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1	Effects of land use intensity on the natural attenuation capacity of				
2	urban soils in Beijing, China				
3	Meie Wang ^a Jack H. Faber ^b Weiping Chen ^{a*} Xiaoma Li ^a Bernd Markert ^c				
4	^a State key laboratory of urban and regional ecology, Research centre for eco-environmental				
5	sciences, Chinese academy of sciences, Beijing, 100085, China				
6	^b Alterra, Wageningen UR, PO Box 47, 6800 AA Wageningen, The Netherlands				
7	^c Environmental Institute of Scientific Networks, Fliederweg 17, 49733 Haren/Erika, Germany				
8					
9					
10	Corresponding author. Tel.: +86-01-6284-3981; fax: +86-01-6284-3981.				
11	E-mail address: wpchen@rcees.ac.cn				

1 Abstract:

Urban soils are major sinks that provide the services of attenuating and 2 3 detoxifying environmental pollutants. This significant ecosystem service of urban soil can be evaluated by the natural attenuation capacity (NAC). In this research, we 4 develop a method to calculate the natural pollutant attenuation capacity of urban soils 5 on the basis of 5 chemical and physical measurements. By selecting municipal parks 6 soils for reference, we assessed the spatial and temporal changes of NAC in Beijing 7 city soils under influences of rapid urbanization. Results indicated that NAC was 8 9 increasingly impacted by land use in the order: parks < schools < woods < residential areas < traffic areas. Sealed area rate and construction age are two main factors 10 affecting the urban soil NAC. However, their roles are opposite. It would take dozens 11 of years to reach the maximum soil NAC by soil self-recovery. The spatial 12 distribution of NAC in Beijing built-up area resembled the age of urbanization. 13 Regional hot spots of NAC corresponded to the land use distribution and the 14 urbanization progress in Beijing city. The developed index can be used to assess the 15 impacts of urbanization on soil ecosystem services of natural attenuation of 16 contaminants. 17

18 Keywords: Urban expansion; ecosystem service; urban contaminated soil; natural
19 attenuation; soil quality mapping

20

1 **1 Introduction**

Worldwide, the urban population has reached 52% and is expected to rise at 0.5 to 2 3 0.87% per year for the next 50 years (United Nations, 2012). China is in the midst of an incredibly rapid process of urbanization. Shanghai, Beijing and Guangzhou are 4 amongst the 10 most densely populated metropolis of the world (United Nations, 5 2012). Energy and resource consumptions and waste and pollutant emissions are 6 intense in urban areas (Pataki et al., 2011). The urbanization processes drastically 7 affect the indigenous soil ecological template (Kaye et al., 2006; Pavao-Zucherman, 8 9 2008).

The risks of environmental harms associated with depositions of urban pollutants 10 may be indicated by the extent of ecosystem services (Faber and Wensem, 2012; 11 12 Galic et al., 2012; Nienstedt et al., 2012; Pataki et al., 2011; Thomsen et al., 2012). Ecosystem services are benefits men gain from their habitat, including benefits of 13 providing provisions, regulations, and cultural stimulations and auxiliary services that 14 15 compliment the primary eco-functions (Millennium Ecosystem Assessment, 2005). Urban soils are major sinks that provide the services of attenuating and detoxifying 16 environmental pollutants (Dominati et al., 2010; Rittmann, 2004; NRC, 2000). 17

18 Soils possess the ability to reduce the mass, toxicity, mobility, volume, and/or 19 concentration of incoming pollutants. This ability is deployed through reactions of 20 biodegrading, dispersing, adsorbing, diluting, volatilizing, stabilizing, and 21 transforming the soil borne pollutants (US Environmental Protection Agency; EPA, 22 1999). The significance of a reaction is dependent on properties of soils and the nature of pollutants. Van Wijnen et al. (2012) articulated the natural attenuation capacity
(NAC) of soils with respect to their ability to biodegrade organic contaminants. The
resulting model included multiplying effects of 3 microbial indicators, i.e. functional
microbial activity, potential carbon mineralization rate, and potential mineralization
rate of organic nitrogen, and 3 abiotic indicators, i.e. soil organic matter content, soil
pH, and phosphorus content as proxy indicators (Van Wijnen et al., 2012).

7 Identifying proper pollutants and employing appropriate metrics would be challenging for assessing natural pollutant attenuation capacities of urban soils as they 8 9 undergo changes due to rapid urbanization, and there are many pollutants and potential indicators for natural pollutant attenuation capability of soils (van Wijnen et 10 al., 2012). In China, heavy metals and poly aromatic hydrocarbons (PAHs) are the 11 12 most persistent pollutants in the urban areas. Therefore, the soil's filtering and immobilizing reactions are more relevant than the degrading and destructing reactions 13 in deciding the soil attenuation capacities. The concentrations of soluble heavy metal 14 and PAHs in soils might be correlated to solid-solution dissociation constant, K_d , 15 which in turn were functions of organic matter content, clay content, and pH of soils. 16 In this regard, the soils' pH and organic matter and clay contents would be the 17 appropriate metrics to assessing natural pollutant attenuation capacity of urban soils. 18

In this research, we developed a method to calculate the natural attenuation capacity of urban soils by modifying the ecosystem-service performance index proposed by Rutgers et al. (2012) and Van Wijnen et al. (2012). Proper soil property parameters and reference values were selected to evaluate the impacts of urbanization on the NAC of urban soils. Beijing is used as a case to illustrate spatial and temporal
 changes of NAC in soils across the city with respect to the attributes of urbanization.

3 2 Methods and Materials

8

4 **2.1 Calculation of natural attenuation capacity**

The ecosystem services are not well defined quantitatively (Luck et al., 2009; van
Wijnen et al., 2012). Rutgers et al. (2012) and Van Wijnen et al. (2012) calculated the
ecosystem-service performance index (EPX) of soil using the following equation:

$$EPX = 10^{-}$$

$$\begin{bmatrix} \frac{VAR_{obs}^{i}}{VR_{ref}^{i}} \\ n \\ n \\ n \\ \end{bmatrix}^{+...-\log \left[\left(\frac{VAR_{obs}^{j}}{VAR_{ref}^{i}} \right) \right]}{n} \\ \end{bmatrix}$$

$$(1)$$

where VAR^{i...j} are soil parameters from *i* to *j* that contribute to EPX of soils. Subscripts *obs* and *ref* denote the parameter's observed and reference values, respectively
(Rutgers et al., 2012). The symbol *n* denotes number of parameters in the computation.
Generally, 4 to 6 parameters with the highest scores were selected among a group.
The reference values represent a "maximum ecological potential", which could be
brought forward by independent measurements and/or evaluations by professional
panels.

For the natural attenuation capacity (*NAC*) of urban soils, we selected 5 soil property parameters (Table 1) that may determine the fate of heavy metals and PAHs in soils, namely soil organic carbon content (*SOC*), clay content (*Clay*), bulk density (*BD*), pH measured in pore water (*pH*), and total soil N contents (*TN*). The soil total N content was included as a supplemental parameter to clay and organic carbon contents of soils (Hassink, 1997). For biodegradation of organic pollutants (Eq. 1), the

contributing parameters had multiplying or dividing effects toward ecosystem-service 1 performance index (EPX). The soil's capacity to react with or attenuate heavy metals 2 3 and PAHs are additive in nature. It is the sum of surface reaction sites in [soil organic matters + clays + organic N]. In addition, the capacities are also susceptible to the 4 multiplying/dividing influences of the soil's pH and bulk density that respectively 5 adjust the attenuation capacity up and down and account for the net soil mass per unit 6 7 volume. Equation 1 was modified accordingly to obtain the natural pollutant attenuation capacity of urban soils (NAC): 8

$$NAC = 10^{\left[\frac{\log\left(\frac{SOC}{SOC_{ref}} + \frac{Clay}{Clay_{ref}} + \frac{TN}{TN_{ref}}\right) + \log\left(\frac{pH}{pH_{ref}}\right) - \log\left(\frac{BD}{BD_{ref}}\right)\right]}$$
(2)

In the above equation, the variables had all been defined. They represent the key soil parameters under the current land use. The variables with subscript *ref* refer to the reference value representing the parameters when the NAC of the soil is at its optimal. We used the arithmetic average of soils obtained at the public parks in Beijing for the reference values per reasoning in van Wijnen et al. (2012).

15 **2.2**

9

2.2 Study area and soil sampling

Beijing as a human habitat dates back for more than 3,000 years. The built-up area now covers about 700 km². Starting from the city center, the city expands over time and outward and is encircled by 5 concentric ring roads, the traffic thoroughfares. The urbanization began from the central area inside the 2nd ring road, then sequentially toward the north, west, east and south directions (Figure 1).

Soils were sampled according to a 1 min latitude \times 1 min longitude

(approximately 1.9 km by 1.0 km) grid. One composite sample was obtained inside a 1 500 m \times 500 m representative landscape of each grid. In this manner, two hundred 2 3 thirty three 0 to 10 cm surface soil samples were collected. Each sample was composed of 5 subsamples of the four corners and the center point in a 10 m \times 10 m 4 square. Among them, 25 were from public parks, 58 from traffic areas, 53 from 5 schoolyards and public areas, 28 from agricultural and wooded area (excluding parks), 6 and 69 from residential areas (Figure 1). These habitats were chosen based on the 7 dominated landscape in each grid. 8

9 2.3 Measurements of soil parameter and paved area

Soil parameters were determined as described in Wang et al., (2011), Wang et al., 10 (2012) and Peng et al., (2012). Soil organic carbon contents were determined using 11 12 HCl treated method (Nam et al., 2008). Briefly, soil samples were treated with 1M HCl for 24 hrs to decompose carbonate associated carbon. And then, the treated soil 13 was dried at 60°C before determination of carbon content by an elemental analyzer 14 (Elementar, Hanau Germany). Soil pH was determined in distilled water at a 15 soil-to-solution ratio of 1: 2.5. Surface soil (0-10 cm) bulk density was determined 16 using stainless cutting rings (100 cm³). The ring soil samples were dried at 105 °C for 17 24 hrs to calculate bulk density. Five repeats were sampled for each 10 m×10 m 18 square. Clay content was determined using a laser particle size analyzer and 19 calculated according to the USDA soil classification scheme. Total nitrogen content 20 21 was measured using an elemental analyzer (Elementar, Hanau Germany).

The percentage of impervious paved area of the 500 m \times 500 m sampling grids

1 were identified using GIS Arcgis 9.3.

2 2.4 Data analysis and mapping

Spearman and Pearson correlation analysis and post-hoc multiple comparisons were conducted using SPSS (PASW Statistics 18.0). SigmaPlot 12.0 was used for plot and regression analysis. The spatial distribution of NAC was mapped using ordinary kriging interpolation techniques in Arcgis 9.3. Hotspots of NAC were identified using local Moran's I. "Regional hotspots" (high values in high value neighborhood) and "cool spots" (low values in low value neighborhood) were marked. All raw data was standardized before further analyses by statistics and GIS.

10 **3 Results and Discussion**

3.1 Spatial factors affecting natural attenuation capacity

12 The natural pollutant attenuation capacities of soils inside Beijing in descending order are parks > schools > wooded areas > residential areas > traffic areas (Figure 2). 13 Those of the residential and traffic areas were significantly lower than those in the 14 parks. The soils in the residential and traffic areas were more susceptible to physical 15 disturbances and anthropogenic activities than soils in the parks and schools (Pouyat 16 et al., 2002). Spearman correlation analysis showed that NAC in traffic areas 17 exhibited a negative significant nonlinear correlation with the sampling location's 18 distance to city centre ($r^2 = -0.373$), the closer to city centre the higher of soil NAC 19 was. The urban areas away from the city center would experience more frequent 20 disturbances in terms of urbanization and have shorter time to recover from it. The 21 NAC versus distance correlations were not significant for soils of the parks and 22

residential areas because parks and residential areas are evenly distributed across
 inside the 5th ring road, i.e. the entire developed area.

The relative size of the paved surface showed significant negative impacts to NAC of soils in the parks (Table 2) in which the soil's NAC decreased with increasing relative paved surface according to a linear function relationship:

$$NAC = 1.596 - 0.231x, (0 \le x \le 1), R^2 = 0.204$$
 [Eq. 3]

7 where x represent the paved surface (%).

8 Contrary, the NAC of soils in the roadside traffic area was significantly positive 9 correlated the relative size of the paved surface, while the NAC of soils in residential 10 area was not significantly impacted by the pavement (Table 2). Compared to the parks, 11 the traffic and residential areas always contained high percentages of paved surfaces. 12 From NAC of soils in the parks to NAC of soils in traffic areas represented the two 13 extremes of how did pavements in urban area impact the soil's natural pollutant 14 attenuation capacities (Figure 2).

15 **3.2 Temporal changes in natural attenuation capacity**

Urbanization in Beijing has a temporal gradient that depicts how long ago (in years) did the location become urbanized. We labeled this time horizon "construction age" and accordingly every sampling grid was assigned a construction age. The NAC of soils in parks and residential areas significantly increase with the constructing age (Table 2). Following the urbanization, the soils needed time to recover from the initial disruptions. Gradually, the physical, chemical and biological properties of the soils would stabilize into a new equilibrium with the surroundings (Scharenbroch et al., 2005). We were unable to establish the temporal gradients for the traffic areas.
 However, we noted that the NAC of soils in the traffic areas covered a wide range and
 we expected they would exhibit the same trend as the park and residential areas
 (Figure 2).

To explore the temporal changes of NAC in urban soils, we used the residential areas that composed of a 1 to 50 year temporal gradient and the park area that composed of a 1 to 800 year temporal gradient for further elaborations. The NAC of soils in the parks and residential areas increased with construction age according to the exponential function relationships (Figure 3A). For park area:

10
$$NAC = 1.577 - 0.262e^{-0.013t}, R^2 = 0.417$$
 [Eq. 4]

11 For residential area:

12
$$NAC = 1.45 - 0.193e^{-0.144t}, R^2 = 0.159$$
 [Eq. 5]

13 where *t* represents the construction age in years.

Two NAC temporal gradients of different time horizons and different urban land 14 15 uses yielded different outcomes. However, it was clear, the natural pollutant attenuation capacity of urban soils would grow, become stabilized, and approach a 16 maxima. It was suggested the maximum and initial soil NAC in parks was slightly 17 higher than that in residential area. The rate of soil NAC increases for residential soils, 18 r = 0.144, was considerably higher than that of the park area, r = 0.013. Derivations 19 for Eq. 4 and Eq. 5 suggested that t = 16 was the demarcation. When t < 16, the soil 20 21 NAC of residential areas increased faster than those in the park areas. When t > 16, the results were the opposite. The soil NAC of residential areas took approximately 20 22

years to reach the maximal plateau while that of the park areas would need about 200
 years to do the same (Figure 3B).

3

Using the soils of the park areas as the example, the temporal gradient and paved surfaces were significant factors in determining the soil NAC, explained 41.7, and 20.4 % of the variances of NAC in urban soils, respectively. Other inherent soil properties and spatial elements might have affected the NAC (Pouyat et al., 2002; Raciti et al., 2011).

8 **3.3 Spatial distribution of the natural attenuation capacity**

9 The natural attenuation capacities of urban soils in Beijing were spatially coded 10 and grouped into low, middle and high NAC zones (Figure 4). The low NAC zone 11 was located in the south-west quadrant of the city, while the high NACs zone was 12 found toward the city center and the north-east-south expansion. The footprint of the 13 high NAC zone overlapped the areas that were earliest in undergoing urbanization, 14 while the low NAC zone was found to cover the more recently urbanized city 15 quarters.

In terms of regional distributions, there were NAC hot and cool spots throughout. The hot spots were isolated high NAC locations inside the high NAC zone and the cool spots were isolated low NAC locations inside of the low NAC zone. Regionally, the hot spots were found exclusively in the north half the city between the 2nd and 5th roads where parks, university campuses, and old residential neighborhoods are located, in other words they represented the long time horizons in urbanization. The regional cool spots were distributed in the south between the 4th to 5th ring roads. This distribution corresponds to the land use distribution and the urbanization progress in
Beijing. Land use in the South 2nd to the 5th ring road where majority of the new
developments are located.

4 4 Conclusions

Natural attenuation of contaminants by urban soils is an important ecosystem
service to protect the human population and other sensitive receptors from hazardous
exposure. Urbanization may disturb the natural soil template and the capacity to
mitigate forthcoming environmental risks. Our results suggested that:

9 1) The natural pollutant attenuation capacity of the soil would be decimated during
10 the course of urbanization. It would gradually recover, become stabilized over time,
11 and eventually approached a maximum.

In Beijing, soils in public parks showed the highest natural pollutant attention
 capacities in comparison to other urban land uses, such as residential and traffic areas.
 The natural pollutant attenuation capacities of soil in the traffic area throughout
 the city are inversely correlated to location's distance to city centre through nonlinear
 functions and the natural pollutant attenuation capacities of soil in public parks were
 inversely correlated to the location's percentage of paved surfaces and how long ago
 the location becoming urbanized in nonlinear functions.

4) The spatial distribution of natural pollutant attention capacities in Beijing
coincided with the city's pattern of urban development. Footprint of high capacities of
natural pollutant attenuation zone overlapped with areas of the earliest in undergoing
urban development. Soils with low capacity of natural pollutant attention cover the

1 most recently developed of the city.

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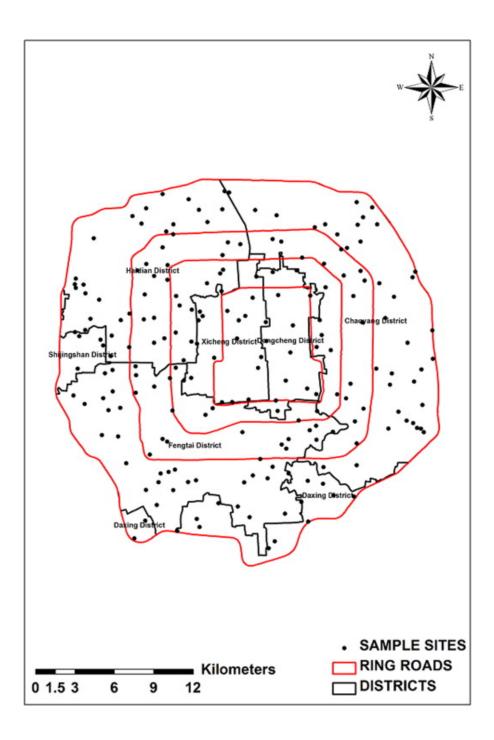
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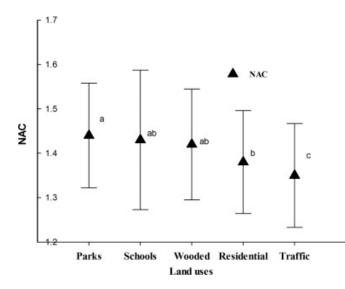
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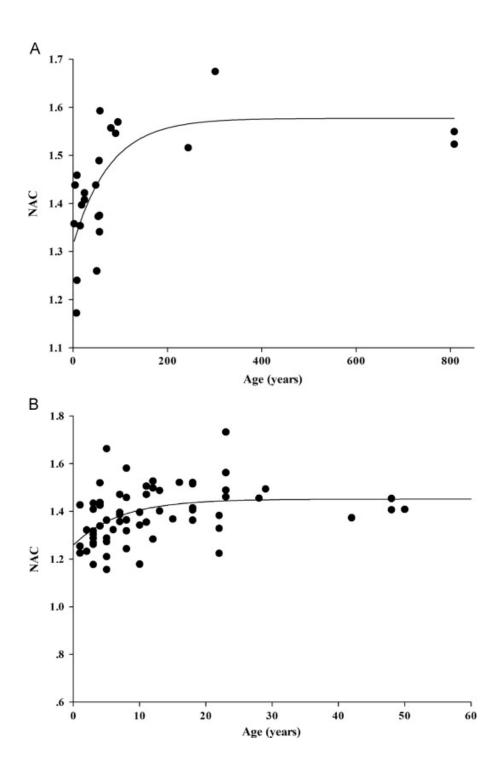
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2	Figure 1. The spatial distribution of sample sites in the built-area of Beijing city.
3	
4	Figure 2. Natural pollutant attenuation capacity of urban soils of different land uses in Beijing.
5	Values reported(Mean \pm S.D.) are of the dimensionless parameter in reference to the optimal
6	capacity. Relatively higher value denotes greater capacity.
7	
8	Figure 3. Exponential function relationships between soil NAC in parks (A) and residential areas
9	(B) and the construction age.
10	
11	Figure 4. Spatial distribution maps of soils' natural attenuation capacity urban soils in Beijing.
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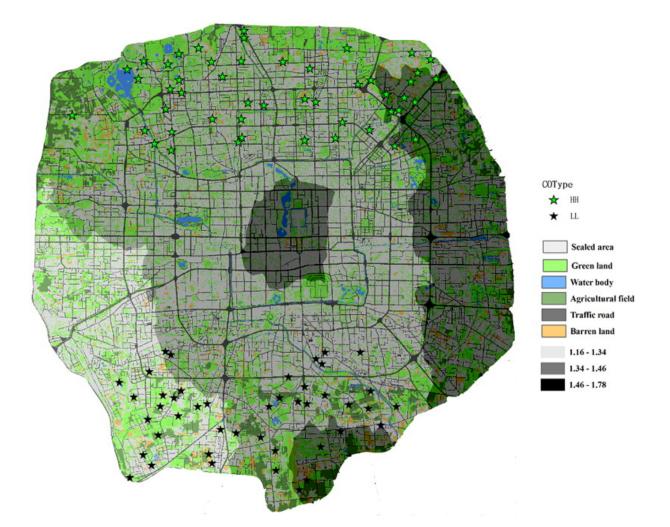


Table 1.

Key soil parameters used in NAC calculation<comma> their ranges and ecological processes involved.

Soil parameters	Range	Ecological process involved
Soil organic carbon content (SOC) (%)	0.241-5.11	Adsorption of heavy metals and PAHs in soils and degradation of PAHs
Clay content (Clay) (%)	2.51–17.7	Adsorption of heavy metals in soils
Bulk density (BD) (g/cm3)	0.968–1.77	Leaching of heavy metals and PAHs
pH measured in pore water (pH)	7.06-8.4	Adsorption of heavy metals and biodegradation of PAHs
Total soil N contents (TN) (%)	0.031-0.205	Supplemental parameter to clay and organic carbon contents of soils

Table 2.

Spearman correlation coefficients for soil NAC as related to distance from city center<comma> ages and sealed area rate around sampling site.

Urban development factor	Land use		
Parks	Traffic	Residential	
Distance to city center (km)	-0.286	-0.373?	-0.017
Percent paved surface area (%)	-0.4052	0.328	0.112
Construction age (year)	0.701??	-	0.366??