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Fingerprinting sedimentary and soil units by their natural metal contents: A new approach to assess metal contamination

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HIGHLIGHTS

- Sedimentary facies and soil units are fingerprinted by their natural metal contents.
- Source-rock composition, grain size and soil weathering control metal distribution.
- Background concentrations of Cr and Ni commonly exceed the Italian guidelines.
- Predetermined background values are inadequate to depict local pollution.
- Geochemical maps based on soil/geological data allow assessing metal contamination.

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ABSTRACT

One of the major issues when assessing soil contamination by inorganic substances is reliable determination of natural metal concentrations. Through integrated sedimentological, pedological and geochemical analyses of 1414 (topsoil/subsoil) samples from 707 sampling stations in the southern Po Plain (Italy), we document that the natural distribution of five potentially toxic metals (Cr, Ni, Cu, Zn and Pb) can be spatially predicted as a function of three major factors: source-rock composition, grain size variability and degree of soil weathering. Thirteen genetic and functional soil units (GFUs), each reflecting a unique combination of these three variables, are fingerprinted by distinctive geochemical signatures. Where sediment is supplied by ultramafic (ophiolite-rich) sources, the natural contents of Cr and Ni in soils almost invariably exceed the Italian threshold limits designated for contaminated lands (150 mg/kg and 120 mg/kg, respectively), with median values around twice the maximum permissible levels (345 mg/kg for Cr and 207 mg/kg for Ni in GFU B5). The original provenance signal is commonly confounded by soil texture, with general tendency toward higher metal concentrations in the finest-grained fractions. Once reliable natural metal concentrations in soils are established, the anthropogenic contribution can be promptly assessed by calculating metal enrichments in topsoil samples. The use of combined sedimentological and pedological criteria to fingerprint GFU geochemical composition is presented here as a new approach to enhance predictability of natural metal contents, with obvious positive feedbacks for legislative purposes and environmental protection. Particularly, natural metal concentrations inferred directly from a new type of pedogeochemical map, built according to the international guideline ISO 19258, are proposed as an efficient alternative to the pre-determined threshold values for soil contamination commonly established by the national regulations.

1. Introduction

The assessment of soil contamination by risk elements and the estimate of anthropogenic disturbance are increasingly important issues when dealing with environmental problems. In this regard, establishing the natural concentrations of potentially toxic metals with respect to the anthropogenic contribution is essential for defining the pollution status of soils, and thus developing adequate policies of environmental protection (Salminen and Tarvainen, 1997). Total element concentrations in the natural environments may vary by several orders of magnitude (Blaser et al., 2000; Tarvainen and Kallio, 2002). This is especially true for certain metals, such as Cr and Ni, whose naturally elevated concentrations in ultramafic rocks can be orders of magnitude higher than values

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from continental crust rocks (Hiscott, 1984). As a consequence, natural metal concentrations in soils may vary markedly from area to area, within a region and between regions, making definition of global background values impossible (Reimann and Garrett, 2005).

The Po Plain, one of the widest alluvial plains in Europe, is a heavily urbanized area that hosts about one third of the Italian population. This region is characterized by intense agricultural and industrial activities, and for this reason it is seriously at risk of metal pollution. Recent studies carried out south of Po River (Emilia-Romagna plain), have documented that Cr and Ni, among all potentially toxic metals, may serve as powerful tracers of sediment provenance, and that they play a major role for the reconstruction of sediment dispersal patterns throughout the system (Amorosi et al., 2002, 2008; Curzi et al., 2006; Amorosi, 2012; Bianchini et al., 2013, 2014). Particularly, relatively high Cr and Ni values in alluvial and coastal plain sediment have been inferred to reflect the abundance of ultramafic detritus supplied by the Po River via its tributaries that drain the ophiolitic complexes of the Western Alps and NW Apennines (Fig. 1). Such "anomalous" high concentrations may exceed the national standards for potentially toxic metals (Bianchini et al., 2002; Amorosi and Sammartino, 2007), and for this reason they are a matter of concern and a serious problem for the environmental agencies.

A huge amount of data produced in the Emilia-Romagna plain in the framework of soil (Regione Emilia-Romagna, 2010) and geological (Regione Emilia-Romagna, 1999) mapping projects allows today to examine the natural distribution of selected elements within a mixed pedological and geological framework, through integration of geochemical data with detailed soil and facies characterization.

A general framework for standardizing methods for geochemical mapping at the global–regional scale has been developed during the 1990s (Darnley, 1997; Plant et al., 1997; Salminen and Tarvainen, 1997). However, there is still no established technique for mapping geochemical data, and an integrated system of geochemical mapping with detailed geological and soil data is far from being achieved. The vast majority of the existing geochemical maps is built on either single point representations or computer-assisted, geostatistical interpolation methods (see Reimann and Filzmoser, 2000; Reimann et al., 2002; Cheng, 2007; Micó et al., 2008, for a review of the statistical approaches). A pure statistical approach, however, in general fails to consider soil and geological properties and, as such, cannot provide adequate representation of spatial metal distribution away from the sites where data are available. In these types of geochemical maps, delineation of class boundaries may represent a highly subjective and interpretive exercise, and the resulting maps can hardly meet the needs of land-use planning.

The major objectives of this work, which focuses on a wide spectrum of alluvial, deltaic and coastal deposits, are: (i) to assess the controlling factors of natural metal distribution in the southern Po Plain, (ii) to document the possibility of fingerprinting sedimentary and soil units by their natural metal contents, and (iii) to show to what extent a new type of pedogeochemical map (Regione Emilia-Romagna, 2012), largely based on sedimentological and soil properties, may impact the determination of natural metal concentrations and the reliable estimates of anthropogenic pollution.

We use here the term "pedogeochemical content" (or "natural background value", according to the international guideline ISO, 19258, 2005) to refer to metal contents resulting from natural geological and pedological processes, excluding any addition of human origin (Micó et al., 2008). This term is commonly referred to by the geochemists as "background value" (Lepeltier, 1969; Rose et al., 1979; Reimann and Garrett, 2005), and varies according to the nature of the parent material for any particular element. The "pedogeochemical content" is conceptually separated from the term "baseline" (or "usual background value" of ISO, 19258, 2005), which is commonly meant to define a concentration of a substance that includes a diffuse anthropogenic contribution due to atmospheric deposition and agricultural practice (Tarvainen and Kallio, 2002; Cicchella et al., 2005; Albanese et al., 2007).

2. Geological setting

The Po Plain is the superficial expression of a subsiding foreland basin (Po River Basin) of Pliocene to Quaternary age. It is made up of the longest Italian river (the Po), 652 km long, which flows in W-E direction from the Western Alps to the Adriatic Sea, and by a series of transverse tributaries. The Po Plain is bounded by two mountain chains: the Alps to the north, and the Apennines to the south (Fig. 1). The Alpine catchments show contrasting compositional signatures, which reveal the complex geological history of this orogen. Two major structural

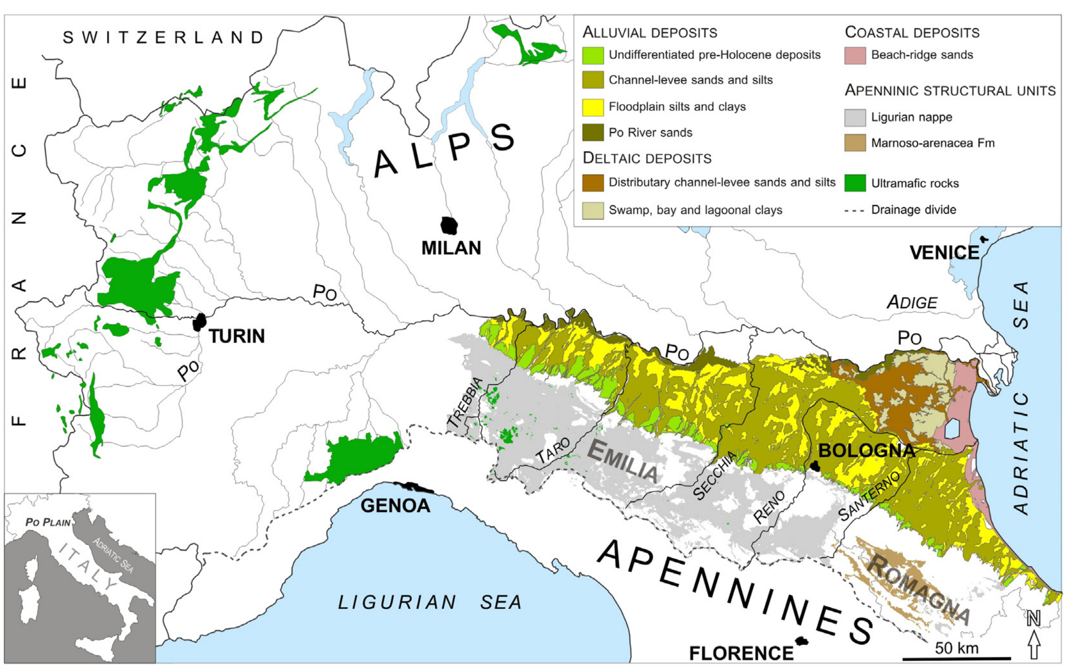

Fig. 1. Simplified geological map of the Emilia-Romagna plain (modified from Regione Emilia-Romagna, 1999) and adjoining areas.