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Impact of river overflowing on trace element contamination of volcanic soils in south Italy: Part I. Trace element speciation in relation to soil properties

P. Adamo [a,*], M. Zampella [a], L. Gianfreda [a], G. Renella [b], F.A. Rutigliano [c], F. Terribile [a]

[a] *Dipartimento di Scienze del Suolo, della Pianta e dell'Ambiente, Università di Napoli Federico II, Via Università 100, Portici, 80055 Napoli, Italy*
[b] *Dipartimento di Scienza del Suolo e Nutrizione della Pianta, Università di Firenze, P.le delle Cascine 28, 50144 Firenze, Italy*
[c] *Dipartimento di Scienze Ambientali, Seconda Università di Napoli, Via Vivaldi 43, 81100 Caserta, Italy*

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River overflowing adds up soil with Cr-rich sediments which, although chemically low reactive, transfer metal along the soil pore network during water movement.

Abstract

Volcanic soils affected by different numbers of polluted river flooding events were investigated. Chromium and Cu were the major soil contaminants. Nickel, Fe, Zn and Mn total content never exceeded the Italian mandatory limits. The distribution of Cr and Cu total contents among studied soils indicated that only Cr contamination was related to overflowing events. In polluted soils, sequential chemical extractions revealed a preferential association of Cr and Cu with organic forms. A progressive Cr insolubilization with ageing was observed. Significant amounts of Cr and Cu were extracted by NH_4-oxalate, suggesting metals association with short-range-order aluminosilicates and organo-mineral complexes. Possible methodological drawbacks in the use of the EU-BCR chemical speciation protocol on volcanic soils are discussed. Micromorphology and SEM/WDS analyses revealed Cr and Cu enriched silt and clay coatings in surface and subsurface soil horizons, suggesting a transfer of metal-rich sediments along the soil pore network with water movement.
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1. Introduction

The Solofrana river valley (Campania Region, south Italy) is characterised by thick, fertile volcanic soils with moderate to high andic properties. Agricultural and industrial activities occurring in this area have produced a widespread degradation of local natural resources. In particular, tanning plants (~160) operating in the upper valley caused in the past a Cr-enrichment of the Solofrana river waters (Basile et al., 1985). Recently, a Cr content decline in river waters was observed (Adamo et al., 2001), while the river sediments (De Vivo et al., 2003) and the valley soils still contain Cr concentrations above natural background (Adamo et al., 2003). Besides the use of polluted river waters for irrigation (prohibited since 1990), a key role, both in the past and at present time, in the Cr enrichment of the valley soils might have been played by repeated flooding events, due to river embankments weakness, after intense rainfall. About 400 ha of the valley are interested by overflowing (Consorzio Bonifica Integrale Agro Sarnese Nocerino, 1996) which release on the adjacent soil 20–30 cm layers of coarse and fine sediments, usually mechanically removed by farmers after drying.

Impact of flooding on soil trace metal contamination and its consequences on soil biota depend on metal total amount, metals forms and soil properties, such as pH, texture and organic matter content (Kabata-Pendias, 2004). High metal

* Corresponding author. Tel.: +39 81 253 9172; fax: +39 81 253 9186.
E-mail address: adamo@unina.it (P. Adamo).

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retention capacity of volcanic soils may increase the trace metal retention time but also might reduce their mobility, attenuating their toxicity over time.

From 2002, a multidisciplinary study was performed in the Solofrana valley focused on soils subjected to flooding events. Objectives of the study are: i) to analyse the main physico-chemical and mineralogical soil properties, ii) to determine Cu, Cr, Ni, Zn, Al and Fe total content and speciation, iii) to describe micromorphological features produced by sediment deposition, iv) to analyse soil eubacterial communities composition by PCR-DGGE approach, v) to measure microbial biomass, total and active fungal mycelium, and several soil enzymes activities. In this paper results concerning i–iii points are presented, with emphasis on metal availability in relation to andic properties. Some of these data are reconsidered in the second manuscript of this series (D'Ascoli et al., 2006) for interpretation of metal effect on selected soil biological and biochemical functions.

2. Description of the area

The Solofrana river valley, located between the towns of Solofra (NE) and Nocera Inferiore (SW), constitutes the inland portion of the Sarno plain, located in Campania Region (south Italy) between the volcanic complex of Somma-Vesuvius (NW), the Sarno Mountains (NE), the limestone Lattari Mountains (S) and the Tyrrhenian cost (W). It covers an area of approximately 3000 ha of cultivated soils originated by pyroclastic material from Somma-Vesuvius colluviated to the valley (Terribile and Di Gennaro, 1996). The slopes vary between 1–5% and the elevation from 42 to 150 m above sea level. The area has a Mediterranean climate regime, with average annual temperature of 17.2 °C and average annual rainfall of 1203 mm (Ufficio Idrografico e Mareografico di Napoli, 1960–1995). Field horticulture, orchards and greenhouse horticulture and floriculture are the main productions of the valley very intensive agriculture. Land use on the southern slope generally consists in terraces with coexisting horticulture, fruit trees and vineyards, while chestnuts are widely present on the north-facing slopes.

3. Materials and methods

3.1. Study areas selection and soil sampling

Combining in a GIS environment land information (soil, hydrology, flooding and land use maps), three plots of about 700 m^2 with the same soil type (Humic Haplustand, Soil Survey Staff, 1998) were selected for this study: E1 (from 14°45′47″E, 40°47′57″N to 14°45′54″E 40°47′55″N), E2 (from 14°45′44″E, 40°47′50″N to 14°45′52″E, 40°47′49″N), E3 (from 14°45′50″E, 40°47′43″N to 14°45′47″E, 40°47′44″N). Plots were not cropped by at least 5 years, covered by spontaneous herbaceous vegetation and affected by different numbers of flooding events: 1) E1, flooded in 1981; 2) E2, flooded in 1981 and 1993; 3) E3, flooded in 1981, 1993 and 1998. At the E3 site, flooded again in October 2002, sediments (SED) were sampled soon after the event and before mechanical removal by farmers. Location of the studied sites is given in Fig. 1. Another site (C), located in the same area (from 14°46′00″E, 40°49′16″N to 14°46′08″E, 40°49′15″N), but never flooded by the Solofrana waters, was considered as control soil.

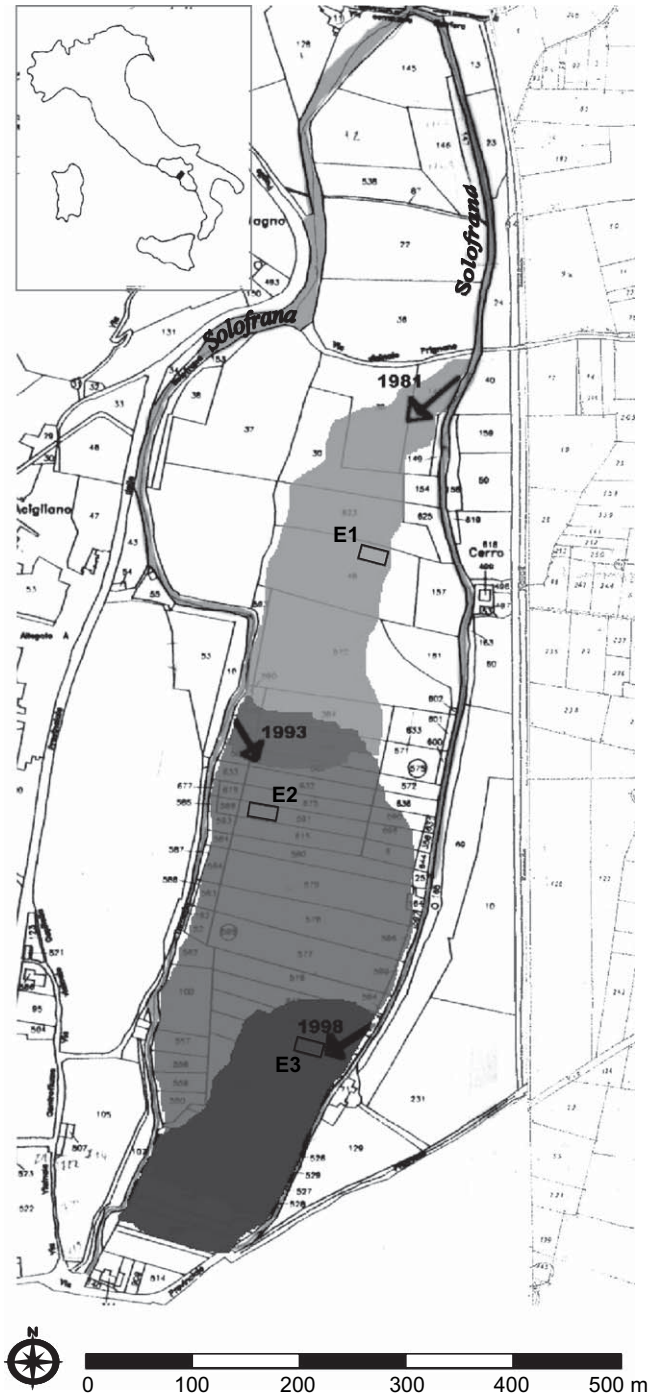

Fig. 1. Location of selected study sites in the Solofrana river valley. Arrows indicate overflowing departing location and directions. The areas affected by floods at different times are shown in different grey gradations. Rectangles indicate the sampling plots.

The selection of not cultivated sites was produced in order to avoid the influence of agriculture treatments on soil microbial activities, biomass and diversity, covering the trace metals influence.

Soil sampling was carried out in all selected sites following a "W" shaped sampling scheme. Surface soils were sampled at a depth of 0–10 cm, using plastic cores and avoiding any pollution in the sampling procedure. For each study site, five independent subsamples, each composed of 20 soil cores mixed together, were sampled and kept separate. The samples were stored at 4 °C and analysed within 20 days after sampling.

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