Geoderma 326 (2018) 1–8

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Method for reconstructing the initial baseline relationship between potentially harmful element and conservative element concentrations in urban puddle sediment

Andrian A. Seleznev[a,*], Ilia V. Yarmoshenko[a], Alexander P. Sergeev[a,b]

[a] Institute of Industrial Ecology, Ural Branch of Russian Academy of Sciences, S. Kovalevskoy St., 20, 620219 Ekaterinburg, Russia
[b] Ural Federal University, Mira St., 19, 620002 Ekaterinburg, Russia

A R T I C L E I N F O

Keywords:
Urban geochemical baseline
Urban baseline relationship
Potentially harmful elements
Conservative elements
Puddle sediments
^{137}Cs

A B S T R A C T

This paper presents a method for reconstructing the initial baseline relationship between potentially harmful element (PHE) and conservative element (CE) concentrations in urban puddle sediment samples. This method is based on an analysis of the relationship between PHE and CE concentrations in urban puddle sediment samples a considerable time after landscape development. After development, pollution increases the PHE concentration and changes the initial PHE–CE relationship. The ultimate goal is to restore it taking into account environmental pollution. The approach is to assign lower weights to more polluted samples and apply linear weighted fitting. To test the developed method, reconstruction of the initial baseline PHE–CE relationship was performed by applying the results of a survey of PHE concentrations in contemporary urban puddle sediments in Ekaterinburg, Russia, in 2007–2010. The reconstructed relationships between the PHE (mg/kg) and CE (Fe, g/kg) concentrations are as follows: Pb = 45 + 0.1·Fe, Zn = 141 + 1.7·Fe, and Cu = 32 + 1.2·Fe. The developed approach demonstrated consistency with results of the ^{137}Cs chronological tracer approach for Pb, Cu, and Zn pollution.

1. Introduction

Landscape planning and construction result in artificial geochemical conditions of urban environments (i.e. the content of elements in environmental compartments). The initial concentrations of elements in urban environmental compartments reflect the contributions of components of natural and anthropogenic origin. Environmental compartments can be created artificially, and different compartments can be added to urban landscapes (e.g. as a result of renewing pavement and landscaping), transforming the geochemical conditions of an urban area. Over time, pollutant entry also significantly modifies the geochemical conditions of a given urban landscape.

Several widespread approaches are used in environmental studies to assess the geochemical reference concentrations of potentially harmful elements (PHEs). However, in studies of artificial environments, most approaches possess some disadvantages. For example, the Clarke value (natural abundance of a particular element), which reflects the average content of the element in the Earth's crust, does not account for the significant anthropogenic influences on the geochemical processes occurring in urban environments (Salminen and Gregorauskiene, 2000; Reimann and De Caritat, 2000; Liénard et al., 2014). The PHE background concentrations at an unpolluted sampling site located far from the source of pollution may not be associated with the studied area, considering the geological and geochemical factors. Finally, the permissible concentrations (i.e. concentrations suitable for environmental management) may not be related to the specific geochemical conditions of the studied area.

The complex patterns of geochemical processes occurring in landscapes over time are critical for understanding the geochemical baseline concept (Salminen and Gregorauskiene, 2000; Reimann and Garrett, 2005; Matschullat et al., 2000; Guillén et al., 2011). Geochemical baseline theory defines specific concentrations of an element (baseline values) characterising prevailing variations in the content of an element in the surficial environment at a given point in time (Salminen and Gregorauskiene, 2000). The baseline theory introduces baseline levels as reference values, which include “ambient background”, “natural background”, geochemical “threshold”, etc. (Matschullat et al., 2000; Reimann et al., 2005; McGrath and Zhao, 2012; Reimann and Garrett, 2005; Salminen and Gregorauskiene, 2000). Baseline levels correspond to separate geochemical processes and stages during landscape development, and the baseline of an element includes its background content (geogenic or natural content reflecting its bedrock lithology) (Albanese

* Corresponding author.
E-mail addresses: seleznev@ecko.uran.ru (A.A. Seleznev), ivy@ecko.uran.ru (I.V. Yarmoshenko).

https://doi.org/10.1016/j.geoderma.2018.04.003
Received 16 August 2017; Received in revised form 29 March 2018; Accepted 1 April 2018

et al., 2007). Matschullat et al. (2000), Reimann and Garrett (2005), Reimann et al. (2005) and others have described techniques for assessing baseline values. Elemental baseline values are calculated based on statistical analysis, normalization procedures, and analysis of the cumulative distribution frequency curves. Under some conditions, the sample population mean (median or geometric mean) ± 2 standard deviations (or median absolute deviations) are interpreted as the central and upper and lower background values (thresholds), respectively (e.g. Fok et al., 2013; Johnson and Ander, 2008; Chiprés et al., 2009; Reimann et al., 2005; Matschullat et al., 2000). Linear regression using "conservative" elements (Mn, Fe, or Al) that are not influenced by anthropogenic activities can be used to define geochemical thresholds (e.g. McGrath and Zhao, 2012; Matschullat et al., 2000; Jiang et al., 2013).

In terms of the baseline concept, the initial geochemical conditions (the initial baseline relationship between the contents of PHEs and conservative elements (CEs)) of an urban environment can be represented as the background for artificially created landscapes. Baseline levels have been used as reference values in assessments of the degree of pollution based on soil surveys (e.g. Guillén et al., 2011; Flight and Scheib, 2011; Karim et al., 2015), sediment in water body surveys (e.g. Albanese et al., 2007; Appleton and Ridgway, 1993; Davenport et al., 1993), studies of dry atmospheric deposition (Matschullat et al., 2000), and biological objects (Gough et al., 1988).

Environmental assessments of urban areas are complicated by the continual natural process of contemporary sedimentation. The origin of various types of urban contemporary anthropogenic sediments is associated with soil erosion, atmospheric deposition of dust and particulate matter, and the transfer of traffic-related material (Murakami et al., 2009; Wei et al., 2009; Apeagyei et al., 2011). Recent natural and anthropogenic processes affect pollutant migration. Thus, sediments can characterise and reflect the geochemical conditions of urban landscapes accumulating elements over space and time. Contemporary sediments can be investigated to obtain information on the environmental state of an area (e.g. Murakami et al., 2009; Wong et al., 2006; Duzgoren-Aydin et al., 2004). Sediments from water bodies, road dust, atmospheric depositions, street deposition, soakaway, and sewage sediments, as well as puddle sediment (PS), have been examined in urban environmental studies (e.g. Gunawardana et al., 2012; Selbig et al., 2013; Hilliges et al., 2013; Seleznev and Yarmoshenko, 2014).

The environmental role of PS as a type of contemporary anthropogenic sediment was studied in the city of Ekaterinburg, Russia. PS accumulated pollutants over space and time, characterising the generally unknown migration processes within the urban residential area (Seleznev and Yarmoshenko, 2014). The ages of PS and pollution in the urban territory were determined from the ^{137}Cs content (Seleznev et al., 2015). The ^{137}Cs chronological approach enabled the assessment of the initial concentrations of the elements in PS in an urban landscape.

Baseline values for contemporary anthropogenic sediment surveys could offer information corresponding to different periods of construction and urban landscape formation. Moreover, the initial baseline PHE concentration for contemporary sediment could be used as a reference value in environmental assessments of cities. Samples in a sample population that are polluted to different degrees indicate that the studied area has different sources of pollution (especially nonpoint sources) and that various components of the landscape are exposed in various degrees of pollution. Reconstructing the initial urban baseline relationship corresponding to the moment the landscape was formed could provide reference values that are suitable for environmental monitoring and assessing the degree of pollution in dense urban areas.

Understanding the geochemical background concentrations of elements in PS is important for several reasons. For example, environmental assessments of residential blocks can be conducted directly. PS begins forming during the construction of residential districts, and accumulation of pollutants in PS occurs simultaneously with the sedimentation of material from various landscape zones, thereby accounting for unknown migration processes. Therefore, PS reflects the geochemical conditions of an area and the environmental changes that have occurred over the course of the existence of a given urban landscape, and the concentrations of elements in PS reflect the long history of urban and industrial development.

The ^{137}Cs chronological tracer approach enables the assessment of the age of the PS and age of pollution in urban environments. Analysing the correlations between metal concentrations and ^{137}Cs enables the identification of the most important pollutants in an urban area and assessment of the background values and average annual input.

In this study, we suggest a new method assessing the initial geochemical conditions of contemporary anthropogenic sediments in urban areas. This method is based on the relationship between PHE and CE concentrations while accounting for the fact that some or all samples may be polluted to some degree. The concentrations of PHEs of interest are then used for the analysis by weighting their importance as inversely proportional to their concentration.

2. Materials and methods

The method was implemented using the results of a PS survey conducted in Ekaterinburg, Russia, as an example.

2.1. Puddle sediments

PS accumulated in local surface-depressed zones of relief represents a particular type of recent anthropogenic sediment in urban environments (Seleznev and Yarmoshenko, 2014). PS reflects the contemporary geochemical conditions of an area and environmental changes over the course of the existence of the urban landscape. PS accumulates pollutants over space and time characterising the pollutant migration processes. PS begins to form simultaneously with the development, construction, and landscape planning of a residential district.

Local surface-depressed areas are filled with sedimentary material represented by solid and suspended particles of soil, erosion material, and other particles transported from various urban landscape zones (Seleznev et al., 2010, Seleznev and Yarmoshenko, 2014, Seleznev et al., 2015), such as roofs, ground, pavement, local roads, and green zones.

2.2. Results of the PS survey

The PS sampling survey for the assessment of heavy metal pollution was conducted in Ekaterinburg, a city in the Ural Mountains of Russia. In total, 210 PS samples were collected in residential districts throughout the city in 2007–2010. The PS sampling sites were located within an irregular grid. Samples were collected in the courtyards in the blocks of multistorey apartment buildings (Seleznev and Yarmoshenko, 2014). The samples were taken from the upper 5 cm layer, with a sample mass of approx. 1.5 kg (dry weight). The PS samples were air-dried, and the dried samples were crushed, homogenised, and passed through a 1-mm sieve. Then, a representative subsample (20 g) of each sample was pulverised with an agate mortar and pestle.

Table 1 lists the parameters (mean, geometric mean, range, standard deviation, excess kurtosis, skewness, and coefficient of variation (CV)) and type of distribution of the metal concentrations in the PS samples.

The results of the PS sampling survey enabled the assessment of background concentrations of Pb, Zn, and Cu based on the ^{137}Cs chronological approach (Seleznev et al., 2015). Table 2 presents the results of the regression analysis of the relationship of PHE concentration and ^{137}Cs. Parameter A in the regression model represents the background metal concentration under the zero-level of ^{137}Cs concentration, which corresponds to the moment the urban landscape was formed. These background concentrations were used as an alternative to verify the approach presented in this study.