.33)	0.022 (0.022/0.022)
2NFLT [c]	8.6 (3.8/11)	0.32 (nd/0.45)	0.040 (nd/0.080)	15 (13/18)	0.78 (0.54/0.95)	0.054 (0.035/0.050)
1NPYR	0.75 (0.21/1.4)	0.33 (0.00/0.58)	0.061 (nd/0.14)	1.1 (1.1/1.2)	0.82 (0.76/0.88)	0.030 (0.031/0.029)
2NPYR	2.5 (0.92/3.3)	0.53 (0.19/0.69)	0.058 (0.060/0.055)	1.3 (0.73/2.0)	0.93 (0.83/0.97)	0.070 (0.040/0.061)
7NBAA	<LOQ	nd	nd	2.5 (0.77/4.2)	0.91 (0.56/0.97)	0.074 (0.038/0.057)
6NCHR	0.02 (<LOQ/0.07)	1.00 (nd/1.00)	2.12 (nd/2.12)	0.01 (<LOQ/0.02)	1.00 (nd/1.00)	0.022 (nd/0.022)
Σ_{11}3-4rNPAH	23.7 (11.8/32.0)	0.22 (0.01/0.22)	0.34(0.33/0.34)	58 (56/59)	0.16 (0.13/0.17)	0.039 (0.036/0.040)
PM$_{10}$ (µg/m^3)	34.9 (21.0/55.5)		0.58 (1.13/0.62)	22.1 (19.5/24.5)		nd
EC (µg/m^3)	0.11 (0.09/0.17)		0.03(0.05/0.03)	0.31 (0.28/0.33)		0.21(0.19/0.22)
OC (µg/m^3)	1.9 (1.5/3.0)		0.17(0.16/0.15)	3.6 (3.3/3.9)		0.16(0.13/0.18)
T (°C)	25.6 (27.0/22.2)			23.1 (28.8/17.5)		

[a] 2 filter and 4 PUF samples i.e., No. 9, 10, 19 and 22 in Fig. S3

[b] 1 filter and 1 PUF sample i.e., No. 1 and 2 in Fig. S3

[c] co-eluted with 3NFLT, assuming $c_{3NFLT} = 0$