Mass balance-based regression modeling of PAHs accumulation in urban soils, role of urban development

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ABSTRACT

We investigated the polycyclic aromatic hydrocarbons (PAHs) contents in 68 soils samples collected at housing developments that represent different length of development periods across Beijing. Based on the data, we derived a mass balanced mathematical model to simulate the dynamics of PAH accumulations in urban soils as affected by the urban developments. The key parameters were estimated by fitting the modified mass balance model to the data of PAH concentrations vs. building age of the sampling green area. The total PAH concentrations would increase from the baseline of 267 ng g⁻¹ to 3631 ng g⁻¹ during the period of 1978–2048. It showed that the dynamic changes in the rates of accumulations of light and heavy PAH species were related to the shifting of sources of fuels, combustion efficiencies, and amounts of energy consumed during the course of development.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in urban environments. The United States Environmental Protection Agency (USEPA) listed 16 PAHs as priority pollutants because of their frequent occurrences, environmental toxicities, and potential human exposures in urban settings (Hao et al., 2007). Natural processes including volcanic eruptions, forest fires and biosynthesis have emitted PAHs (Gocht et al., 2007; Ravindra et al., 2008). The PAHs found in atmospheric and terrestrial environment however came primarily from anthropogenic emission sources due to incompleteness combustions of fuels in industrial processing, power generations, waste incineration, vehicle emissions, cooking and space heating, and wood and biomass burnings (Heywood et al., 2006; Liu et al., 2006). Once released, the airborne PAHs would be suspended for a long time and subject to long distance transportation (Sun et al., 2009) and eventually 90% of the PAHs would be deposited on soil surfaces in and surrounding population centers (Gocht et al., 2007; He et al., 2009). The strong adsorption by soil

organic matter would inhibit their degradation, leaching, and volatilization losses (Yu et al., 2006) resulting in accumulation of PAHs in top soils (Gocht et al., 2007).

Geographically urban centers are hot spots of PAH emissions (Wong et al., 2004). Dense population, teeming commercial and industrial activities in urban metropolises create heavy traffic volumes, consume huge amount of energy, and produce vast wastes, all PAH generators (Peng et al., 2011). Urban soils being in close proximity of emission sources are expected to accumulate a great deal of fugitive PAHs (Nam et al., 2008) and PAH concentration of urban soils appear to change in proportion with extent of cities are being urbanized and industrialized (Augusto et al., 2009; Jensen et al., 2007; Wei et al., 2014). If the temporal trends in urban development parallel the PAH accumulation pattern of soils (Guo et al., 2006; Harrison et al., 1996; Yan et al., 2009), the inter-relationships are imperative for better planning of urban land uses, traffic networks, and residential communities. The current database consisted of primarily one time survey of PAH accumulation in urban soils with the soil samples collected at uncoordinated times and unrelated locations. How may the dynamic processes of PAH accumulation in urban soils be tracked over the time of development?

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Mathematical models might be employed to envision fates, transport, interactions, spatial distribution and potential risk of pollutants persisting in the environment (Kubosova et al., 2009; Poggio et al., 2008; Tao et al., 2003; Wania and McLachlan, 2001). Environmental models designed for some specific purposes would be less effective in other research fields, such as fugacity models were expert in modeling pollutants partitioning between media (Mackay, 2001), GIS-based watershed model were suitable for modeling pollutants transport and distribution with water flows (Galván et al., 2009), and mechanism models were commonly employed for predicting a specific environmental process of pollutants in the environment, e.g. leaching or plant uptake (Chen et al., 2013; Chiou et al., 2001). The mass balance model was able to track long-term accumulation of pollutants in soils with minimal mathematical parameters. Chen et al. (2007) demonstrated the long-term accumulation of fertilizer-borne As and Cd in cropland soils using a mass balance model that included key reactive processes governing the input and out fluxes. However, validating efficacy of the model would be problematic as required data were often unavailable.

The accumulation of PAHs in soils are affected simultaneously by the duration soils have been exposed to pollutant fallouts and spatial factors including sources distribution, land use categories, vegetation structures, population density, and soil properties (Jensen et al., 2007; Nam et al., 2008; Peng et al., 2012; Staci L. and Simonich, 1994; Yu et al., 2006). The residential neighborhoods are sheltered from intense emission sources and allowed discharged PAHs to intermingle before falling out (Peng et al., 2013). The open and green spaces inside these housing developments are similar in ecological settings and in soil and vegetation management strategies reducing interferences of spatial factors over the time. Therefore, community housing developments would be idea to examine the dynamics of soil PAH accumulation over urban development.

In this research, we chose Beijing, a city experiencing rapid urbanization and deep transformation in terms of demographics, infrastructural renewals, and industrialization in last 30 years, as an example to study temporal changes of soil PAHs accumulation during the course of urban development. The main objectives are to: 1) Use soil samples that represented varying lengths of development period, from 1 to 30 years, to deduce the dynamics of PAH accumulation over time in Beijing. 2) Develop a mathematical model to simulate the dynamic changes of soil PAH concentrations over time. 3) Evaluate impacts of urban development on PAH accumulation of urban soils in Beijing.

2. Material and analysis

2.1. Study area

Beijing has doubled the urban area, undergone complete overhaul of infrastructures, and changed the energy consumption patterns in last 30 years. From 1978 to 2008, its population grew from 8.7 to 17.0 million people and the gross domestic product (GDP) increased from 10.9 to 1111.5 billion Yuan RMB (BSB, 2009). It evolved from a traditional heavy industry based smock stack city into a politico-commercial-cultural center. All aspects of the environment have vastly improved as the traditional industries were replaced by the tertiary industries. In 1978, the gross industrial production was 64.5% of the GDP. In 2008, 19.0% of the GDP associated with the industrial sector. The urban green space had risen from 22.3% of the old city in 1978 to 44.4 % of the expanded new metropolis in 2008 (BSB, 2009). With the redevelopments and new developments, the PAH emission patterns continued to evolve.

2.2. Sampling

We collected 68 soils (0–10 cm depth) at the green areas of randomly selected housing development projects inside the 5th ring road of Beijing (roughly 650 km²). Detailed sampling strategy could be found in reference (Peng et al., 2013). The previous study suggested that 59% of the PAHs in those soils were resulted from a citywide uniform baseline deposition (Peng et al., 2013). The establishment time was known for each sampling sites. They represented soils of Beijing that had exposed to different durations of urban development (*x*). Each specimen was the mixture of 5 soil cores obtained within boundaries of the community green space. The samples were stored in paper bags, transported to the laboratory, dried at room temperature, ground to pass a sieve of 2 mm openings, and stored in amber color glass containers in freezer at −25 °C waiting for the chemical analysis.

2.3. Chemical analysis

The method employed to determine PAH contents of soils was detailed in Peng et al. (2011). Briefly, 5 g aliquot of soil was mixed with 5 g sodium sulfate, extracted in an automated Soxhlet extraction apparatus with 120 ml equal volume mixture of acetone – dichloromethane for 2 h. The extract was concentrated and then purified by pass through a silica gel solid-phase extraction column (Supco, Inc., USA). The collected drainage were analyzed by an Agilent 6890 gas chromatography equipped with a 5975C mass selective detector (GC-MSD, Agilent, Inc., USA) through external standard method. Sixteen USEPA priority PAHs were determined namely naphthalene (NAP), acenaphthylene (ACPY), acenaphthene (ACP), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), chrysene (CHR), benzo(a)anthracene (BaA), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), dibenzo(a, h)anthracene (DBA), indeno(1, 2, 3- cd)pyrene (IND), and benzo(g, h, i)perylene (BghiP).

2.4. Data preparation and statistical analysis

SigmaPlot (vision 12.0) was used for regression analysis and parameter estimation. In urban areas, some unforeseeable causes would lead to unusual high/low concentrations of PAH in the soils. To reduce the impacts of data variance on the regression estimates, we log-transformed the data to obtain an approximation of normal distribution (passed Kolmogorov–Smirnov test). Moreover, in the regression practices, the data points with large studentized residuals (outside the 95% confidence) were marked as outlying data and were eliminated from the raw datasets (e.g. four data points for PHE, and five data points for BaP). Other statistical analyses (e.g. Pearson correlation analysis) were carried out by using SPSS (version 18.0).

3. Model development

For PAHs accumulating in soils, the annual change of PAH concentrations may be described by a one-dimensional mass balance equation that:

$$\frac{dM}{dt} = I - L \quad (1)$$

where *M* is total PAH concentration of soil (μg kg^{−1}), *I* is annual PAH input flux (μg kg^{−1} yr^{−1}), *L* is annual PAH outflux of the soil (μg kg^{−1} yr^{−1}). Beijing has experienced fast urban expansion in recent decades. The population, coal consumption, vehicle number and GDP of Beijing showed approximate exponential increases

during the period of 1978–2008 (BSB, 2009). The PAH accumulation in the surface soils has been considerable. We assume that annual changes of PAH input with respect to time (i.e. input flux) follows a first order reaction and is proportional to the input, I :

$$\frac{dI}{dt} = k_i * I \quad (2)$$

where k_i is the input change rate constant (yr^{-1}). Pathways for output of soil PAHs include leaching, degradation, volatilization, and uptake by plants. We assume that total loss is a constant fraction of the PAH concentration of soil (Mackay, 2001):

$$L = k_l * M \quad (3)$$

where k_l is the soil PAH loss constant (yr^{-1}). Combing the Equation (1) through (3), the changes of total PAH concentration with respect to time is:

$$M(t) = \int_{t_0}^t (I_0 e^{k_i t} - k_l * M(t)) \quad (4)$$

or

$$M(t) = \frac{I_0}{k_l + k_i} e^{k_i t} + \left(M(0) - \frac{I_0}{k_l + k_i} \right) e^{-k_l t} \quad (5)$$

where t_0 represents the initial time when it begins to urbanize, I_0 is the baseline input of PAHs at t_0 ($\mu\text{g kg}^{-1} \text{yr}^{-1}$), $M(0)$ is background concentration of PAHs in Beijing ($\mu\text{g kg}^{-1}$), and t is the number of years PAHs have been accumulating in a given soil. A set of data, $M(t)$ vs. t , is needed to define the equation parameters, k_l and k_i , and initial values, I_0 and $M(0)$.

The modernization and urban renewal of Beijing began in 1978 and the developments expanded stepwise over time across the entire city. For the study, it would not be possible to go back in time and obtain retroactively soil samples from 1978 to the present. Instead, we were only able to collect soil samples at locations that represented different length of time (years) in housing development in 2008. While PAH accumulations in all soil samples followed the dynamics described in Equation (5), each sample nevertheless was represented by a different set of I_0 and had different initial time, t_0 . As soil samples were collected at 2008, there has been a 30 year span since the advent of urbanization in Beijing. A location began urbanizing t years after 1978 would have $30 - t$ years of development, namely, the soils received t years of the background inputs of PAH but not the added PAH inputs due to the urbanization. The time this location had been urbanized is x (year) then:

$$x = 30 - t \quad (6)$$

In this manner, Equation (5) would have a different initial input, I_x , and the same equation parameters k_l and k_i and initial soil PAH, $M(0)$. Mathematically, the initial inputs of the soil samples might be determined as:

$$I_x = I_0 e^{k_i(30-x)} \quad (7)$$

Substituting I_x for I_0 in Equation (5) and integrating.

$$M(x) = \frac{I_0 e^{30k_i}}{k_l + k_i} + M(0) e^{-k_l x} - \frac{I_0 e^{30k_i}}{k_l + k_i} e^{-(k_l + k_i)x} \quad (8)$$

The mathematical form of Equation (5) applicable to data of $M(t)$

vs. t was transformed into a new mathematical form of Equation (8) applicable to data of $M(x)$ vs. x .

Fitting soil PAH concentrations vs. time (i.e. years the location had been urbanized at the time of soil sampling) to Equation (8), the background concentrations of PAH in Beijing $M(0)$, the 1978 baseline PAHs input I_0 and parameters k_i and k_l might be obtained. When the model parameters and initial values obtained in this manner were adopted in Equation (5), the temporal dynamics of PAHs accumulations in Beijing soils from 1978 to 2008, were delineated.

The distribution patterns of PAH congeners in urban soils affected by diffuse sources were rather stable (Peng et al., 2012), and therefore compounds representing a range of physicochemical properties of PAHs could be selected for parameter estimation (further details can be found in Section 4.1). Due to the high degrees of freedom in Equation (8), priori information was prerequisite for a robust result. The previously reported decay rates (half-lives) of PHE and BaP in soils at low concentration condition were used as the loss constants k_l in Equation (8) (Aronson et al., 1998; Wild et al., 1991). After that, the results of parameter estimation became robust and rarely changed when up to 30% of data points were randomly deleted.

4. Results and discussion

4.1. Soil PAHs accumulation and classification

The greeneries in the housing projects have similar ecological settings and were managed more or less in the same fashion. To facilitate vegetation transplanting, the original soils of these green spaces were covered with fertile and fresh soils, which were normally transported from outskirts of the city during the processes of land use change. In most cases, the new soil layer had a higher horizontal plane than the surrounding impervious grounds. As the soils were disturbed and moved at the time of development, it would be reasonable to assume that in each housing project the PAH accumulation began at same baseline level. The housing projects with various building age suggesting that the green soils were exposed to the urban atmospheric deposition for different years. The total PAH concentrations of Beijing residential soils ranged from 180 to 4092 ng g^{-1} with an arithmetic mean of 865 ng g^{-1} . The average concentrations were comparable with outcomes of previous PAH investigations in Beijing (mean = 694 ng g^{-1} , $n = 12$) and Shanghai (mean = 1260 ng g^{-1} , $n = 12$) (Jiang et al., 2009; Liu et al., 2010). The distribution of data was skewed towards the lower PAH concentrations showed lognormal distributions. The wide range distribution of PAH concentrations reflected the progression in urban development over time. The high concentrations were found at locations representing longest periods of exposures (Fig. 3).

The 16 PAH species have different physicochemical properties and once released will experience different extent of environmental fate and transport (Ma et al., 2011; Ravindra et al., 2008; Tao et al., 2003; Wang et al., 2011). As molecular weight, octanol–water partitioning coefficient (K_{ow}) and Henry's Law constant of PAHs characterize their environmental fate and transport (Table S1), it is commonly group the 16 PAHs into two classes according to their molecular weight and environmental behavior, namely low molecular weight PAHs (LMW PAHs including NAP, ACPY, ACP, FL, PHE, and ANT) and high molecular weight PAHs (HMW PAHs including FLT, PYR, BaA, CHR, BbF, BkF, BaP, IND, DBA, and BghiP). LMW PAHs would be environmentally more reactive. It spreads farther from the emission sources and disappears from the urban ecosystems more rapidly than HMW PAHs. On the other hand, HMW PAHs are more environmental resistant to degradation and prone to adsorb

Fig. 1. Concentrations of the 16 PAH congeners in the residential soils of Beijing.

Fig. 2. Linear regressions of PHE vs. LMW PAHs and BaP vs. HMW PAHs in the residential soils of Beijing.

Fig. 3. Measured PAH concentrations and $M(x)$ vs. x according to Equation (8).

on soil organic matter. They accumulate in soils for a longer time than LMW PAHs.

The soil samples were collected to represent different durations of PAH exposures. While 16 PAHs were all found in the soils, species belonging to HMW PAHs were prominent (Fig. 1), especially at locations of earlier development. The 16 PAH congeners were strongly correlated with each other as well as the total PAH concentrations (Table 2). To simplify the modeling processes, we tend to simulate one or two PAH congeners that could represent the general deposition trend of the whole PAH species. LMW PAHs and HMW PAHs were considered separately due to their difference in environmental behavior. Among the 16 PAH species, PHE and BaP had the highest correlation with LMW PAHs and HMW PAHs

respectively (Table 2). Liner regressions showed the determination coefficients (R^2) were 0.984 for PHE vs. LMW PAHs and 0.988 for BaP vs. HMW PAHs suggesting that modeling the accumulation of

Table 1
Nonlinear regression fitting field data to Equation (8).

Compound	R^2	p	$M(0)$	k_i (yr ⁻¹)	k_i (yr ⁻¹)	l_0^a
PHE	0.47	<0.0001	1.39 (24.7 ngg ⁻¹) ^a	0.0693 ^b	0.0062	0.1439
BaP	0.37	<0.0001	1.25 (17.7 ngg ⁻¹)	0.0475 ^c	-0.0006	0.1178

^a Values in brackets indicate antilog of $M(0)$.
^b The degradation rate of PHE were from Wild et al. (1991).
^c The degradation rate of BaP were from Aronson et al. (1998).

Table 2
Correlations between PAH congeners and total PAH concentrations.

	LMW-PAHs ^a	HMW-PAHs ^b	ΣPAHs
NAP	0.373**	0.157	0.195
ACPY	0.780**	0.762**	0.773**
ACP	0.895**	0.868**	0.882**
FL	0.909**	0.821**	0.844**
PHE	0.979**	0.937**	0.954**
ANT	0.933**	0.954**	0.961**
FLT	0.931**	0.988**	0.989**
PYR	0.917**	0.987**	0.985**
BaA	0.905**	0.994**	0.990**
CHR	0.923**	0.994**	0.992**
BbF	0.919**	0.990**	0.989**
BkF	0.918**	0.993**	0.991**
BaP	0.916**	0.996**	0.993**
IND	0.903**	0.983**	0.980**
DBA	0.891**	0.985**	0.980**
BghiP	0.895**	0.985**	0.980**

**Correlation is significant at the 0.01 level (2-tailed).

^a LMW PAHs denotes low-molecular-weight PAHs containing 2–3 rings.

^b HMW PAHs denotes high-molecular-weight PAHs containing 4–6 rings.

PHE and BaP were enough to predict the dynamics of total PAH concentrations in the soils (Fig. 2).

4.2. Regression estimates of PAHs accumulation

The model parameters $M(0)$, k_i , and I_0 were essential for prediction of PAH accumulation in urban soils. We fitted the data to the modified mathematical form, Equation (8), from which k_i , $M(0)$, and I_0 were estimated (Fig. 3). The k_i was preset to 0.0693 for PHE and 0.0475 for BaP based on references (Table 1). The dynamic accumulations of PHE and BaP over development time were simulated to represent the accumulation processes of semi-volatile and resistant PAH species. The regressions of $M(x)$ vs. x according to Equation (8) were significant at $p < 0.001$ and R^2 were 0.47 for PHE and 0.37 for BaP (Table 1). The data uncertainty had several causes, including (1) the simplicity of model hypothesis on the inputs and outputs of soil PAHs, (2) The strategy of trading space for time since we were unable to obtain a long-term *in situ* monitoring data, (3) and the high complexity and heterogeneity of the urban area. Yet, the regression estimates were robust and should be the statistically

optimal solutions to explore the general patterns of PAHs accumulation accompanied by urban development.

Parameter k_i denoted the PAH input change rate over the 1978 to 2008 development period in Beijing. The k_i for PHE, and BaP were $6.2 \times 10^{-3} \text{ yr}^{-1}$ and $-6.0 \times 10^{-4} \text{ yr}^{-1}$, respectively. The fitted k_i of BaP were slightly below zero suggested a changeless or decrease trend of BaP deposition in the period. This fact was supported by BMEPB (2003) results of the airborne BaP concentrations in the urban area of Beijing from 1980 to 2002 (see Fig. 4). In addition, Ma et al. (2011) reported that the total atmospheric concentration of BaP in the gas and particle phases of urban Beijing were 9.3 ng m^{-3} in 2008, which was similar to BMEPB results at 2002. On the contrary, the fitted k_i of PHE were slightly above zero suggesting that recent emissions played a more significant role for the LMW PAHs. Unfortunately, PHE was not monitored by the BMEPB air quality monitoring network due to its relatively low toxicity.

Parameter $M(0)$ indicated the start point of PAHs accumulation in the new development green spaces, namely the average PAH baseline of Beijing soils. Table 1 showed the model fitted $M(0)$ of PHE and BaP in Beijing soils were 24.7 ng g^{-1} and 17.7 ng g^{-1} respectively. According to the regression equations in Fig. 2, we could calculate the baseline concentration of the total PAHs was 267 ng g^{-1} . The result was in agreement with the independent investigations of Ma et al. (2005) and Jiao et al. (2009) who reported the median concentrations of PAHs in pristine soils of Beijing as 228 ng g^{-1} and 260 ng g^{-1} , respectively.

4.3. Predictions of PAHs accumulation

The dynamics of PHE and BaP accumulation in urban soils of Beijing might be delineated by Equation (5), in which k_i , $M(0)$, and I_0 were obtained from Equation (8) (Table 1). The PHE and BaP of the soils steadily increased over the duration of urban development (Fig. 5). As a scenario simulation, we assumed the boundary conditions of the model will stay stable in the next 40 years. According to antilog of the results, the average concentrations of PHE and BaP were 24.7 ng g^{-1} and 17.7 ng g^{-1} in the year of 1978 then increased gradually with time and would reach to 866 ng g^{-1} and 230.6 ng g^{-1} in 2048 respectively.

The accumulation trends of the LMW PAHs, the HMW PAHs and the total PAHs were estimated based on the predictions of PHE and BaP (Fig. 6). The total PAH concentrations in urban soils of Beijing increased from the baseline of 267 ng g^{-1} to 1854 ng g^{-1} in the past 30 years (1978–2008) and continue growing to 3631 ng g^{-1} in the following 40 years. The concentration ratio of LMW PAHs to total PAHs were 18.0% in the year of 1978 but rising to 33.1% in the year of 2048 (Fig. 6). The LMW PAHs would become the more important contributor to the increases of total PAH contents in the future.

The dynamics of PAHs accumulations over time depended on the physicochemical characteristics of PAH species and the origins of PAH emissions. Over the development period, Beijing had continually evolving PAH emission sources as the nature of combustions and consumption patterns of fuels changed. From 1978 to 2008, the total energy consumption in Beijing increased 3 folds (Fig. 7) and the number of motor vehicle expanded by 40 times. Meanwhile, efficiency of energy utilization increased beginning in 1990s (Fig. 7) resulting in reduced PAH emissions. The coal-fired industrial combustions that favor emissions of HMW PAHs were gradually being replaced by the more efficiency and cleaner combustion of fossil-based liquid fuels and natural gas (Gulyurtlu et al., 2003; Oanh et al., 1999). Consequently, emissions of LMW PAHs increased (Liu et al., 2001) resulting in faster accumulation of PHE over time. The shifts of PAH species was demonstrated by the relative contributions of LMW PAHs and HMW PAHs toward the total PAHs over the time of development (Fig. 6). Similar

Fig. 4. Atmospheric BaP concentrations in the urban Beijing, 1980 to 2002 (BMEPB, 2003).

Fig. 5. Predictions of PHE and BaP accumulating in urban soils of Beijing, 1978 to 2048.

Fig. 6. Predictions of PAHs accumulating in urban soils of Beijing, 1978 to 2048.

Fig. 7. Total energy consumption and energy utilization efficiency in Beijing, 1980 to 2008.

trends were documented in the United States in the 1970s as coal was being replaced by oil and natural gas in space heating (Lima et al., 2002; Liu et al., 2005) and cooking (Chuang et al., 1991; Zhu and Wang, 2003).

5. Conclusions

We used the regression modeling approach to simulate the historical processes of PAHs accumulation in urban soils. The key

parameters of k_i , $M(0)$, and I_0 were estimated from the nonlinear regression analysis. The impacts of urbanization and industrial transformation on PAH emissions were revealed. The total PAH concentrations in the urban soils of Beijing were increasing with time during urbanization processes. LMW PAHs had higher accumulation rates than HMW PAHs. It suggested that the increments of PAH emissions in Beijing were shifting to LMW PAHs, such as PHE, owing to the improving energy efficiency of the city.

The regression modeling approach was an effective way to reconstruct the pollution history of urban soil and to study the connections between urbanization process and soil pollution. The model concept was simple and the data requirements of this approach could be readily satisfied. This approach was applicable in other metropolitan cities as long as we have the building age of green spaces and their soil pollutant concentrations. The low regression performance (R^2 values) of the current study mainly due to inadequate of the dataset. The model uncertainty could be reduced by predetermining the key parameters k_i or k_j in target city, or obtaining more sampling data of PAH concentrations in residential soils.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2014.11.025>.

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