**S1 Methodology - Organic trace analytical quality assurance parameters**

The instrument limit of quantification (ILOQ), which is based on 3 times the instrument limit of detection, which in turn is based on 3 times the chromatogramme baseline noise level, was 0.002-0.033 ng for NPAHs (except for 1NNAP for which it was 0.414 ng) and 0.006-0.06 ng for 4-ring PAHs (except for FLT and PYR for which it was 0.282 and 0.115 ng, respectively) (Table S1).

Table S1: Recoveries including their relative standard deviations (RSD) (a), instrument limits of quantification (LOQ) (b), given as masses and concentrations, the latter for a typical sample volume (650 $m^3$; range of sample volumes: 612-3130 $m^3$ at the marine site and 578-885 $m^3$ at the continental site) and (c) field blank values for various type of sampling media (pg)

a.

| Analyte | Recovery (%) | RSD (%) |
|---|---|---|
| D8-NAP | 72 | 14 |
| D10-PHE | 95 | 12 |
| D12-perylene | 102 | 9 |
| 1NNAP | 70 | 14 |
| 2NNAP | 71 | 16 |
| 3NACE | 85 | 12 |
| 5NACE | 83 | 9 |
| 2NFLU | 89 | 14 |
| 9NPHE | 91 | 20 |
| 3NPHE | 90 | 16 |
| 9NANT | 88 | 15 |
| 2NFLT | 92 | 9 |
| 3NFLT | 88 | 13 |
| 1NPYR | 110 | 12 |
| 2NPYR | 105 | 16 |
| 7NBAA | 99 | 19 |
| 6NCHR | 89 | 9 |

b.

| Analyte | mass (ng) | concentration (pg $m^{-3}$) |
|---|---|---|
| FLT | 0.282 | 0.43 |
| PYR | 0.115 | 0.18 |
| BBN | 0.006 | 0.010 |
| BAA | 0.014 | 0.021 |
| TPH | 0.031 | 0.048 |
| CHR | 0.060 | 0.092 |
| 1NNAP | 0.414 | 0.64 |
| 2NNAP | 0.014 | 0.021 |
| 3NACE | 0.002 | 0.004 |
| 5NACE | 0.005 | 0.008 |
| 2NFLU | 0.005 | 0.008 |
| 9NPHE | 0.033 | 0.051 |
| 3NPHE | 0.005 | 0.008 |
| 9NANT | 0.005 | 0.008 |
| 2NFLT [a] | 0.025 | 0.038 |
| 1NPYR | 0.007 | 0.011 |
| 2NPYR | 0.005 | 0.008 |
| 7NBAA | 0.005 | 0.008 |
| 6NCHR | 0.005 | 0.008 |

c.

| Analyte | PUF (n = 4[b]) | QFF | |
|---|---|---|---|
| | | 0.49-10 µm stages (n = 4[b]) | backup filter (n = 4[b]) |
| FLT | 1046±220 | 496±98 | 509±116 |
| PYR | 602±148 | 172±64 | 153±33 |
| BBN | 57±19 | 20±9 | 16±3 |
| BAA | 66±13 | 20±14 | 14±5 |
| TPH | 89±26 | 42±10 | 40±9 |
| CHR | 147±41 | 90±42 | 73±12 |
| 1NNAP | <410 | 72±124 | 363±17 |
| 2NNAP | 50±44 | 54±12 | 60±1 |
| 3NACE | < 5.0 | < 5.0 | < 5.0 |
| 5NACE | < 5.0 | < 5.0 | < 5.0 |
| 2NFLU | < 5.0 | < 5.0 | < 5.0 |
| 9NPHE | < 5.0 | < 5.0 | < 5.0 |
| 3NPHE | < 5.0 | < 5.0 | < 5.0 |
| 9NANT | 22±19 | 60±68 | 81±78 |
| 2NFLT [a] | 45±39 | 53±8 | 68±1 |
| 1NPYR | 14±12 | 15±93 | 21±1 |
| 2NPYR | < 5.0 | < 5.0 | 5.5±0.7 |
| 7NBAA | < 5.0 | < 5.0 | < 5.0 |
| 6NCHR | < 5.0 | < 5.0 | < 5.0 |

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

[b] 3 PUF, 10 QFF for the stages corresponding to 0.49-10µm and 2 QFF for particles <0.49 µm at the continental site

## S2 Results

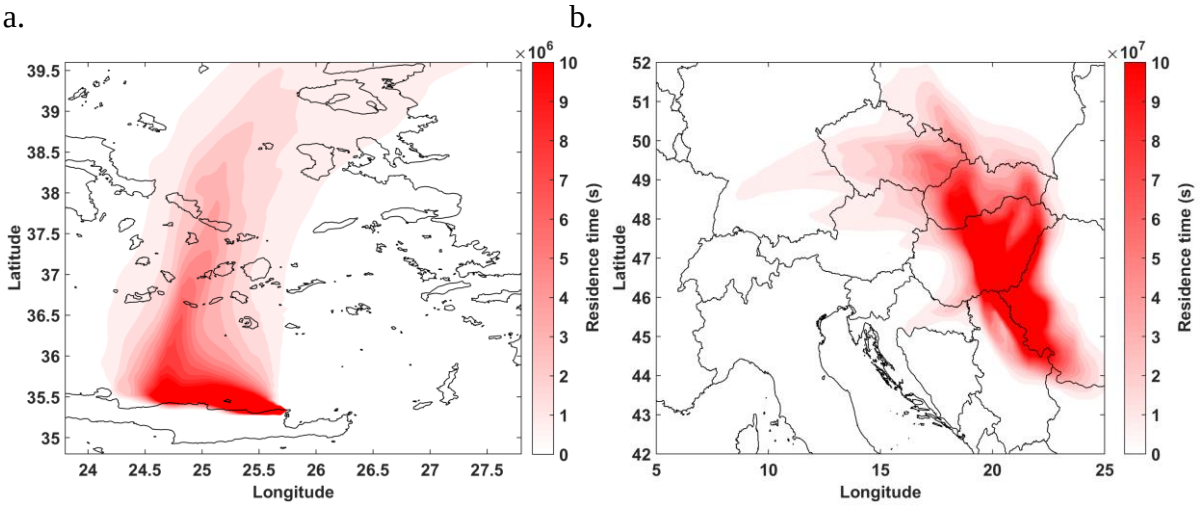
### S2.1 Meteorology and transports

#### S2.1.1 Meteorological situations

Marine site: During 2-11 July 2012 the Aegean was mostly influenced by northerly, and in its northern part easterly advection over the Marmara Sea as part of a cyclonic system which resided over Romania during 1-3 July and moved over western Russia during 4-10 July. The sky was cloud-free all the time. No frontal passage occurred, such that for all samples taken in the study region the hypothesis of horizontal homogeneity of air mass collected can be applied. Under the influence of a strong westerly flow towards Europe the flow in the northern part of the Aegean switched to westerly during the night 11-12 July, such that air which was residing over the SW Balkans was advected as well as air from beyond, i.e. central Italy and the NW Mediterranean Sea and the Iberian Peninsula.

Continental site: During 5-16 August 2013 mostly northwesterly and northerly flow, directed by anti-cyclonic systems slowly moving eastward over northern France, Germany and Poland dominated the flow to the Gt. Hungarian Plain. These air masses travelled over industrialised areas of Hungary (Budapest), Slovakia, Czech Republic, Germany and Poland. During 10-13 August advection from southeast contributed, too.

Fig. S1. Back trajectories from the (a) marine and (b) continental site during the measurements in summers 2012 and 2013, respectively. FLEXPART simulations 48 h backward in time.




#### S2.1.2 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, 38.25-38.85°N/26.2-27.3°/E), Athens (≈300 km, 37.8-38.1°N/23.5-23.85°E) and Istanbul (≈500 km away, 40.82-41.1°N/28.58-29.55°E). (Figure S3)

The urban fraction of a total dose, $D_{u\,i}$, an air mass collected in sample i had received (for a given simulation period $\Delta t = \Delta t_{sample} + 48h$, $\Delta t_{sample}$ being the sampling time) can be derived as:

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

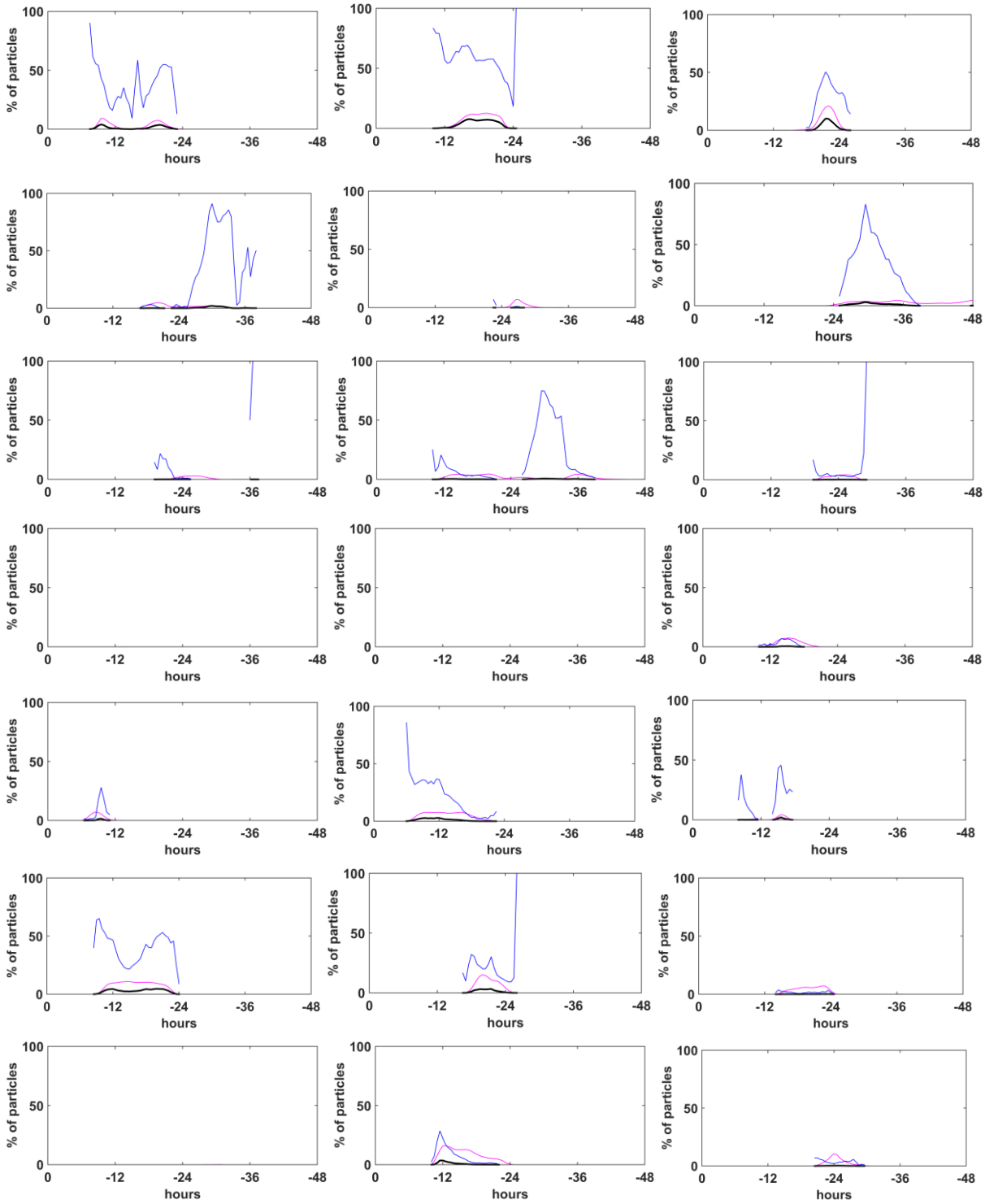
$t_{Rblua}$ = 0.5 h (model output resolution), $N_{tot}$ = number of virtual particles present during the specific time step, $N_{blua}(t)$ = number of particles within the urban boundary layer. $D_{u\,i}$ takes values between 0 and 1, corresponding to none or all, respectively, of the entire sample air that had crossed the urban boundary layer (Fig. S3).
Comparison of urban influence in samples of various sample volume requires normalisation to sample volume, V, a relative dose (with n = total number of samples collected):

$D_{ru\,i} = [\sum_n V_n/(nV_i)] \times D_{u\,i}$

Values of $D_{ru\,i}$ may exceed 1.

As an implication of the impactor sampling protocol at the marine site, individual samples encompass up to 4 days/nights. The sampling periods selected for the sub-dataset representing marine background conditions are the day-times 7 and 13 July and the nights of 6-7 and 11-12 July (i.e. samples No. 9, 10, 19 and 22 in Fig. S3), while the sampling periods selected for the sub-dataset representing background with urban influence are the day-times 3 and 10 July and the nights 2-3 and 10-11 July (i.e. samples No. 1, 2, 16 and 17 in Fig. S3).

Fig. S2. Tracking of air mass history for urban influence: Fraction of Lagrangian particles (or air parcels) continuously released in FLEXPART runs, travelling from the marine site back in time that crossed the Izmir area (purple), the fraction of these particles which had crossed the Izmir area within the boundary layer (blue), and product of these two fractions (black) for arrival time periods. 22 sequential day/night samples 2-13 July 2012.



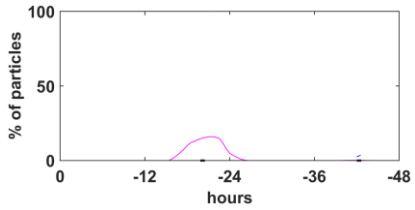
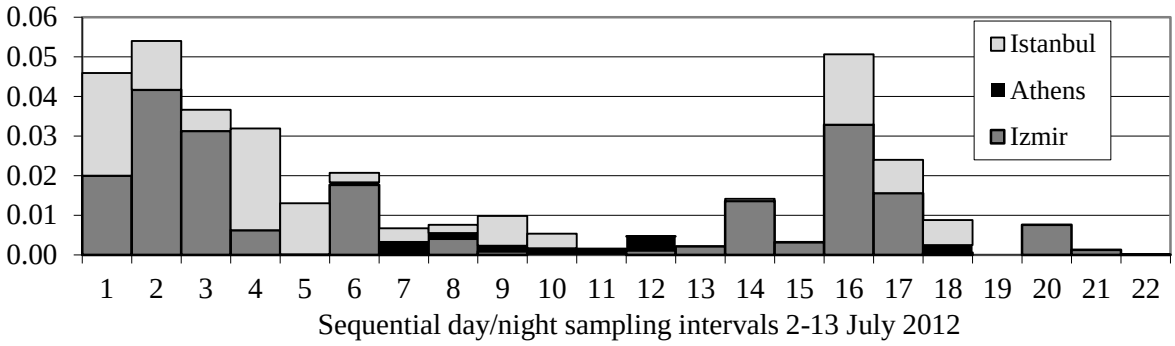


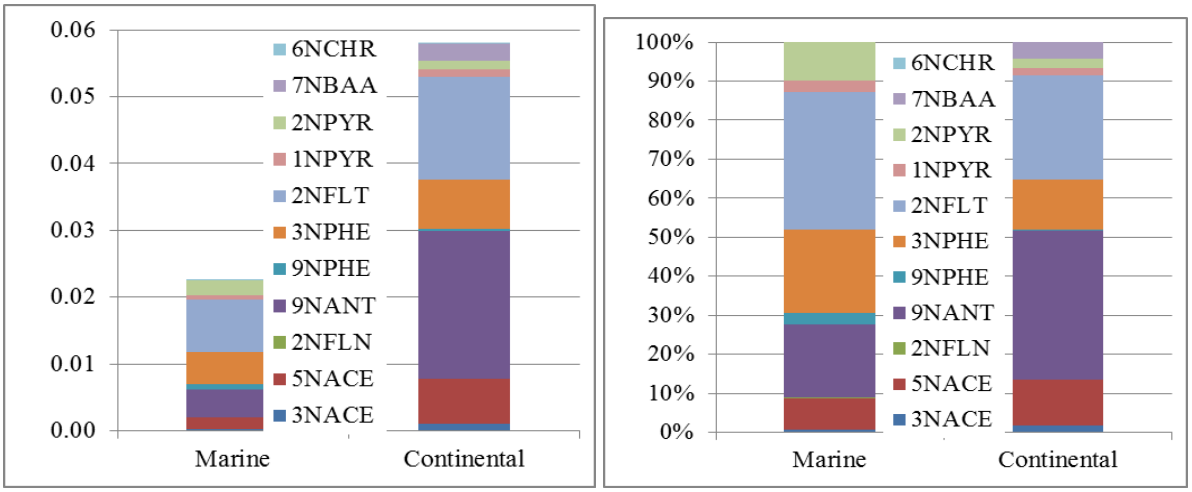

Figure S3. Tracking of urban influence in air mass history: Time series of urban dose, $D_u$, of samples collected at the marine site on the Island of Crete. FLEXPART simulations 48 h backward in time (see Fig. S2).




## S2.2 Concentrations

Fig. S4: Mean absolute (a; ng $m^{-3}$) and relative (b) total (gas + particulate) 2-4 ring NPAH substance patterns at the marine and continental sites

a. b.



## S2.3 Gas-particle partitioning

### S2.3.1 Prediction by ppLFER

Deviations between predicted and observed (Fig. 3):
Root-mean square errors (RMSE) of log $K_p$ ($m^3$ $g^{-1}$) predictions by the poly-parameter linear free energy relationship (ppLFER) model for 5NACE, 1NPYR, 2NPYR, and 2NFLT were 1.63, 1.48, 1.49, and 0.81, respectively, at the marine site. At the continental site, the RMSE values for 5NACE, 9NANT, 9NPHE, 3NPHE, 2NPYR, 3NACE, and 2NFLT were between 0.50 and 0.84, and 1.11 and 1.86 for 1NPYR and 7NBAA, respectively.

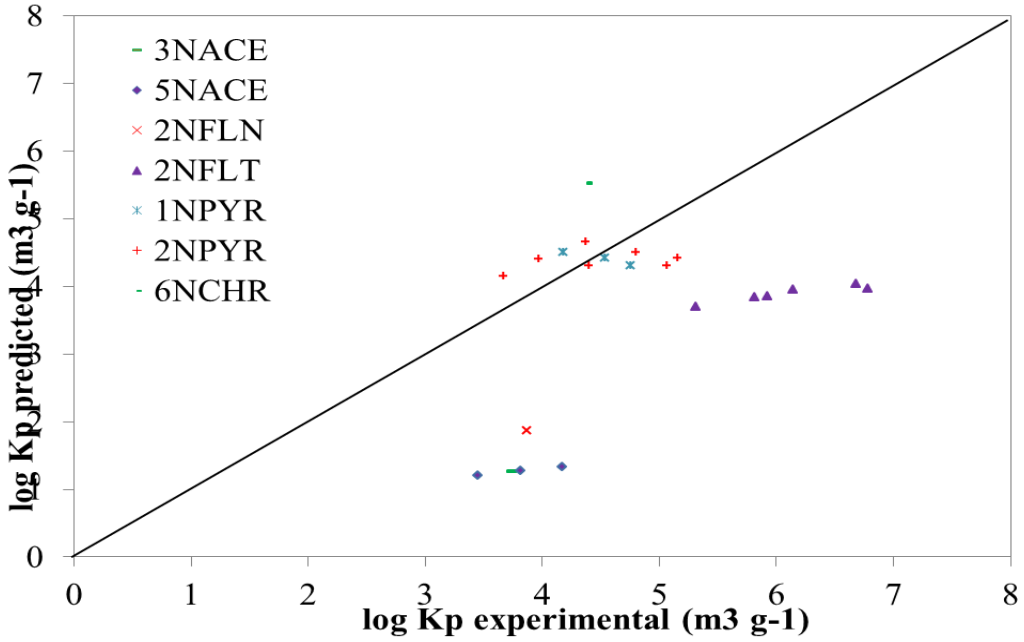
### S2.3.2 Prediction by spLFER

A single-parameter linear free energy relationship (spLFER), namely the $K_{oa}$ model (Finizio et al., 1997) was applied. This model was slightly modified, as $K_{oa}$ and enthalpies of liquid-gas phase transfer were derived using Abraham solute descriptors and ppLFER equations suggested by Abraham et al. (2010) and Mintz et al. (2007). The model is presented in detail and discussed in Shahpoury et al., 2016, and Tomaz et al., 2016.

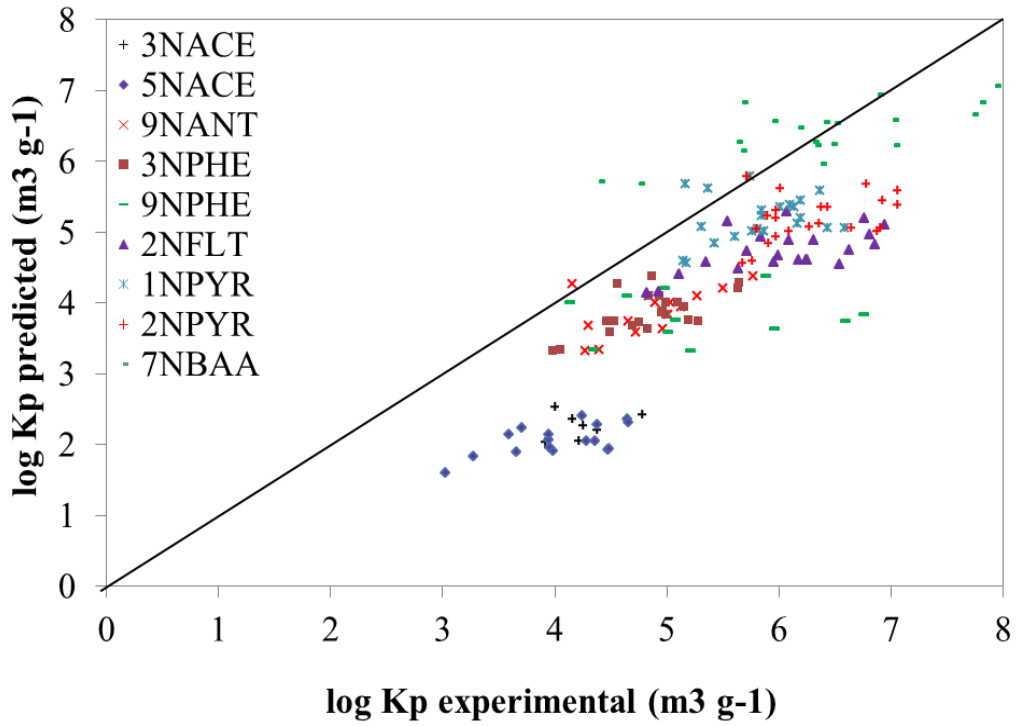
Deviations between predicted and observed (Fig. S5): At the marine site, the RMSE values of log $K_p$ ($m^3$ $g^{-1}$) predictions by the spLFER were 0.9 and 1.3 log-units larger than determined for ppLFER predictions (S2.3.1, above) for 5NACE and 2NFLT, respectively, and were 1.1 and 1.0 log-units smaller for 1NPYR and 2NPYR, respectively. At the continental site, the RMSE values were between 0.2 and 0.9 log-units larger than the values determined for ppLFER predictions (S2.3.1, above), with the exception of 1NPYR and 7NBAA for which the RMSE values were 0.4 and 1.1 log-units smaller.

Fig. S5. Predicted versus experimental log $K_p$ ($m^3$ air $g^{-1}$ PM) for NPAHs using the $K_{oa}$ model at the (a) marine and (b) continental sites

a.




b.



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