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Mass balance-based regression modeling of Cd and Zn accumulation in urban soils of Beijing

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ABSTRACT

Accumulation of heavy metals in urban soil can pose adverse impacts on public health and terrestrial ecosystems. We developed a mass balance-based regression model to simulate the heavy metal accumulation in urban soils as a function of time and to explore connections between metal concentration and urbanization processes. Concentrations of Cd and Zn in 68 residential soil samples in the urban area of Beijing were used. The background concentrations, the loss rates and the input fluxes of Cd and Zn in urban soils of Beijing during the last three decades were estimated using a regression of the time series of accumulations of the metals. Based on the regression estimates, we simulated the general trends of Cd and Zn accumulation in the soils from 1978 to 2078. The concentrations of Cd and Zn in urban soil generally increased with the population growth, vehicle use and coal consumption. The mean concentrations of Cd and Zn in urban soil of Beijing would increase by 3 fold over the next 70 years for the current development scenario. The mass balance-based regression approach, which is able to reconstruct the history data of urban soil pollution, provides fundamental information for urban planning and environmental management.

Introduction

With increased urbanization, many potentially hazardous heavy metals such as Cd and Zn are released to near human habitats by transportation, coal use and resource consumption (Kong et al., 2011; Maas et al., 2010). Accumulation of heavy metals in urban soils has drawn great attention as it poses adverse impacts on public health and threatens the integrity of terrestrial ecosystems, plants and soil microbes (Maliszewska-Kordybach and Smreczak, 2003). The distribution patterns of heavy metals in urban soils have been broadly delineated (Wang et al., 2012a; Wei and Yang, 2010). However, the static spatial distributions of heavy metals in soil are inadequate to understand their complex accumulation processes and their ever changing emission sources in terms of urbanization progression.

Heavy metal accumulation in urban soil is complex and a dynamic process (Wong et al., 2006). Atmospheric deposition is the main influx of persistent pollutants accumulating in urban soils (Moller et al., 2005; Peng et al., 2012). Airborne

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heavy metals are emitted from diffused and scattered sources such as commercial establishments, traffic networks, and residential activities (Ajmone-Marsan and Biasioli, 2010; Xia et al., 2011). After they are released, pollutants from various sources may mingle with the wind and form a regional blanket baseline atmospheric deposition for a given urban area (Peng et al., 2013). This baseline input causes an increase of metals in urban soils which increase over time as the urban system continues to develop. Unfortunately, the long-term metal deposition fluxes were not recorded in the most of cities. The losses of heavy metals from soils are mainly caused by solute leaching, plant uptake and physical disturbance (Keller et al., 2001; Pouyat et al., 2007). The transport fluxes of heavy metals in soils are not easily measured and are impacted by soil pH, soil organic matter and physical disturbance (Mahanta and Bhattacharyya, 2011; Wang et al., 2011). The annual increments of heavy metal concentrations in urban soils are small and not readily detectable using short-term sampling and monitoring (Sun et al., 2011), while long-term in situ monitoring records of soil metals are often unavailable because soil environmental quality surveys are laborious and time-consuming (Cheng et al., 2014). Consequently, it is difficult to establish the time-dependent heavy metal accumulation pattern and to systematically predict the future trends using conventional soil surveys.

Historical trend of heavy metals accumulation in soil can be reconstructed by measuring the heavy metal contents in bricks manufactured at different time periods, moss/leaf collections from museums, downstream sediments, and sectioned soils layers (Cao et al., 2008; Liu et al., 2005; Rodríguez Martín et al., 2015; Shrivastav et al., 1998; Zhang et al., 2005). However, these approaches are only applicable to estuarine and coastal areas or at geologic timescales. None of those approaches is able to deduce the metal deposition patterns that have evolved through urban development.

Long term changes of heavy metals in soils can be modeled if the pathways and mass flows are properly quantified and validated (Chen et al., 2007). Previous studies adopted mass balance model to simulate the long term trends of heavy metal accumulation in agricultural soils (de Vries and McLaughlin, 2013; Oporto et al., 2012; Six and Smolders, 2014). However, those models require detailed information on metal input loads, soil properties, and plant growth and hydrogeological data. Qian and Follett (2002) described the changes of soil organic matter over a 45 year period based on the building age of the sampling golf courses using a quadratic with plateau model. Peng et al. (2015) introduced a mass balance-based nonlinear regression model to simulate the historical and future changes of polycyclic aromatic hydrocarbons in urban soil. The time series data of pollutant concentrations were obtained using a sampling strategy of trading space for time. Similarly, the mass balance of heavy metals accumulation in soils can be tracked with nonlinear regression model approach. For back casting, the pollution history may be revealed, and the impacts of urban expansion and industrialization on metal emissions can be evaluated. For forecasting, the future trends of metal concentrations in urban soil may be predicted, and the critical loads of emission sources can be established. These forecasts can be used to establish policies that prevent heavy metal accumulations that exceed health risk thresholds (Posch and de Vries, 2009).

Beijing has experienced a rapid urbanization in past decades. Since 1978, the population of Beijing grew from 8.7 to over 20.0 million and the total coal consumption has doubled (BSB, 2009) (Fig. 1). As a result, the heavy metal emissions of urban Beijing have increased over time (Chen et al., 2005). Okuda et al. (2008) reported clear trends of increasing Cd, Cu, Pb and Zn levels in the total suspended particles in Beijing from 2001 to 2006. Wang et al. (2005) found increasing Cu, Zn, As, Ba and Pb concentrations in the growth rings of trees during 1982 to 2004 in a suburban area of Beijing. In summary, the urban renewal and expansions have shifted the patterns of heavy metals deposition as well as their concentrations in the air, plant, and soil.

The objective of this research is to uncover the long-term trends of Cd and Zn accumulation in urban soils, which are expected to be closely related to urban activities, especially traffic and coal combustion in urban areas. A mass balance-based regression model is developed to delineate the dynamic changes of heavy metal in urban soils for yearly changes to inputs and outputs. The heavy metal concentrations in soils of urban green spaces with different building age are used to develop a model of heavy metal accumulation in soils. We then used the model to simulate the concentrations of Cd and Zn in urban soil of Beijing from 1978 to 2078. Uncertainties associated with model simulations are discussed.

1. Mass balance approach

For heavy metal accumulation in urban surface soil, the mass balance is given by Chen et al. (2007) s following:

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

where, $M(t)$ (mg/kg) is the metal content per unit soil mass. I (mg/kg/year) and L (mg/kg/year) represent annual input and output fluxes per unit soil mass, respectively.

For the first year, we assume that the soil receives an input of metal, I_0 (mg/kg/year). During the course of urbanization, this baseline input would change over time according to population, traffic and energy consumption in the city. For the cities facing rapid urbanization, such as Beijing, the population and economic statistics showed linear and exponential increases (BSB, 2009). Cheng et al. (2015) found that atmospheric emissions of heavy metals in China were approximate linear for 2000 to 2010. Consequently, we assumed the annual baseline metal input at the tth year after urbanization, I_t, would be described by Eq. (2):

$$I_t = I_0 + k_i t \tag{2}$$

where, k_i (mg/kg/year^2) is the increment of metal input fluxes per year.

The output fluxes of heavy metal in urban surface soil include leaching loss, plant absorption, and soil physical disturbance (Pouyat et al., 2007; Wong et al., 2006). The mobility of metal in soils is mainly affected by soil properties, such as soil organic matter and soil pH, which change little in a small urban area especially under a similar land cover (Chen et al., 2010). We assumed that the metal was even distributed in the soil pool; and, hence, the metal loss from soil physical disturbance should

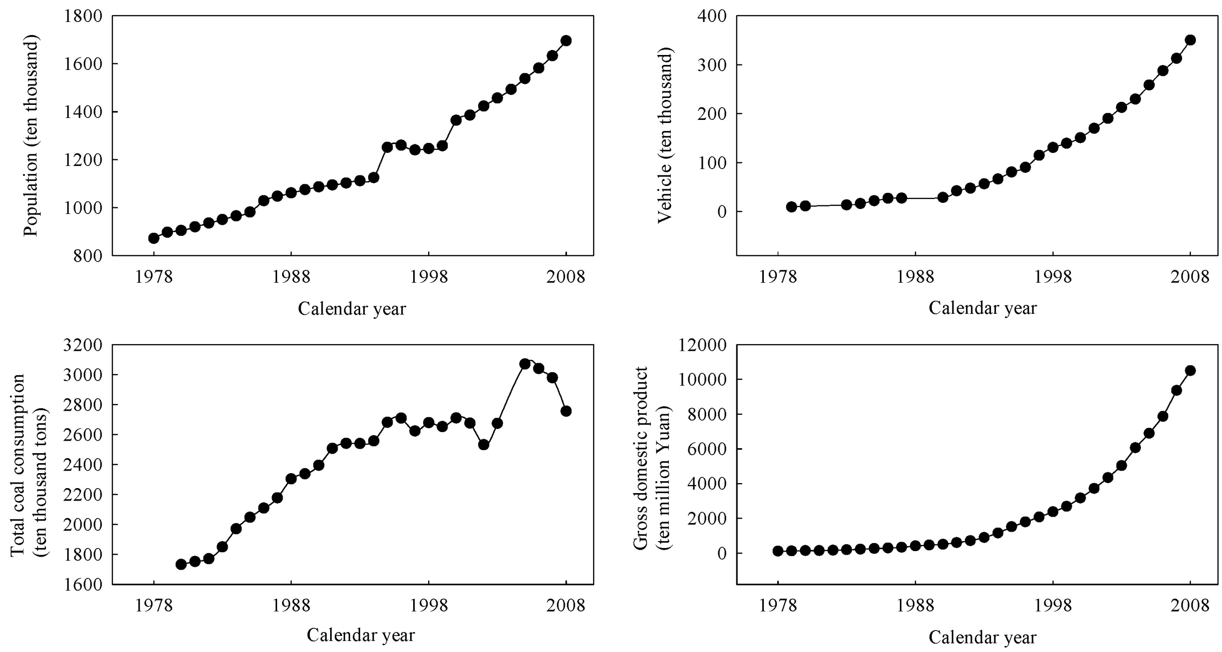

Fig. 1 – Changes in the permanent population, vehicle ownership, total energy consumption and gross domestic product of Beijing during 1978 to 2008.

be linked to the total metal content. Therefore, for a given soil and vegetative cover, the annual output flux of heavy metal can be described by a simplified equation (Keller et al., 2001, 2002):

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

where k_l ($k_l > 0$, year^{-1}) is the annual metal loss rate, describing the proportion of total metal mass lose from soil per year. Combining Eqs. (1), (2), and (3), the total concentration of a metal in the soil at time t, $M(t)$ can describe as:

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

Where, time$t_0 = 0$ is the start of metal accumulation. The following Eq. (5) is obtained from Eq. (4) after integration.

$$M(t) = \left(M_0 - \frac{I_0}{k_l} + \frac{k_i}{k_l^2}\right) e^{-k_l t} + \frac{k_i}{k_l} t + \frac{I_0}{k_l} - \frac{k_i}{k_l^2} \quad (5)$$

where M_0 (mg/kg) is the background metal concentration of the soil at $t = 0$.

Eq. (5) expresses the change of metal concentration in urban soils as a function of time ($M(t)$ *vs.* t). If the metal concentration are tracked yearly from $t = 0, 1, \ldots\ldots n$, the annual input increment k_i, annual loss rate k_l, and initial values M_0 and I_0 may be obtained and Eq. (5) can be used to estimate the future trends.

The rapid urbanization and modernization of Beijing began in late 1970s (BSB, 2009). It would be impossible to travel back in time and sample soils yearly from 1970s to the present. Instead, we can sample soils in residential green spaces with different building age (x). The residential green spaces of Beijing have similar vegetative cover and maintenance processes. At the time of the green spaces were established, the original soils would be covered with fertile soils that were commonly transported from rural areas along with vegetation transplanting and were nearly uncontaminated by urban activities (Peng et al., 2013). The accumulation time of metal in these soils would be equal to the building age (x) of the green spaces. For the green space constructed in 1978, the period of the soil exposed to the urban environment would have reached $t = 30$ in 2008. Therefore, soil samples we collected in 2008 from green spaces represent 30 years of metal accumulation. To apply the model, we found locations (x) that had x years of housing development before 2008. Similar to Eq. (2), I_x is related to start of the simulation in 1978 (as compared to 2008) and is shown in the following Eq. (6):

$$I_x = I_0 + k_i(30 - x) \quad (6)$$

Correspondingly, substituting I_x for I_0 in Eq. (5) and integrating using x (a location with development times, t), we can use the data with the building age of green spaces x instead of the calendar timescale:

$$M(x) = \left(M_0 - \frac{I_0 + 30k_i}{k_l} + \frac{k_i}{k_l^2}\right) e^{-k_l x} + \frac{k_i}{k_l} x e^{-k_l x} + \frac{I_0 + 30k_i}{k_l} - \frac{k_i}{k_l^2} \quad (7)$$

Fitting the data of soil metal concentrations *vs.* building age of the green spaces ($M(x)$ *vs.* x) to Eq. (7), we can obtain the background metal content in urban soils (M_0), the baseline metal input of urban soils at the beginning of urban development (I_0), and the rate constants (k_i and k_l) that characterize the dynamic changes in metal accumulation. By using the fitted parameters (M_0, I_0, k_i and k_l) in Eq. (5), the historical accumulation (1978 to 2008 in the present case) and future changes (2008 to 2078 in the present case) of heavy metals in urban soils can be simulated and predicted, respectively.

2. Data collection and regression analysis

2.1. Data collection

Data on Cd and Zn concentrations in the urban soils from 68 residential green spaces inside the 5th ring road of Beijing were collected. These data have been previously reported (Peng et al., 2013). The sampled residential areas are spatially distributed in the urban center of Beijing, surrounded by high traffic density and population (Appendix A Figs. S1 and S2). These residential areas were enclosed by containment walls and separated from surrounding landscape. Therefore, the heavy metals in the residential soils were mainly resulted from the citywide atmospheric deposition (Peng et al., 2013).

The surface soil of green spaces in those communities were disturbed and covered with fertile and clean soils for lawn growth at the time of the communities constructed, and the residential green spaces were 10 cm higher than the surrounding impermeable surface (*e.g.*, roadway or side walk). The age of the residential green spaces was documented on the basis of construction history (Peng et al., 2013). As a result, these samples could be temporal data for the model regression.

2.2. Data preparation and regression analysis

SigmaPlot (vision 12.0) was used for curve fittings and SPSS (version 18.0) was used for statistical analyses. In urban areas, the high spatial heterogeneity and unforeseeable disturbances would cause unusually high/low concentrations of heavy metal in the soils that are beyond the influence of deposition time. To reduce the impacts of data variance on the regression estimates, we excluded the outliers that lay beyond the 95% confidence bounds of the regression curves during the fitting process (3 outliers for Cd and 7 outliers for Zn).

We restricted $M(t) > M(t-1)$ when we fit the data. We felt it is reasonable to assume that the soil metal concentrations would substantially increase with time because of the rapid urbanization in Beijing.

3. Results and discussion

3.1. Descriptive statistics of dataset

Table 1 summarizes the concentrations and background values of Cd and Zn in soils of Beijing. The mean concentrations of Cd and Zn in the residential soils of urban Beijing were 0.106 and 88.540 mg/kg respectively, which were considerably higher than that in the deep soils and rural soils of Beijing (Cheng et al., 2014; Luo et al., 2010). The previously reported soil background values of Cd and Zn showed large variances (Table 1). Those background values would fluctuate between sampling sites and were affected by the choice of analytical methods. Therefore, the reported background values were insufficient to identify the extent of heavy metals accumulation in Beijing soils. The Cd and Zn concentrations in urban soils of Beijing had been elevated by anthropogenic activities such as vehicular wear and emissions, as well as domestic and industrial coal burning (Wang et al., 2012b; Xia et al., 2011). The accumulation process of heavy metals in the residential soils can be described using our mass balance model (Eq. (7)).

3.2. Model parameter estimation

We fit Eq. (7) to soil Cd and Zn data of residential green spaces with different building ages to determine the model parameters. The data points are scattered in the 95% prediction bands and the regression curves show higher slope in the younger residential areas (Fig. 2). The estimated model parameters are shown in Table 2. The regression results were significant ($p < 0.0001$).

We compared those fitted parameters with previously reported values. Table 2 shows that the background Cd and Zn concentrations (M_0) in residential soils of urban Beijing were 0.039 and 48.03 mg/kg, respectively. The M_0 indicates the metal concentrations in soils of newly developed residential green spaces. These values are comparable to the Cd and Zn concentrations in the clean soils surrounding the Miyun Reservoir, the water source of Beijing, and slightly lower than the reported background values (Table 1).

The baseline metal input (I_0) and the annual increase rate of metal input (k_i) in Table 2 display the fitted metal input fluxes from 1978 to 2008. Based on the estimated (I_0) and k_i, we calculated that the Cd and Zn input fluxes were 7.84 and 8720 g/ha/year in 1978 increased to 36.64 and 24,027 g/ha/year in 2008, respectively. The increments of metal inputs are likely to be atmospheric deposition. Therefore, the annual atmospheric deposition of Cd and Zn inside the 5th ring road of Beijing (about 650 km^2) is close to 2.4 tons and 1561 tons in 2008. Cheng et al. (2015) estimated the total emission of Cd in the greater Beijing was 3.30 tons in 2010, which is comparable to our results. Yang et al. (2011) monitored that the total input fluxes of Cd, Pb, Cu, and Zn in the rural areas of Beijing, and Tongzhou and Daxin districts, were 17.3 and 2732.1 g/ha/year respectively during 2007 to 2008. Compared with these reported input fluxes, our estimates of the mean input fluxes of Cd and Zn in urban soils of Beijing were 2 and 8.8 times higher respectively. Beijing is a highly industrialized city with 20 million people and 5 million cars. The emissions of Cd and Zn are related to population density, urban traffic and industrial activities (Wang et al., 2014). The urban soils of Beijing should receive more metal inputs than the rural soils. Judging from comparison to the literature data, our estimate metal inputs for the study period of 1978 to 2008 are reasonable.

The estimated average metal loss rates k_l were 0.138 $year^{-1}$ for Cd and 0.120 $year^{-1}$ for Zn in the urban soils (Table 2). These k_l values are considerably larger than the previously estimated removal rate of Cd and Zn in agricultural soils through crop uptake and leaching (Hu et al., 2013; Six and Smolders, 2014). The physical disturbance may be an important output pathway of metals in urban soil. The two parameters, k_i and k_l are optimized values and are interdepended during the model fitting. While there is very limited information in the literature to validate these loss rates, it is an alternative way to use these mechanisms to forecast the accumulation rate of Cd and Zn in urban soils of Beijing.

Table 1 – Concentrations and background values of Cd and Zn in soils of Beijing.

Location			Cd (mg/kg)	Zn (mg/kg)	Reference
Beijing	Urban residential soil (0–10 cm)	Mean	0.106	88.540	This study
		Geom. M	0.096	84.518	
		SD	0.039	27.392	
Beijing	Urban soil (150–180 cm)	Mean ± SD	0.089 ± 0.02	58 ± 8.5	Cheng et al. (2014)
Beijing Miyun Reservoir	Rural soils (0–20 cm)	Geom. M ± SD	0.049 ± 0.022	55 ± 18	Luo et al. (2010)
Background (2010)	Rural soils	Geom. M ± SD	0.053	74.8 ± 11.41	Xia et al. (2011)
Background (2004)	Forest soils	Geom. M ± SD	0.119 ± 0.112	57.5 ± 16.29	Zheng et al. (2008)
Background (1990)	Rural soils	Geom. M ± SD	0.053 ± 0.058	97.2 ± 35.37	CNEMC (1990)
Background (1988)	Agricultural soils	Mean ± SD	0.119 ± 0.91	55.53 ± 5.2	Li and Zheng (1988)
Environmental Standard (1995)	Class 1		0.2	100	SEPA (1995)
Environmental Standard (1995)	Class 2		0.6	300	

SD: standard deviation; Geom. M: geometric mean.

3.3. Accumulation trend of heavy metal in urban soils

According to Eq. (5), the general trends of heavy metals accumulation in Beijing soils can be predicted using our estimates of M_0, I_0, k_i and k_l. By assuming that the boundary conditions were constants, we could predict the future trends of heavy metal accumulation in those soils. Consequently, we predicted the heavy metal dynamics in urban soils of Beijing for one hundred years by substituting the estimated parameter values in Table 2 into Eq. (5) (Fig. 3).

The metal sources in a metropolitan city like Beijing are highly spatial heterogeneity and changed with the processes of urbanization and industrialization. Over the period of 1978 to 2008, the Cd and Zn contents in the soils continued to rise with the calendar time (Fig. 3). They reflect the increases of emissions due to urbanization represented by the vehicles, coal consumptions, population and economic activities (Fig. 1). Registered motor vehicle in Beijing had risen from <90,000 in 1978 to over 3.5 million in 2008 (BSB, 2009). The vehicle wear and tear is part of the emission sources of Cd and Zn. In recent years, Beijing has relocated the heavy industries associated with coal combustions and coke productions. However, the total coal consumptions of the city continues to grow due to the increasing energy needs for tertiary industries and space heating since 2000 (Fig. 1). The more efficient modern burners are burning coal at higher temperatures release more heavy metals (Okuda et al., 2008). Accordingly, additional metal emission results from the increasing number of urban residents. Their daily routines more or less causes releases of metals from ingredients of paints, pigments, decorations, alloys, batteries, electronic components and pesticides (Lin et al., 2002). Generally, the increases of Cd and Zn concentrations in soils were consistent with the urbanization processes represented by the increases of GDP, resident population, vehicle numbers and total coal consumption in the city (Table 3).

We assumed Beijing would continue urbanization at the usual pace after 2008, and the annual increases of the baseline metal inputs would remain the same rate in the future. In this case, the Cd and Zn concentrations would increase 3.3 and 2.8 times within the next 70 years (Fig. 3), unless the surface soil is disturbed by land use change. The second class of the national soil environmental standard (SEPA, 1995) indicates the threshold value for the need of human health, and the third class indicates the critical value for the safety of plant growth. None of the mean metal concentrations would exceed the second national criteria. However, the metal concentrations in urban soils are not deterministic values but vary with sampling locations. The standard deviation curves in Fig. 3 suggested both the prediction error and the spatial variation of Cd and Zn in urban soils. Cd had the possibility to reach the second pollution criteria, and Zn might be exceeding the third pollution criteria. Soils are readily accessible to children through hand to mouth and dermal contact (Peng et al., 2011). To ensure the safety of the children

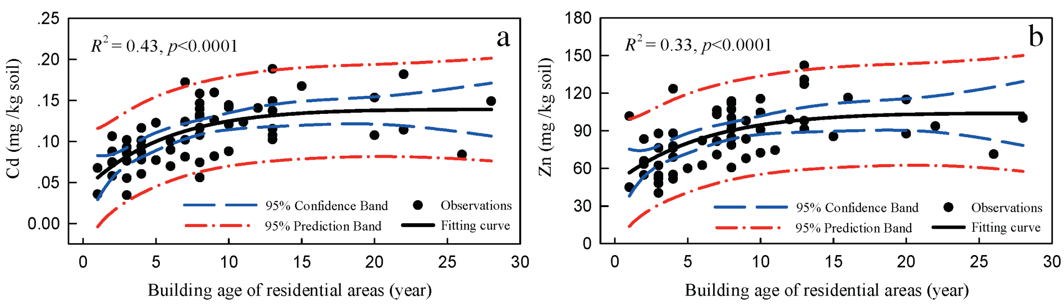

Fig. 2 – Model fit of heavy metals in soils of residential green spaces as a function of building age.

Table 2 – Model performances and parameter estimates.

	R^2	Sig.	Standard Error of Estimate (mg/kg)	M_0 (mg/kg)	k_1 (y^{-1})	k_i (mg/kg/year^2)	I_0 (mg/kg/year)	I_{1978} (g/ha/year)	I_{2008} [a] (g/ha/year)
Cd	0.43	<0.0001	0.0268	0.039	0.138	0.0006	0.0049	7.84	36.64
Zn	0.33	<0.0001	19.23	48.03	0.120	0.3189	5.45	8720	24,027

[a] The unit conversion was based on the average soil bulk density of Beijing, 1.6 g/cm^2.

playing on the ground, we need to pay attention and implement control measures to control the increase of metal emissions, especially Zn emissions.

3.4. Model uncertainties

We used nonlinear regression model to estimate the long term changes of metal concentrations in urban soils. However, there are some uncertainties. The standard errors of estimate were 0.0268 mg/kg for Cd and 19.23 mg/kg for Zn respectively. The current regression modeling approach provided a good prediction on the average metal concentration in soils of an urban area (Table 2). In the fitting process, the estimated parameter values are optimal solutions and had high degree of freedom. The standard errors of parameters are following this trend: $I_0 > k_i > k_1 > M_0$. Therefore the regression performance could be improved by independently determining I_0, k_i or k_1.

The model uncertainties came from two major causes. Firstly, the simplified empirical regression model was only capable to describe metal input and output fluxes as zero or first order changes during the urbanization processes. The regression model in the current study requires less input data and reveals the general pattern of nature based on field measurements therefore is suitable for simulating long-term trends of metal accumulation. Secondly, the strategy of trading space for time inevitably causes uncertainties due to ignoring the spatial variances of the metal inputs and outputs. However, it is hard to obtain a long-term *in situ* monitoring data of metal concentration or to measure spatial data of metal inputs in a complex urban area. The current approach has minimized the data spatial variances by adopting metal concentrations in residential green spaces that have parallel management policy and similar ambient environment. Yet, expanding the observing dataset is expected to improve the regression performance. Through the results remain some uncertainties, the regression approach can reconstruct the history data of soil pollution by one time soil survey and reveals the connection between urbanization process and urban soil contamination that provides fundamental information for urban planning and environmental management.

4. Conclusions

We demonstrated that the mass balance-based regression model was able to describe the general trends of heavy metal concentration in Beijing urban soils. Data of residential soils installed at different location and times could be used for substituting long-term *in situ* monitoring data, and to reconstruct the pollution history of heavy metals in urban soils. Based on the regression estimates, we forecasted the accumulation and uncertainties of Cd and Zn in urban soils of Beijing. Concentrations of Cd and Zn may increase 3.3 and 2.8 times in the next 70 years (from 2008 to 2078). The results reveal the connection between urbanization process and urban soil contamination that are useful for urban planning and environmental management.

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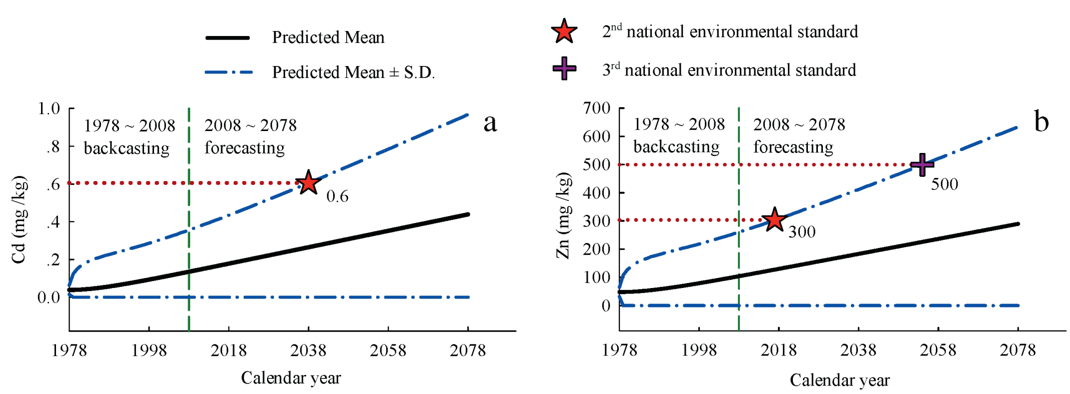

Fig. 3 – Simulations of heavy metals accumulating in urban soils of Beijing (1978–2078).

Table 3 – Correlations between the predicted metal concentrations in urban soil and the statistic data of Beijing (1978 to 2008).

	GDP	Population	Vehicle numbers	Total coal consumption
Cd	0.917 **	0.990 **	0.962 **	0.905 **
Zn	0.922 **	0.990 **	0.966 **	0.901 **

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.05.012.

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