Journal of Geochemical Exploration 170 (2016) 30–38

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

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

Composite vs. discrete soil sampling in assessing soil pollution of agricultural sites affected by solid waste disposal

Claudia Rocco [a,b,*], Ida Duro [a], Salvatore Di Rosa [c], Massimo Fagnano [a,b], Nunzio Fiorentino [a,b], Angela Vetromile [c], Paola Adamo [a,b]

[a] Department of Agricultural Sciences, University of Naples Federico II, Portici, Naples, Italy
[b] CIRAM–Interdepartmental Centre for Environmental Research, University of Naples Federico II, via Mezzocannone, 16, 80132 Naples, Italy
[c] ARPAC – Campania Region Environmental Protection Agency, Naples, Italy

ARTICLE INFO

Article history:
Received 15 February 2016
Revised 5 August 2016
Accepted 7 August 2016
Available online 11 August 2016

Keywords:
Heavy metal(loid)s
Soil pollution
Spatial distribution
Soil sampling
Pollution indices

ABSTRACT

The choice of an appropriate sampling scheme is a crucial step in the process of soil pollution assessment and risk management. In agricultural systems, where soil is mixed by ploughing, the bulking of discrete samples to obtain composite samples improves soil sampling precision, unless strong concentration gradients exist. In this case, the compositing may significantly underestimate the risk posed by the contaminants. In this paper, the degree and spatial variability of soil pollution by potentially toxic elements in three agricultural sites, subjected to unauthorized waste disposal, were assessed applying a soil sampling scheme based on a two-level grid resolution. On the first level, a regular low-resolution 10 × 10 m grid was defined. On the second level, each grid was subdivided into nine high-resolution 3.33 × 3.33 m subplots. Discrete soil samples were taken from each 3.33 × 3.33 m plot. Composite soil samples were made bulking aliquots from the discrete soil samples. Soil samples were collected at 0–30 and 30–60 cm depths to evaluate vertical variations. When statistical analyses were applied to composite data and various pollution indices were calculated, only one site appeared to be slightly polluted by Cu and Zn, with mean contents of 131 and 95 mg kg^{-1} and peaks of 275 and 174 mg kg^{-1}. When the same analysis and indices were applied to discrete soil data a much worse scenario emerged. The slightly polluted site became highly polluted by Cu (mean and max of 276 and 1707 mg kg^{-1}) and Zn (174 and 972 mg kg^{-1}), and slightly polluted by Sb and As (max of 15 and 30 mg kg^{-1}). Plots classified as unpolluted on the basis of composite data revealed metals above legal limits. Pollution always interested both the 0–30 and 30–60 cm depth soil samples, with the deeper samples showing only in few cases higher values than the surface samples. The adopted two-level soil sampling scheme succeeded to show dishomogeneity in soil pollutant spatial distribution, with pollution hot spots emerging only when sampling was done at a very short spatial scale.

1. Introduction

The determination of potentially toxic elements (PTEs) total or 'pseudototal' content in soil is considered a valuable preliminary aid in establishing the risks for biota and human health, assuming that pollutants transference to water resources or biota are correlated with the contamination level (Adamo and Zampella, 2008). In contrast, relevant paradigms in environmental monitoring, risk assessment and remediation feasibility are the natural levels of PTEs in soil, the spatial variability of soil pollution, the mobility and bioavailability of pollutants to microorganisms, plants, animals and humans. In agricultural land, contamination of soil with PTEs represents a serious risk to human and animal health due to the potential accumulation of pollutants in the food chain (Wuana and Okieimen, 2011). Moreover, in all parts of the world, agriculture is a primary sector of economy playing a key role in food security and rural environment sustainability, and any abandonment or change of land use would result in increased environmental pressures and deterioration of valuable farm habitats with serious economic and social consequences (Washa et al., 2014). Hence, the adequate choice of sampling scheme, assessment of the level and geographical extend of soil contamination and consequently the adoption of the most appropriate remediation strategy, is of vital importance in croplands (de Abreu et al., 2012, Loska et al., 2003).

Although field soil sampling is a crucial step in the description of the type, patterns and spatial distribution of soil pollution, its study has lagged behind in relation to soil analysis techniques. According to Markert (1995) the uncertainty arising from representative soil

* Corresponding author at: Department of Agricultural Sciences, University of Naples Federico II, Portici, Naples, Italy.
E-mail addresses: claudia.rocco@unina.it (C. Rocco), paola.adamo@unina.it (P. Adamo).

http://dx.doi.org/10.1016/j.gexplo.2016.08.004
0375-6742/

sampling is by far larger than that linked to pre-analysis treatment and instrumental measurement. Not all EU countries have standard soil sampling guidelines imposed by law neither similar soil sampling protocols. Some countries follow ISO/DIS guidelines, others soil sampling guidelines suggested by scientific societies or research institutions (Theocharopoulos et al., 2001). Most guidelines require the collection of composite instead of simple samples, while some prefer sampling soil profiles. The current Italian legislation (D.Lgs 152/06 integrating the M.D. 471/99) provides only indicative criteria, such as sampling depth (0–1 m as 'superficial' soil) and sampling density based on the total dimension of the study area (<1 ha, at least 5 samples; 1–5 ha, 5 to 15 samples; 5–25 ha, 15 to 60 samples). These indications, far from enrolling the complexity of soil pollution, are becoming standard reference in the characterization of Italian polluted sites without any distinction about land use.

For agricultural fields, simplified schemes to obtain representative composite samples are provided by the European Protection Authority (NSW EPA, 1995) using patterns as double diagonal or zig-zag lines (ISO, 2002). Similar simple sampling schemes are applied in artificially polluted sites (Argyraki et al., 1995), although the larger heterogeneity and spot-like nature of the contaminations often would require more sophisticated approaches (Taylor et al., 2005). Simplified sampling schemes are preferred in many situations where the increased effort of more elaborated sampling is not commensurate with the purpose of the sampling (i.e. fitness for purpose) (Ramsey and Thompson, 2007; Buczko et al., 2012). In agricultural system, where the soil is homogenised by ploughing, the bulking of discrete samples, taken from several points of field plots, to form composite samples is a widely applied technique of soil sampling. The PTEs total content measured on the composite soil samples can be considered representative of the sampled field plots. Nevertheless, if in the soil there are strong horizontal or vertical gradients of pollutant concentration, the compositing scheme may miss important information with a significant underestimation of the risk posed by the contaminant. In this case, different strategies of soil sampling have to be used in order to appreciate the spatial variability of soil pollution and to locate the areas that effectively require remediation (Correll, 2001).

Excavation, addition of extraneous materials and mixing of the soil matrix are frequent in the urban and peri-urban areas as a consequence of the intensive use of the territory and the rapid land-use changes (Ajmone-Marsan and Zanini, 2013). In agricultural areas, the importance of soil as a medium for waste disposal is increasing with increase in industrialization and population (Lal and Pimentel, 2007). Intense anthropogenic activities, add to the natural spatial variability thus intensifying soil heterogeneity (Behera and Shukla, 2014; Li et al., 2011). The spatial variability of PTE pollution in agricultural soils is important for designing site specific agricultural and environmental soil and crop management practices. The scales of spatial variation may differ between different soil properties, because the processes that cause variability may occur at different scales, e.g. from the single plant scale to larger topographical scales (Zhang et al., 2014). Understanding the pattern and processes of soil spatial variability is key for an efficient soil resource management. Disregarding spatial variability may cause unreliable results.

Main aim of this study was to highlight the difficulties to appropriately assess the level of PTEs pollution in agricultural soils interested by illegal waste disposal when only composite soil sampling is applied. For this reason, in three agricultural sites, subjected to unauthorized solid waste disposal, we applied a soil sampling scheme based on a two-level grid resolution, contemplating both discrete and composite soil sampling. Data concerning the total content of PTEs in composite and discrete soil samples were compared using classical statistical methods to provide evidences of the potential loss of information when only composite samples are used. The need for soil-specific sampling guidelines for contamination assessment is discussed taking into consideration the risk to human health posed by contamination.

2. Materials and methods

2.1. Study area

The Litorale Domitio Agro Aversano is an area of Campania Region (southern Italy), with a total surface of about 1564 km^2 (Bove et al., 2011; Capra et al., 2014), encompassing the plains of the Garigliano and Volturno Rivers and partially the Phlegrean Fields volcanic area. It includes a large part of the agricultural land belonging to >77 municipalities in the Naples and Caserta provinces (Capra et al., 2014) formerly identified by the Italian State as one of 54 National Interest Priority Sites (NIPS), where severe environmental pollution and degradation is supposed to occur and, therefore, where characterization and remediation activities have to be implemented. Since January 2014, the area has been recognized as a Regional Interest Priority Site (RIPS) remitting any requalification activity to Campania Region (Fig. 1).

Soils in the area are characterized by the presence of both detrital-alluvial sediments and the fall of pyroclastic material from Phlegrean Fields. Soil formation in the valley is strongly influenced by alluvial processes forming very thick, fertile soils which show moderate to high vertic properties (Capra et al., 2014). The slopes are between 1 and 5% and the elevation ranges from 42 to 150 m above sea level. The area has a Mediterranean climate, with an average annual temperature of 18.7 °C and an average annual rainfall of 818 mm (Capra et al., 2014). In the Litorale Domitio Agro Aversano, agriculture is very intensive, mainly consisting of fodder crops (mostly maize and alfalfa), field horticulture, orchards and buffalo livestock. It is well known the production of the famous "mozzarella di bufala campana D.O.P." (Denomination Origin Protected) recognized with the Ministerial Decree on May 10, 1993.

Ancient Romans used to call this region *Campania felix* because of the fertility of its soils. Now this area is depicted in the media as an open-sky landfill. In 2004, the territory comprising the municipalities of Acerra, Nola and Marigliano, was named the "triangle of death" by the medical magazine The Lancet (Senior and Mazza, 2004) due to its high incidence of cancer-related deaths and shorter life span of people living in this area. More recently, its moniker was changed to "land of fire", a reference to the common practice of burning rubbish in the area.

The area is actually characterized by a diffuse land abuse mainly through an intense and chaotic urbanization with most of municipalities reaching a population density higher than 425 inhabitant km^{-2} (ISTAT, 2013). Furthermore, the intensive agriculture and livestock, the presence of numerous dumping sites (both legal and illegal), the usual practice of waste incineration and the common sewage network leakage, has produced groundwater and soil contamination, with many wells showing very high nitrate concentration (Corniello and Ducci, 2014) and soil pollution by PTEs, hydrocarbons and pesticides (Bove et al., 2011; Capra et al., 2014; Grezzi et al., 2011).

This situation has driven Italian Government to carry out a survey of the pollution levels in agricultural soils of Campania. The survey, combining pre-existing and new data, mostly based on composite soil sampling and 100 × 100 m grid pattern, has confirmed until now only 22 ha of polluted soils within an agricultural area of 50.000 ha. The results of the survey were published on February 12th and July 7th, 2015 with two Interministerial decrees (GU n.56, 9-3-2015 and GU n.191, 19-08-2015). Nevertheless, the soil sampling scheme used in this characterization could lead to a significant underestimation of the risk posed by contaminants.

Authoritative researchers have recently suggested that Campania region could be a perfect field study for a monitoring research programme, as their poisoned fields could serve as a giant experiment in the new science of 'exposomics' (Nature, 2014). In three pilot sites of the Litorale Domizio Agro Aversano RIPS, subjected to unauthorized waste disposal, the EU-LIFE-Ecoremed2011 (www.ecoremed.it) project is working to implement eco-compatible protocols for agricultural soil remediation.