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Trace elements of concern affecting urban agriculture in industrialized areas: A multivariate approach

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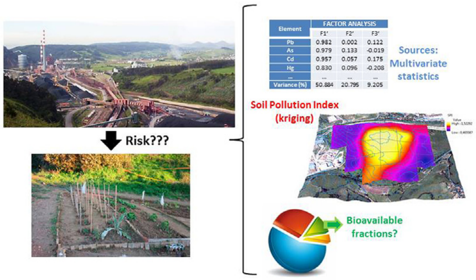
HIGHLIGHTS

- Trace element in peri-urban soils devoted to agriculture exceeded threshold levels.
- Multivariate statistics revealed anthropogenic activity, mainly coal combustion.
- A novel soil pollution index was applied to identify subareas of concern.
- Bioavailability assessment demonstrated low potential risks for human health.

GRAPHICAL ABSTRACT



Element	FACTOR ANALYSIS		
	F1′	F2′	F3′
Pb	0.982	0.002	0.122
As	0.979	0.133	-0.019
Cd	0.957	0.057	0.175
Hg	0.830	0.096	-0.208
...	...	...	...
Variance (%)	50.884	20.795	9.205

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ABSTRACT

The urban and peri-urban soils used for agriculture could be contaminated by atmospheric deposition or industrial releases, thus raising concerns about the potential risk to public health. Here we propose a method to evaluate potential soil pollution based on multivariate statistics, geostatistics (kriging), a novel soil pollution index, and bioavailability assessments. This approach was tested in two districts of a highly populated and industrialized city (Gijón, Spain). The soils showed anomalous content of several trace elements, such as As and Pb (up to 80 and 585 mg kg^{-1} respectively). In addition, factor analyses associated these elements with anthropogenic activity, whereas other elements were attributed to natural sources. Subsequent clustering also facilitated the differentiation between the northern area studied (only limited Pb pollution found) and the southern area (pattern of coal combustion, including simultaneous anomalies of trace elements and benzo(a)pyrene). A normalized soil pollution index (SPI) was calculated by kriging, using only the elements falling above threshold levels; therefore point-source polluted zones in the northern area and diffuse contamination in the south were identified. In addition, in the six mapping units with the highest SPIs of the fifty studied, we observed low bioavailability for most of the elements that surpassed the threshold levels. However, some anomalies of Pb contents and the pollution fingerprint in the central area of the southern grid call for further site-specific studies. On the whole, the combination of a multivariate (geo) statistic approach and a bioavailability assessment allowed us to efficiently identify sources of contamination and potential risks.

1. Introduction

During the last century, the growth of cities worldwide led to an increase in urban agricultural practices (Szolnoki et al., 2013). The

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term “urban agriculture” encompasses farms in inner cities, which are called urban gardens, and also to those located on the outskirts of cities (Leake et al., 2009; Rodríguez Martín et al., 2015). Regardless of the location of cities, their growth implies increased exposure of urban farming to air and soil pollution caused by heavy industry and dense traffic (Wiseman et al., 2013). Among the many contaminants derived from these anthropogenic sources, trace elements (such as Pb, As, Cu or Zn) are of particular concern (Argyropoulos et al., 2012; Boente et al., 2016). Trace elements, but also organics such as PAHs (Polycyclic Aromatic Hydrocarbons), enter soil through atmospheric deposition (Davis and Birch, 2011), and they can pose a public health problem when they exceed certain thresholds. In this regard, heavy metal(loid)s have long residence times and are easily assimilated by natural organisms (Kabata-Pendias, 2011). As a result, in the case of urban agriculture, trace elements can be taken up by plants, thus entering the food chain in significant amounts (Säumel et al., 2012). Therefore, the consumption of fruit and vegetables grown in soils with elevated concentrations of potentially toxic elements (Szolnoki et al., 2013; Tóth et al., 2016) poses a public health concern.

In order to determine whether trace elements contamination affects urban and peri-urban agriculture, plant and soil sampling in natural or uncultivated pasturelands—which are supposedly virtually pollution-free—is an appropriate approach to gather valuable information on the source and extent of atmospheric trace metal pollution in urban and industrial environments (Chai et al., 2015). Studies of this sort frequently follow the same approach, namely soil sample collection, preparation and chemical analysis of samples (Theocharopoulos et al., 2001), multivariate statistical and spatial analyses (Facchinelli et al., 2001; Gallego et al., 2002), and the identification of potential areas of risk on the basis of concentration thresholds considered hazardous for human health (Fairbrother et al., 2007). In this regard, SSLs (Soil Screening Levels), better known as RBSSLs (Risk-Based Soil Screening Levels), are threshold levels based on a specified degree of risk or hazard, usually taking also into account natural backgrounds. Thus these levels determine a threshold for several chemical elements at which a soil would require site-specific risk assessment. This value varies depending on soil use; i.e. industrial, residential, recreational, or other uses (natural soils, such as agricultural or forests) (BOPA, 2014). In this context, bioavailability and toxicity data of the potential contaminants should be considered in order to refine the bulk data of total concentrations (Izquierdo et al., 2015; Yutong et al., 2016). In addition, a site-specific risk assessment is sometimes also performed to determine potential effects of contaminants on human health (Hough et al., 2004).

RBSSLs are generally used (Wcisło et al., 2016) in brownfield sites to determine whether risk assessment is required. However, in extensive areas where diffuse pollution caused by atmospheric deposition is expected, an intermediate step should involve the identification of priority subareas in which site-specific risk assessment and/or bioavailability studies should be performed. In this context, soil pollution indexes (SPIs) are commonly used to determine the concentration of heavy metal(loid)s in soil (Zhiyuan et al., 2011). Many SPIs have been reported (Massas et al., 2013; Muller, 1969; Zaharia, 2011); however, in this study, we attempted to go one step further, in order to develop an innovative SPI that determines the global contamination of a position taking into account valid RBSSLs in the study area. This SPI has been configured as a regionalized variable (Matheron, 1971), and therefore it can be implemented and calculated via kriging. Kriging requires a point map (centroids of square grids for example) as input and returns a raster map with predictions. It uses experimental semi-variograms, that must be computed and interpreted (Goovaerts, 1999; Antunes and Albuquerque, 2013), to characterize the spatial relationship between samples (McGrath et al., 2004). It is an interpolation procedure that provides the best unbiased linear estimator and that allows prediction of element concentrations at non-sampled locations (Sierra et al., 2014). Kriging contemplates two groups of distances: the first is the distance between the point of interest and the sample location and the second is the distance between sample locations, giving rise to sample clustering, which impairs the quality of the estimation (Ha et al., 2014).

Given the abovementioned considerations, this study sought to improve and complement the classical characterization methodologies, like (multivariate) statistical and geostatistical analyses (kriging), with a new SPI especially designed for heavy metal pollution and that also considers RBSSLs. To this end, one of the largest industrialized areas of Spain was selected to test the capacity of this SPI. Thus, a comprehensive sampling campaign was undertaken in two districts in the surroundings of the city of Gijón (Asturias, Northern Spain). In this densely populated area, agricultural land coexists alongside several industries that process coal, heavy metals and cement—thus exposing nearby soils to potential contamination via atmospheric deposition of trace elements and other contaminants. The combined methodology carried out had three objectives:

- To determine whether heavy metal(loid)s affect the soil of two rural areas located in the surroundings of an industrialized area next to a large city and, thus, verify whether agricultural practices in this area give rise to a public health risk. A possible concurrent contamination with PAHs has been also addressed.
- To identify patterns and possible sources of pollution by means of multivariate statistics, thereby assigning the origins of the geochemical anomalies either to natural backgrounds, to diffuse contamination (atmospheric deposition), or to point-source contamination (industrial releases, waste disposal or others).
- To define, via kriging, a novel soil pollution index with which to identify areas of concern that merit bioavailability assessment.

2. Materials and methods

2.1. Site description

The districts of Jove and Lloreda are located in the NW and SW of Gijón (Fig. SM1), which is the largest city (almost 300,000 people) in the region of Asturias. Nowadays this city continues to be surrounded by several heavy industries that have been operating since the middle of the 20th century. Industrial processes include a coal power plant, metallurgy industries (including integrated steelworks), a cement plant, a main harbour (dry bulk port), and a number of auxiliary industries distributed in industrial estates, all of them potentially emitting trace elements and organic contaminants. The location of the main principal factories, sampling grids (see below), and points of interest is shown in Fig. 1.

The district of Jove (Northern grid) covers a hill about 150 m high running northeast-southwest, with the main urban area of Gijón situated to the west of the hill and the mouth of the Aboño estuary to the east. On this side, there is an industrial estate with a coal power station and a cement plant. In addition, about 3 km southwest of this district there is an iron/steel factory. Recent studies have revealed Hg pollution in groundwater in this area (González-Fernández et al., 2014).

The district of Lloreda (Southern grid) is also located on another small hill of around 100 m in height, about 4 km to the south of the district of Jove. Lloreda is flanked to the north by the heavily frequented A-8 motorway, to the northwest by the iron/steel factory, and to the northeast by a Zn-oxide plant.