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Geographically Weighted Principal Components Analysis to assess diffuse pollution sources of soil heavy metal: Application to rough mountain areas in Northwest Spain

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ABSTRACT

Heavy metal pollution can result in the degradation of the soil, air and water bodies' quality affecting the health of all living organism. We analyze the spatial distribution of the concentrations of soil heavy metal and relationship with natural or anthropogenic origin. The analysis was performed in Principality of Asturias (mountain region of NW of Spain), where soil heavy metal pollution has become a severe problem. First, a standard Principal Components Analysis (PCA) was performed over a population of 334 soil samples to identify the sources of fourteen heavy metal and metalloids (Ag, As, Ba, Hg, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Zn). Due to the high geological heterogeneity of the territory, the PCA analysis was improved using a variant of PCA known as Geographically Weighted Principal Components Analysis (GWPCA). The first six principal components in a standard PCA account for about 57% of soil heavy metal variability but when GWPCA is performed this figure increases to >80% in some areas. We conclude that GWPC1 corresponds to a geogenetic component with changing winning variables adapted to the geological characteristics of the territory (lithology and mining), while GWPC2 corresponds to a factor related to atmospheric pollution including heavy metal released from vegetation cover via wildfires.

1. Introduction

Soil heavy metal pollution has become a severe problem in many parts of the world due to the fact that the metal pollution is covert, persistent and irreversible (Bini et al., 2011; Zhang et al., 2009; Zhiyuan et al., 2014). This kind of pollution not only degrades the quality of the atmosphere, water bodies and food crops, but also threatens the health and well-being of animals and human beings by way of the food chain (Dong et al., 2011; Nabulo et al., 2012; Wang et al., 2012). Heavy metals such as mercury (Hg), chromium (Cr), cadmium (Cd) or metalloids like arsenic (As) are present in the environment free or as part of different molecular forms (Chen et al., 1999). In natural soils they are present at a background level and usually occur as cations which strongly interact with the soil matrix (Alloway, 1995). Therefore, some physicochemical properties of soils such as pH and organic matter are important parameters that control the accumulation and the availability of heavy metals in the soil environment. Generally speaking, heavy metals are distributed heterogeneously in the Earth's crust as an effect of geological processes, and the elemental contents of non-polluted soils are incorporated by rock weathering processes. Among these, the main factor that dictates the elemental content of a soil is the composition of parent material but this can be increased due to anthropic causes (Alloway, 1995; Kabata-Pendias, 2004; Harmanescu et al., 2011).

In industrial areas, anthropogenic activities such as agriculture, urbanization, industrialization and mining increase the metal concentration baseline (Adriano, 1992; Sheppard et al., 2000; Facchinelli et al., 2001; Wei and Yang, 2010; Zhong et al., 2012). The geological features such as lithology or mineralized areas associated to faults or thrusts exert a strong control on heavy metal concentrations and their variability in soils (Alloway, 1995; Kabata-Pendias, 2004). Smelting from industrial activities and cities is recognized as the most important source of heavy metals in the environment but little is known about the role of wildfires, which are frequent in mountainous areas. Ash is a key component of the land affected by wildfires (Cerda and Doerr, 2007; Bodi et al., 2014; Pereira et al., 2013b). Furthermore, the ability of some natural plant species, named *metalofitas*, to take up, translocate and accumulate heavy metals in their shoots (Nanda et al., 1995; Chaney et al., 1997) is well known. The combustion of these plant species could produce smog, necromasse and ashes enriched in heavy metals that, when deposited in topsoil, contribute to raise the concentration of nutrients and pollutants such as heavy metals in soils. Nowadays, a research effort concerning the legacy of atmospherically-deposited elements (e.g. heavy metals) in burned soils is needed but during the last decade some authors have shown the role of ash in the Earth and Soil System (Bodi et al., 2014; Pereira et al., 2013a). Elemental composition studies carried out

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on ashes from California burned soils reported high concentrations of heavy metals such as Zn > Ba > Cu > Mn > Ag > As > Cd > Cr > Co (Plumlee et al., 2007; Hageman et al., 2008a; Hageman et al., 2008b). Recently, a review about the heavy metal composition in wildfire ashes from Australian soils was published (Santin et al., 2015). All these research studies seem to indicate that wildfires are an important source of heavy metals in soils.

Often geogenetic and anthropogenic sources of heavy metals are superimposed in the territory and it is very difficult to separate the contribution of each one from the soil heavy metal backgrounds, making difficult the identification of the boundary between natural and contaminated soils. Thus, statistical methods such as Principal Components Analysis (PCA) and clustering have been extensively used to identify sources of heavy metals in the environment (Hu et al., 2013). PCA is a useful tool to discover diffuse pollution sources by analyzing metal associations in each principal component (Zhang et al., 2009; Wei and Yang, 2010). However, the PCA method can be complemented using a variant of the method called Geographically Weighted Principal Components Analysis (GWPCA) when spatial heterogeneity occurs in the data (Harris et al., 2011; Demšar et al., 2013). In fact, a statistical hypothesis test is normally performed in GWPCA in order to establish the existence of spatial heterogeneity. In essence, this method consists in performing a local PCA, that is, in the neighborhood of each observation, instead of a global standard PCA.

The main objective of this research is to find the natural soil heavy metal backgrounds in the Principality of Asturias, discovering possible sources of diffuse pollution using PCA over a soil population of 334 taken in the most pristine areas of the territory. The spatial heterogeneity of background levels of metals and its relationship with lithology and human activities was addressed with geographically weighted principal component analysis (GWPCA).

2. Material and methods

2.1. Study area

This research was performed in the Principality of Asturias which is a mountain region with 10,600 km^2 located in the north of the Iberian Peninsula, Spain (Fig. 1). It dates from the Hercynian Orogenic cycle, but its relief was rejuvenated during the Alpine cycle and runs parallel to the coast of the Cantabrian Sea following an east–west direction.

The climate of the area is included within the type known as “oceanic cold–temperate domain”, with mild temperatures and abundant rainfall, being strongly influenced by its proximity to the Cantabrian Sea. Roughly, the average annual precipitation reaches values ranging between 700 and 1300 l/m^2. The temperature has an annual mean of about 13 $\pm$ 1 °C and averages of 9 $\pm$ 1 °C and 19 $\pm$ $-$1 °C in the coldest and warmest months, respectively.

The vegetation is typical of Atlantic areas, composed mainly of deciduous forests (*Quercus petraea* subsp. *Petraea* (Matt.) Liebl., *Quercus pyrenaica* Willd and *Fagus sylvatica* L.) which grow on north-facing hillsides. Away from the industrial and urbanized areas, the land has been traditionally used for farming and cattle grazing. The conversion of forest and scrubland areas to pasture for cattle grazing has led to frequent and recurrent burning of extensive sectors (Vélez, 2000). The use of fire has caused severe degradation of vegetation cover and soils (Fernandez et al., 2005).

2.2. Geological and geomorphological setting

Geologically, a large part of the study area lies within Variscan Orogen which was divided into five zones according to the nature of the rocks, deformation features and metamorphic grade. Two of these zones are present in the study area: The Cantabrian zone (CZ) and the West-Asturian Leonese zone (WALZ). The CZ is constituted by a Palaeozoic sequence thrusted and folded during the Variscan orogeny. Lower Palaeozoic lithological units are predominantly siliciclastic but their content in carbonates substantially increases in the upper part of the sequence, of Devonian and Carboniferous age (Pérez-Estaún et al., 2004). Also, few small intrusive bodies are present in the area in relation to Late Variscan magmatism episodes (Fig. 2). Unconformably over Palaeozoic rocks lies Mesozoic materials which are composed of siliceous conglomerates, carbonate breccias and alternations of argillaceous sandstones, siltstones, clays, marls and limestones. Summarizing, the main lithologies are slate, sandstone, quartzite and several types of limestone while other sedimentary rocks, clay stones and marls, are limited to low relief tertiary-mesozoic basins in the central part of the region.

The relief is very rough with steep slopes. The highest elevations of the area reach 2500 m (a.s.l) and geomorphological processes such as fluvial, mass wasting and creep processes are present. The parent material of the studied soils was mainly quaternary sediments as fluvial sediments and colluvium material deposited at the bottom of hillsides. The sharp relief results in very young soils with properties very similar to the parent material.

2.3. Sources of heavy metals in the Cantabrian range

It is well known that soils and sediments contain heavy metal derived from the bedrock weathering or from anthropogenic sources. The impact of heavy metal pollution on ecosystems due to anthropogenic activities like smelting or mining activities has been frequently

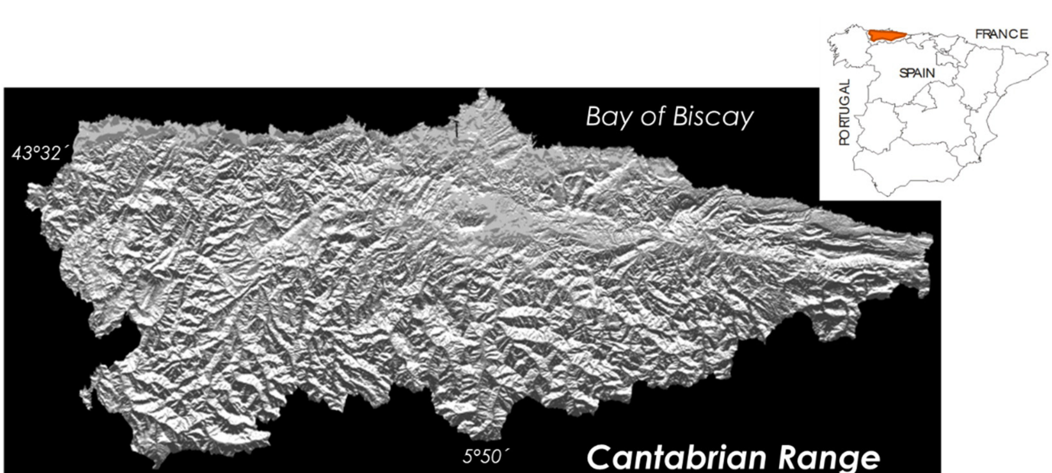

Fig. 1. The Principality of Asturias location and hillshade map.

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