Supporting Information

Modeling the Formation, Degradation and Spatiotemporal Distribution of 2-Nitrofluoranthene and 2-Nitropyrene in the Global Atmosphere

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S2
S1. Formation Chemistry of 2-NFLT and 2-NPYR

\[ Y_{2\text{-NFLT,OH}} \quad Y_{2\text{-NPYR,OH}} \quad \text{and} \quad Y_{2\text{-NFLT,NO}_3} \] is the total yield of either 2-nitrofluoranthene (2-NFLT) or 2-nitropyrene (2-NPYR) from the amount consumed of fluoranthene (FLT) or pyrene (PYR), by their respective reactions. Experimental values can be seen in Table S1 and ranged between 0.5-24%.\(^1\) One key factor contributing to this value of total yield is the % conversion of the PAH-radical adduct into NPAH (reaction with \( \text{NO}_2 \)) instead of other oxygenated products (reaction with \( \text{O}_2 \)) (Fig. S1). Several other factors conflate to reduce the empirical \( Y_{\text{NPAH/PAH}} \) of 2-NFLT and 2-NPYR. These likely include: (1) further reaction and loss of NPAH and (2) formation of other NPAH isomers. The contribution of (2) may be estimated from the theoretical calculations of Zhang et al. (2014), by accounting for the fact that only certain adducts may lead to the formation of 2-NFLT or 2-NPYR (\( \approx 20\text{-}60\% \)).\(^2\)

Initial radical addition is described by experimentally determined rate coefficients (Table S1).\(^1\) The kinetics of reaction of FLT with OH has been measured by Brubaker and Hites.\(^3\) These rate coefficients are in reasonable agreement with theoretical calculations for the reaction of OH and \( \text{NO}_3 \) at specific positions on FLT and PYR.\(^2\) Notably, the rate of reaction between FLT and \( \text{NO}_3 \) is dependent on \( \text{NO}_2 \).

With respect to fate of the PAH-radical adduct, Ghigo et al. (2006), calculated theoretically the ratio \( k_{\text{NO}_2}/k_{\text{O}_2} \) of rate coefficients for benzene and naphthalene (\( 9\times10^3 \) and \( 8\times10^4 \) respectively).\(^4\) This is in good agreement with the experimentally determined value, \( 3.6\times10^4 \), for \( k_{\text{NO}_2}/k_{\text{O}_2} \text{-naphthalene} \) (i.e. rate coefficient for reaction with \( \text{NO}_2 \) and \( \text{O}_2 \) is for the naphthalene- and benzene-OH adducts, respectively).\(^5\text{-}7\) The ratio \( k_{\text{NO}_2}/k_{\text{O}_2} \) for the pyrene-OH and pyrene-\( \text{NO}_3 \) adducts were calculated as \( 5\times10^9 \) and \( 2\times10^9 \), respectively.\(^4\) By using the concentration of \( \text{NO}_2 \) and \( \text{O}_2 \), an analytical expression for the yield scaling factor (\( \Omega \)) may be obtained from the ratio of rate coefficients \( k_{\text{NO}_2}/k_{\text{O}_2} \) (equation 1). In the \( \text{NO}_2 \)-dependent scheme, the yield scaling factor is multiplied by the empirically determined yield to ensure that (a) the model yield is equivalent to the empirically determined one at high \( \text{NO}_2 \) concentrations and (b) decreases towards lower \( \text{NO}_2 \) concentrations.

\[
(1) \quad \Omega = (k_{\text{NO}_2}/k_{\text{O}_2})([\text{NO}_2]/[\text{O}_2]) / (1 + (k_{\text{NO}_2}/k_{\text{O}_2})([\text{NO}_2]/[\text{O}_2]))
\]
Results from a sensitivity study using a formation scheme in which $Y_{2\text{-NFLT},\text{OH}}$, $Y_{2\text{-NPYR,OH}}$ and $Y_{2\text{-NFLT},\text{NO}_3}$ were dependent on NO$_2$ are shown in Fig. S2. In this scheme the value of $k_{\text{NO}_2}/k_{\text{O}_2}$ was set as $1 \times 10^7$ (see Table S1). The dependence of $Y_{2\text{-NFLT},\text{OH}}$, $Y_{2\text{-NPYR,OH}}$ and $Y_{2\text{-NFLT},\text{NO}_3}$ on NO$_2$ in this scheme is shown (Fig. S5) as well as the spatial distribution of $Y_{2\text{-NFLT},\text{OH}}$ for an illustrative month (Fig. S6).

S2. Partitioning Between Gas and Particle Phase
Semi-volatile compounds are distributed to significant mass fractions between the particle and gas phases of aerosols. Polyparameter linear free energy relationships (ppLFERs) are suitable to predict the mass distribution of NPAHs. Experimentally determined ppLFER solute specific descriptors for 1-nitropyrene are used in the model. These parameters are expected to be reasonably well representative for both 2-NFLT and 2-NPYR. Phase equilibrium is re-established at each model time step (30 min).

S3. Particle-phase Loss of 2-NFLT and 2-NPYR
In the gas-phase, NPAHs are generally less reactive than their precursors. Ringuet et al. investigated the reactivity of different NPAH species and found the O$_3$ reaction to be negligible for 2-NFLT (Ringuet et al., 2012). The same reaction was never reported for 2-NPYR. Particle phase 1-nitropyrene was shown to be less reactive than PYR with O$_3$ or NO$_2$.

S4. Comparing Simulated and Measured Concentrations
In order to minimize incommensurability issues, model simulated concentration values were compared with observed values in the following ways:
- Bilinear interpolation within the model grid cell is used to obtain simulated concentrations that better represents the location of each observational site.
- Comparison between model and observations is now solely presented at rural rather than urban sites. Rural sites are less affected by local sources, and make for more representable comparison.
- Temporal incommensurability is addressed by:
  - Comparing measured concentrations with simulated concentrations from the same months (even if not same year).
  - Observation sites where data was available over multiple seasons, were split into separate data points in order to prevent seasonal information being lost by averaging over time.
Table S1. Physicochemical properties and degradation rate coefficients of 2-NFLT and 2-NPYR used.

| Parameter                                           | Units                  | 2-NFLT     | 2-NPYR     | Reference                      |
|-----------------------------------------------------|------------------------|------------|------------|--------------------------------|
| Molar mass                                          | g mol\(^{-1}\)         | 247.25     | 247.25     |                                |
| Molar volume at boiling point                       | cm\(^3\) mol\(^{-1}\) | 245.8      | 242.3      | Le Bas method\(^{14}\)         |
| Total (biotic and abiotic) decay rate in soil       | s\(^{-1}\)             | 2.08 × 10\(^{-8}\) | 3.13 × 10\(^{-8}\) | Estimate. Value for parent compound adopted due lack of data. |
| Total (biotic and abiotic) decay rate in ocean      | s\(^{-1}\)             | 4.20 × 10\(^{-8}\) | 2.80 × 10\(^{-9}\) | Estimate. Value for parent compound adopted due lack of data. |
| Water solubility (at 298K)                          | mg L\(^{-1}\)          | 0.019      | 0.021      | \(^{15,16}\)                   |
| Vapor pressure                                      | Pa                     | 9.91 × 10\(^{-7}\) | 4.40 × 10\(^{-6}\) | \(^{16}\)                     |
| Enthalpy of dissolution, ∆sol\(H\)                 | J mol\(^{-1}\)         | 6.595 × 10\(^4\) | 6.546 × 10\(^4\) | COSMO-RS\(^{17}\)             |
| Heat of vaporization                                | J mol\(^{-1}\)         | 7.64 × 10\(^4\) | 7.64 × 10\(^4\) | \(^{18}\)                     |
| Heat of sublimation                                 | J mol\(^{-1}\)         | 1.25 × 10\(^5\) | 1.25 × 10\(^5\) | \(^{19}\)                     |
| Octanol-water partition coefficient, log\(_{10}(K_{OW})\) | -                      | 4.69       | 4.69       | \(^{16,20}\)                  |
| Property                                      | Value 1                  | Value 2                  | Notes                          |
|----------------------------------------------|--------------------------|--------------------------|--------------------------------|
| Octanol-air partitioning coefficient, \( \log_{10}(K_{OA}) \)^\(^a\) | \( A = 5.2236 \)        | \( A = 5.1659 \)        | COSMO-RS\(^{17}\)              |
|                                              | \( B = 1222.62 \) [K]    | \( B = 1220.86 \) [K]    |                                |
| Henry’s constant. H(T)\(^b\)                | \( H^\theta = 8545 \) [M atm\(^{-1}\)] | \( H^\theta = 9354 \) [M atm\(^{-1}\)] | COSMO-RS\(^{17}\)              |
|                                              | \(-\Delta_{\text{sol}}H/R = 7932\) [K] | \(-\Delta_{\text{sol}}H/R = 7874\) [K] |                                |
| ppLFER solute descriptors                    | E = 2.81                 | E = 2.81                 | Adopted from 1-nitropyrene\(^9\) |
|                                              | S = 2.07                 | S = 2.07                 |                                |
|                                              | A = 0                    | A = 0                    |                                |
|                                              | B = 0.33                 | B = 0.33                 |                                |
|                                              | V = 10.46                | V = 10.46                |                                |
|                                              | L = 1.76                 | L = 1.76                 |                                |
| Enthalpy of adsorption on black carbon       | 1.25 \times 10^5 J mol\(^{-1}\) | 1.25 \times 10^5 J mol\(^{-1}\) | Estimated for 1-nitropyrene using a predictive model and the estimated \( K_{\text{soot/air}} \)^\(^{9,21}\) |

\(^a\) Temperature dependence of \( K_{OA} \) is in the form \( K_{OM}(T) = A + B/T \)

\(^b\) \( H(T) = H^\theta \times \exp\left(\frac{-\Delta_{\text{sol}}H}{R} \times \left( \frac{1}{T} - \frac{1}{T^\theta}\right)\right) \) where \( H^\theta \) is Henry’s constant at the reference temperature \( T^\theta = 298.15 \) K, \( \Delta_{\text{sol}}H \) is the enthalpy of dissolution, \( R \) is the gas constant and \( T \) is temperature.\(^22\)
Table S2. Full collection of NPAH observations used for comparison with the model.

| Location                        | Time Start   | Time End   | Keywords                                      | Classification | Reference |
|---------------------------------|--------------|------------|-----------------------------------------------|----------------|-----------|
| Marseilles_France_A            | Jul-2004     | Jul-2004   | ‘Urban’                                       | Urban          | 23        |
| Marseilles_France_B            | Jul-2004     | Jul-2004   | ‘Suburban’                                    | Urban          | 23        |
| Marseilles_France_C            | Jul-2004     | Jul-2004   | ‘Rural’                                       | Rural          | 23        |
| Los_Angeles_US                  | Jan-2003     | Jan-2003   | ‘Source’, ‘Urban’                             | Urban          | 24        |
| Riverside_US                    | Jan-2003     | Jan-2003   | ‘Downwind receptor’                           | Urban          | 24        |
| São_Paulo_Brazil                | Aug-2002     | Aug-2002   | ‘City’                                        | Urban          | 25        |
| São_Paulo_Brazil                | Jul-2003     | Jul-2003   | ‘City’                                        | Urban          | 25        |
| Araraquara_Brazil               | Aug-2002     | Aug-2002   | ‘Urban’                                       | Urban          | 25        |
| Araraquara_Brazil               | Jul-2003     | Jul-2003   | ‘Urban’                                       | Urban          | 25        |
| Piracicaba_Brazil               | Jul-2003     | Jul-2003   | ‘Sugar cane burning pollution’                | Urban          | 25        |
| Paulinía_Brazil                 | Aug-2002     | Aug-2002   | ‘Sugar cane burning’                          | Urban          | 25        |
| Araraquara_Brazil               | Jun-2010     | Jun-2010   | ‘Vehicular emissions’                         | Urban          | 26        |
| Rayes_Saudia_Arabia             | Sep-2013     | Sep-2013   | ‘Petrochemical works’                         | Urban          | 27        |
| Rabegh_Saudia_Arabia            | Sep-2013     | Sep-2013   | ‘Residential area’, ‘Local industry’          | Urban          | 27        |
| Abhur_Saudia_Arabia             | Sep-2013     | Sep-2013   | ‘Suburb’                                      | Urban          | 27        |
| Baltimore_US                    | Jan-2001     | Jan-2001   | ‘Urban’                                       | Urban          | 28        |
| Fort_Meade_US                   | Jul-2001     | Jul-2001   | ‘Suburban’                                    | Urban          | 28        |
| Finokalia_Crete                 | Jul-2012     | Jul-2012   | ‘Marine background’                           | Rural          | 29        |
| Pusztas_Hungary                 | Aug-2013     | Aug-2013   | ‘Continental background’                      | Rural          | 29        |
| Chamonix_Valley_1_France        | Jan-2003     | Jan-2003   | ‘Suburban’                                    | Urban          | 30        |
| Chamonix_Valley_2_France        | Jan-2003     | Jan-2003   | ‘Traffic’                                      | Urban          | 30        |
| Chamonix_Valley_3_France        | Jan-2003     | Jan-2003   | ‘Altitude’                                     | Rural          | 30        |
| Location                          | Start Year | End Year | Type          | Note                                                                 |
|----------------------------------|------------|----------|---------------|----------------------------------------------------------------------|
| Chamonix_Valley_4_France         | Jan-2003   | Jan-2003 | ‘Rural’       | Rural                                                               |
| Chamonix_Valley_1_France         | Jul-2003   | Jul-2003 | ‘Suburban’    | Urban                                                               |
| Chamonix_Valley_2_France         | Jul-2003   | Jul-2003 | ‘Traffic’     | Urban                                                               |
| Chamonix_Valley_3_France         | Jul-2003   | Jul-2003 | ‘Altitude’    | Rural                                                               |
| Chamonix_Valley_4_France         | Jul-2003   | Jul-2003 | ‘Rural’       | Rural                                                               |
| Maurienne_Valley_1_France        | Jan-2003   | Jan-2003 | ‘Rural’       | Rural                                                               |
| Maurienne_Valley_3_France        | Jan-2003   | Jan-2003 | ‘Suburban’    | Urban                                                               |
| Maurienne_Valley_4_France        | Jan-2003   | Jan-2003 | ‘Rural’       | Rural                                                               |
| Maurienne_Valley_1_France        | Jun-2003   | Jul-2003 | ‘Rural’       | Rural                                                               |
| Maurienne_Valley_2_France        | Jun-2003   | Jul-2003 | ‘Suburban’    | Urban                                                               |
| Maurienne_Valley_3_France        | Jun-2003   | Jul-2003 | ‘Suburban’    | Urban                                                               |
| Maurienne_Valley_4_France        | Jun-2003   | Jul-2003 | ‘Rural’       | Rural                                                               |
| Wanqingsha_China                 | Nov-2010   | Nov-2010 | ‘Rural’, ‘Coal-fired electric power plant’ | Urban                         |
| Rouiba_Algeria                   | Jul-2006   | Jul-2006 | ‘Urban’, ‘Industrial’ | ‘Moderate or scarce vehicle traffic’    | Urban |
| Ouled_Moussa_Algeria             | Jul-2006   | Jul-2006 | ‘Urban’       | Urban                                                               |
| Bouzareah_Algeria                | Jul-2006   | Jul-2006 | ‘Urban’       | Urban                                                               |
| Chrea_Algeria                    | Jul-2006   | Jul-2006 | ‘Park’, ‘Forest’ | Rural                                                               |
| Grenoble, France                 | Jan-2013   | Jan-2014 | ‘Urban’       | Urban                                                               |
| Agra, India_1                    | Oct-2015   | Feb-2016 | ‘Rural’       | Rural                                                               |
| Agra, India_2                    | Oct-2015   | Feb-2016 | ‘Traffic-dominated’ | Urban                         |
| China_Wuwei_1                    | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Yinchuan_1                 | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Taiyuan_1                  | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Beijing                    | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Dezhou_1                   | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Yantai_1                   | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Dalian_1                   | Apr-2010   | Mar-2011 | ‘Urban’       | Urban                                                               |
| China_Rural_Wuwei_2              | Apr-2010   | Mar-2011 | ‘Rural field’ | Rural                                                               |
| China_Rural_Yinchuan_2           | Apr-2010   | Mar-2011 | ‘Rural field’ | Rural                                                               |
| Location                          | Start Date | End Date | Type       | Notes          |
|----------------------------------|------------|----------|------------|----------------|
| China_Rural_Taiyuan_2            | Apr-2010   | Mar-2011 | ‘Rural field’ | Rural          |
| China_Rural_Depzhou_2            | Apr-2010   | Mar-2011 | ‘Rural field’ | Rural          |
| China_Rural_Yantai_2             | Apr-2010   | Mar-2011 | ‘Rural field’ | Rural          |
| China_Rural_Wuwei_3              | Apr-2010   | Mar-2011 | ‘Rural village’ | Rural          |
| China_Rural_field_Yinchuan_3     | Apr-2010   | Mar-2011 | ‘Rural village’ | Rural          |
| China_Rural_field_Taiyuan_3      | Apr-2010   | Mar-2011 | ‘Rural village’ | Rural          |
| China_Rural_field_Depzhou_3      | Apr-2010   | Mar-2011 | ‘Rural village’ | Rural          |
| China_Rural_field_Yantai_3       | Apr-2010   | Mar-2011 | ‘Rural village’ | Rural          |
| China_Rural_field_Dalian_2       | Apr-2010   | Mar-2011 | ‘Rural field’ | Rural          |
| Nepal_Kathmandu                  | Aug-2014   | Oct-2014 | ‘City’      | Urban          |
| Nepal_Pokhara                    | Aug-2014   | Oct-2014 | ‘City’      | Urban          |
| Nepal_Birgunj                    | Aug-2014   | Oct-2014 | ‘City’      | Urban          |
| Nepal_Biratnajor                 | Aug-2014   | Oct-2014 | ‘City’      | Urban          |
| Lampang_Thailand                 | Mar-2013   | Mar-2013 | ‘Urban’     | Urban          |
| ChiangMai_Thailand_DrySeason     | Feb-2010   | Apr-2010 | ‘City’      | Urban          |
| ChiangMai_Thailand_TransitionSeason | May-2010     | May-2010 | ‘City’      | Urban          |
| ChiangMai_Thailand_WetSeason     | Aug-2010   | Sep-2010 | ‘City’     | Urban          |
| HoChi Minh_VNU_Vietnam           | Jan-2005   | Mar-2006 | ‘Urban area’ | Urban          |
| HoChi Minh_ITTE_Vietnam          | Jan-2005   | Feb-2006 | ‘Urban area’ | Urban          |
| HoChi Minh_DOSTE_Vietnam         | Jan-2005   | Feb-2006 | ‘Urban area’ | Urban          |
| Elms_EROS_Birmingham             | Sep-2012   | Sep-2012 | ‘Urban background’ | Urban        |
| Coyhaique_Chile                  | Mar-2007   | Apr-2007 | ‘Remote’   | Rural          |
| Concepcion_Chile                 | Mar-2007   | Apr-2007 | ‘Urban’    | Urban          |
| Xujiahui_Shanghai_China_Spring   | Dec-2007   | Jan-2008 | ‘Urban’, ‘Busy highway’ | Urban        |
| Xujiahui_Shanghai_China_Summer   | Dec-2007   | Jan-2008 | ‘Urban’, ‘Busy highway’ | Urban        |
| Xujiahui_Shanghai_China_Autumn   | Dec-2007   | Jan-2008 | ‘Urban’, ‘Busy highway’ | Urban        |
| Xujiahui_Shanghai_China_Winter   | Dec-2007   | Jan-2008 | ‘Urban’, ‘Busy highway’ | Urban        |
| Baoshan_Shanghai_China_Spring    | Dec-2007   | Jan-2008 | ‘Industrial’, ‘Busy highway’, ‘Residential’, | Urban       |
| Baoshan_Shanghai_China_Summer    | Dec-2007   | Jan-2008 | ‘Industrial’, ‘Busy highway’, ‘Residential’, | Urban       |
| Location                        | Start Date  | End Date  | Features                                      | Setting |
|--------------------------------|-------------|-----------|-----------------------------------------------|---------|
| Baoshan_Shanghai_China_Autumn  | Dec-2007    | Jan-2008  | 'Busy highway', 'Residential', 'Industrial'   | Urban   |
| Baoshan_Shanghai_China_Winter | Dec-2007    | Jan-2008  | 'Busy highway', 'Residential'                 | Urban   |
| Linan_China_Spring             | Dec-2007    | Jan-2008  | 'Regional background'                         | Rural   |
| Linan_China_Summer             | Dec-2007    | Jan-2008  | 'Regional background'                         | Rural   |
| Linan_China_Autumn             | Dec-2007    | Jan-2008  | 'Regional background'                         | Rural   |
| Linan_China_Winter             | Dec-2007    | Jan-2008  | 'Regional background'                         | Rural   |
| HongKong WholeYearAverage      | Sep-2011    | Aug-2012  | 'Urban'                                       | Urban   |
| Beijing_China                  | Mar-2012    | Mar-2013  | 'Urban'                                       | Urban   |
| Jinan_China_(Urban)            | Jun-2015    | Jul-2015  | 'Urban'                                       | Urban   |
| MountTai_China                 | Jul-2015    | Jul-2015  | 'Background', 'Mountain summit'                | Rural   |
| TuojiIsland_China              | Jun-2015    | Jun-2015  | 'Background', 'Marine'                         | Rural   |
| CordobaCity_Argentina_Fall     | Mar-2008    | Apr-2008  | 'City'                                        | Urban   |
| CordobaCity_Argentina_Winter   | Jun-2008    | Jul-2008  | 'City'                                        | Urban   |
| CordobaCity_Argentina_Summer   | Nov-2008    | Dec-2008  | 'City'                                        | Urban   |
| SaoPaulo_Brazil                | Jan-2014    | Sep-2014  | 'Expressway', 'Campus'                         | Urban   |
| SaoPaulo_Brazil                | Jan-2014    | Dec-2014  | 'Expressway', 'Campus'                         | Urban   |
| TlalneplantaNW_MexicoValley_Mexico | Jan-2006 | Dec-2006  | 'Metropolitan zone', 'Residential', 'Commercial', 'Factories', 'Vehicular avenues' | Urban   |
| SanAgustinNE_MexicoValley_Mexico | Jan-2006 | Dec-2006  | 'Metropolitan zone', 'Residential', 'Vehicular avenues' | Urban   |
| MercedCentral_MexicoValley_Mexico | Jan-2006 | Dec-2006  | 'Metropolitan zone', 'Residential', 'Commercial', 'Vehicular avenues' | Urban   |
| CoyoacanSW_MexicoValley_Mexico | Jan-2006    | Dec-2006  | 'Metropolitan zone', 'Residential', 'Vehicular avenues' | Urban   |
| UniversidadAutonomous_MexicoValley_Mexico | Jan-2006 | Dec-2006  | 'Metropolitan zone', 'Residential', 'Commercial', 'Vehicular avenues' | Urban   |
| NorthMexicoCity_Mexico         | Apr-2006    | Feb-2007  | 'City'                                        | Urban   |
| Palaiseau_Paris_France         | Jun-2009    | Jul-2009  | 'Suburban'                                    | Urban   |
| PorteDAuteuil_Paris_France     | Jun-2010    | Aug-2010  | 'Traffic'                                     | Urban   |
| Station                        | Dates          | Background                                | Location       |
|-------------------------------|----------------|-------------------------------------------|----------------|
| Rao_EMEPstation_Sweden        | Dec-2008 - Feb-2009 | ‘Background’                              | Rural          |
| Rao_EMEPstation_Sweden        | Mar-2009 - Mar-2009 | ‘Background’                              | Rural          |
| Rao_EMEPstation_Sweden        | Apr-2009 - Apr-2009 | ‘Background’                              | Rural          |
| Pallas_AMAPstation_Finland    | Feb-2009 - Mar-2009 | ‘Background’                              | Rural          |
| Pallas_AMAPstation_Finland    | Mar-2009 - Apr-2009 | ‘Background’                              | Rural          |
| GoteborgFolketsHus_Sweden     | Dec-2008 - Dec-2008 | ‘Urban’, ‘City/traffic’                    | Urban          |
| GoteborgFolketsHus_Sweden     | Feb-2009 - Mar-2009 | ‘Urban’, ‘City/traffic’                    | Urban          |
| GoteborgGarda_Sweden          | Jan-2009 - Feb-2009 | ‘Urban’, ‘City/traffic’                    | Urban          |
| GoteborgGarda_Sweden          | Jan-2009 - Feb-2009 | ‘Urban’, ‘City/traffic’, ‘Traffic’         | Urban          |
| Lycksele_North_Sweden         | Feb-2009 - Feb-2009 | ‘Urban’, ‘Wood combustion’, ‘Traffic’      | Urban          |
| Lycksele_North_Sweden         | Mar-2009 - Mar-2009 | ‘Traffic’                                  | Urban          |
| Lycksele_North_Sweden         | Apr-2009 - Apr-2009 | ‘Traffic’, ‘Wood combustion’, ‘Traffic’    | Urban          |
| KanazawaCity_Japan_Autumn     | Nov-2016 - Nov-2016 | ‘City’                                    | Urban          |
| KanazawaCity_Japan_Spring     | Mar-2017 - Mar-2017 | ‘City’                                    | Urban          |
| KanazawaCity_Japan_Summer     | Aug-2016 - Aug-2016 | ‘City’                                    | Urban          |
| KanazawaCity_Japan_Winter     | Jan-2017 - Jan-2017 | ‘City’                                    | Urban          |
| Wajima_Japan_Autumn           | Nov-2016 - Nov-2016 | ‘Rural background’                         | Rural          |
| Wajima_Japan_Spring           | Mar-2017 - Mar-2017 | ‘Rural background’                         | Rural          |
| Wajima_Japan_Summer           | Jan-2017 - Jan-2017 | ‘Rural background’                         | Rural          |
| Wajima_Japan_Winter           | Jul-2016 - Jul-2016 | ‘Rural background’                         | Rural          |
| Kigali_Rwanda_Dry season      | Jun-2017 - Jun-2017 | ‘Urban background’                         | Urban          |
| Kigali_Rwanda_Wet season      | Apr-2017 - Apr-2017 | ‘Urban background’                         | Urban          |
| Kigali_Rwanda_Dry season      | Jun-2017 - Jun-2017 | ‘Urban roadside’                           | Urban          |
| Kigali_Rwanda_Wet season      | May-2017 - May-2017 | ‘Urban roadside’                           | Urban          |
| Rwanda_Wet season              | Apr-2017 - May-2017 | ‘Rural’                                   | Rural          |
| AucklandCity_New Zealand_Autumn | Apr-2016 - Apr-2016 | ‘City’                                   | Urban          |
| AucklandCity_New Zealand_Spring | Oct-2016 - Oct-2016 | ‘City’                                   | Urban          |
| Location                        | Season          | Months        | Type         | Notes               |
|--------------------------------|-----------------|---------------|--------------|---------------------|
| Auckland_City_New Zealand      | Summer          | Mar-2017      | Urban        | 'City'              |
| Auckland_City_New Zealand      | Winter          | Jul-2016      | Urban        | 'City'              |
| Tapora_New Zealand             | Autumn          | Apr-2016      | Rural        | 'Rural background'  |
| Tapora_New Zealand             | Spring          | Oct-2016      | Rural        | 'Rural background'  |
| Tapora_New Zealand             | Summer          | Feb-2017      | Rural        | 'Rural background'  |
| Tapora_New Zealand             | Winter          | Jul-2016      | Rural        | 'Rural background'  |
Figure S1. a) Mechanism of 2-nitrofluoranthene formation by the addition of a radical (X = OH or NO$_3$). Following initial radical addition ($k_{\text{add}}$), three processes compete for the fluoranthene-radical adduct: unimolecular decomposition ($k_{\text{rev}}$), reaction with O$_2$ to form oxygenated products ($k_{\text{O}_2}$) or reaction with NO$_2$ to form 2-nitrofluoranthene. b) The same scheme is applicable for 2-nitropyrene with addition of an OH radical.
Figure S2. Dependence of yield on NO$_2$ mixing ratio in the NO$_2$-dependent reactivity schemes for the reaction of FLT or PYR with a) OH or b) NO$_3$. 
Figure S3. Comparison between simulated and measured near-surface concentrations [pg m$^{-3}$] of 2-NFLT (above) and 2-NPYR (below) using the default reactivity scenario and sensitivity test with homogeneous reaction of NPAH with the OH radical.
Figure S4. Comparison between simulated and measured near-surface concentrations [pg m\(^{-3}\)] at rural and urban sites of 2-NFLT comparing alternative scenarios with \(\alpha = 0.05\) (above) and \(\alpha = 0.005\) (below).
Figure S5. Comparison between simulated and measured near-surface concentrations [pg m$^{-3}$] at rural and urban sites of 2-NPYR comparing alternative scenarios with $\alpha = 0.05$ (above) and $\alpha = 0.005$ (below).
Figure S6. Comparison between simulated and measured concentrations [pg m$^{-3}$] of FLT (above) and PYR (below). Observations at rural sites (including remote) are distinguished from urban sites. Error bars represent the upper and lower quartile for simulated results across the entire time period. P = particle phase concentration, P+G = total concentration.
Figure S7. Column densities of 2-NFLT (left) and 2-NPYR (right) of sensitivity study averaged over 2006 – 2008 relative to the default scenario averaged over 2006 - 2008, NPAH_{sensitivity}/NPAH_{default}. For the scenarios with a) no photodegradation, b) with reduced photodegradation ($\alpha = 0.005$), c) with NO$_2$-dependent formation ($\alpha = 0.005$) and d) with NO$_2$-dependent formation (0.05), averaged over 2006 - 2008.
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