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Potentially Harmful Elements and Polycyclic Aromatic Hydrocarbons in the soils of Acerra, southern Italy

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Abstract

In October 2004, Senior and Mazza published a paper on The Lancet Oncology where the villages of Marigliano, Nola and Acerra were included within the vertices of a so-called "triangle of death" where the local population resulted to be strongly affected by a cancer incidence higher than the regional average. The aim of this work has been the evaluation of the geochemical-environmental conditions of this north-eastern sector of the metropolitan city of Naples covering a total surface of ca. 100 sqkm. For the purpose, a total of 154 topsoil samples were collected from the study area to determine the concentrations of potentially toxic elements (PTEs) (in 121 samples) and polycyclic aromatic hydrocarbons (PAHs) (in 33 samples). The analytical data were statistically processed in order to carry out an environmental assessment of the area based on a geostatistical approach and a multivariate analysis of the data. The results showed how the distribution patterns of contaminants in the area are mostly related with the presence of industrial and human settlements in the study area. Diagnostic ratios were applied to PAHs data to assess their origin and distribution. A preliminary quantitative risk assessment (PQRA) was also performed to evaluate the potential effect of soil contamination on local population health conditions.

Keywords: Potentially toxic elements; polycyclic aromatic hydrocarbons; environmental assessment

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1. Introduction

In recent years, Campania region, in southern Italy, has been subject to the attention of media for the alleged wide-scale contamination of an area with an original agricultural vocation interested, nowadays, by the presence of high environmental impact industrial activities and uncontrolled waste dumping. Often dumped waste, specially tyres and other materials containing metals, are also illegally burned in the open countryside by criminal people to recover second raw material to resell. Due to this infamous practice, the territory, around the town of Acerra has been informally renamed as "Land of Fires". Furthermore, Acerra together with the small towns of Marigliano and Nola represent the vertices of an ideal polygon defined by Senior and Mazza (2004) as the “Triangle of death”. According to these authors, the population living in the area, heavily exposed to toxic and carcinogenic substances, is, on the average, affected by an incidence rate of cancer and affine pathologies higher than the regional average.

The individuation of the distribution patterns of potentially harmful elements (PHEs) and polycyclic aromatic hydrocarbons (PAHs) in topsoil allowed an evaluation of the geochemical-environmental conditions of this north-eastern sector of the metropolitan city of Naples, which is one of the areas with the highest population density in Italy and represents an area of great socio-economic interest not only for the urban settlements present, but also for the production activities, infrastructures and existing natural resources.

2. Study area

The study area covers about 100 sqkm, including 6 municipalities (Acerra, Pomigliano D’Arco, Castello di Cisterna, Brusciano, Mariglianella and Marigliano). Local geology reflects the geological history of Campanian plain which has been generated by the surface leveling of a huge graben generated during the Pleistocene and filled by volcanic products and by alluvial deposits consisting in reworked pyroclastic deposits and weathered carbonatic material proceeding from the surrounding mountains (De Vivo et al., 2001).

Population is about 160,000 and the most populous city is Acerra with more than 50,000 inhabitants. Considering the extension of urbanised areas (ca. 20 sqkm), the average population density is of 6-7000 inhabitants per sqkm. Non urbanized areas are mostly occupied by agricultural activities (crops, orchards and vineyard) and by 3 principal industrial settlements. In facts,

- a branch of the Italian automotive industries FIAT, which came into activity in the early 70’s and nowadays has ca. 6000 employees, is present in the area between Acerra and Pomigliano**;**
- the ASI industrial settlement (covering a total area of 2.6 sqkm) characterized by the presence of both a factory which produced polyester fibers until 2015 and a thermoelectric power plant fueled with palm oil since 2008, is located in the middle of the plain north of Acerra**;**
- an incinerator for urban waste treatment stands close to the ASI area.

3. Materials and methods

A total of 121 topsoils samples (within a depth interval between 0 and 15 cm from the surface) were collected across the study area, at an average sampling density of 3 samples

per sqkm in urbanised areas and 1 sample per sqkm in suburban and agricultural/uncultivated areas, to determine the concentrations of 53 inorganic analytes including major and trace elements. After being prepared at the Environmental Geochemistry Laboratory (LGA) at University of Naples Federico II, the samples were sent to ACME Analytical Laboratories Ltd, now Bureau Veritas, (Vancouver, Canada), for analysis by ICP-MS after solubilization in Aqua Regia. In addition, further 33 soil samples were collected, with an average density of 1 sample per 4 sqkm, to determine concentrations of polycyclic aromatic hydrocarbons (PAHs). These latter samples were sent to the Key Laboratory of Biogeology and Environmental Geology (BGEG), at China University of Geosciences in Wuhan, for analysis by GC-MS after solubilization in dichloromethane.

For the purposes of this study, we evaluated the geochemical distribution of both 15 potentially harmful metals (PHEs) (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) and the 16 PAHs defined as priority pollutant by USEPA (2013) (i.e. naphthalene [NAP], acenaphthylene [ACY], acenaphthene [ACE], fluorene [FLO], phenanthrene [PHE], anthracene [ANT], fluoranthene [FLA], pyrene [PYR], benzo[a]anthracene [BaA], chrysene [CHR], benzo[b]fluoranthene [BbF], benzo[k]fluoranthene [BkF], benzo[a]pyrene [BaP], indeno[1,2,3-cd]pyrene [IcdP], dibenzo[a,h]anthracene [DahA] and benzo[g,h,i]perylene [BghiP]).

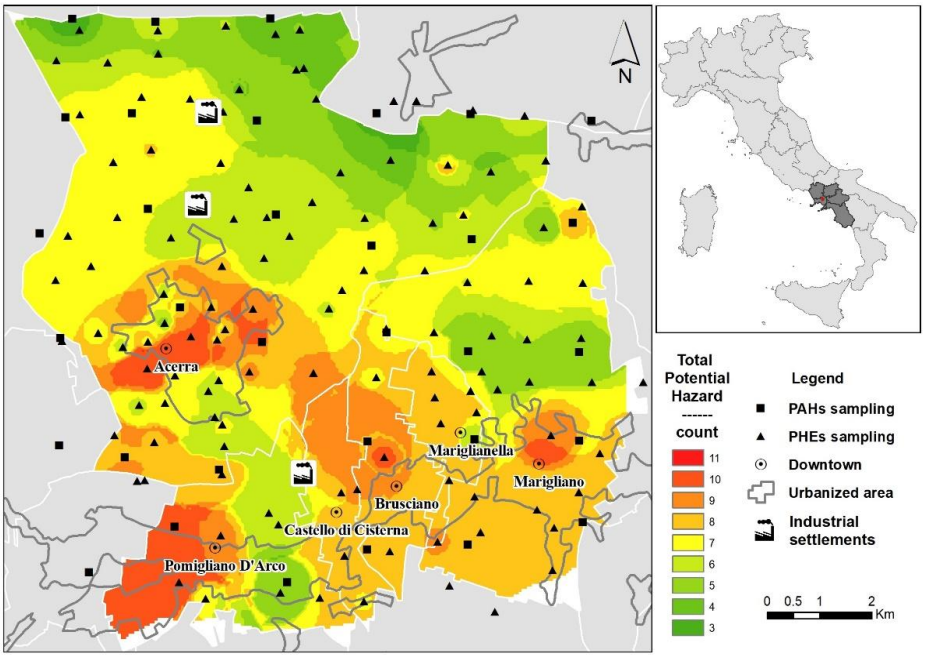

Fig. 1. The map of the Potential Hazard (PH) has been generated by reclassifying the pixels of the interpolated map, generated by mean of a Multifractal IDW algorithm, of each element by using as a criterion the overcoming or not of the corresponding guideline value. Each pixel is characterized by an integer value corresponding to the total number of elements not in line with Italian environmental guidelines within its own spatial domain

For each of the considered elements and compounds multifractal IDW (MIDW) (Lima et al. 2008) interpolated maps were generated to analyse their distribution patterns.

The pixels of the MIDW maps of each analyte were compared with the corresponding guidelines established by Italian Environmental Law (IEL) to generate individual maps of the potential hazard. All the single potential hazard maps were, then, synthesized into a unique total hazard map were the integer assigned to each pixel indicate the total number of single analytes overcoming the own corresponding reference value (as reported in IEL) (Fig. 1).

Following the previous outcomes, we further proceeded with a more detailed environmental analysis on both types of the considered contaminants (PHEs and PAHs) aiming at defining both the spatial distribution of the degree of contamination in the study area and the characteristics of the possible contamination sources and their impact on the context.

For each element the Contamination Factor has been calculated as CF=Ci/Cb, where: Ci is the concentration value of the i-element in the pixel of the interpolated grid and Cb is the reference values of the element for the local natural background retrieved from De Vivo et al. (2006).

As far as PHEs are concerned, for an assessment of the level of contamination, the Contamination Degree (CD) and Pollution Load Index (PLI) maps have been developed. Both maps derive from some raster based algebraic operations involving the Contamination Factors (CF): the first derives from the sum of the factors while the second from their multiplication.

A factor analysis was also developed on PHEs data with the aim of finding associations of elements that could suggest the existence of contaminating sources with well-defined characteristics. A total of three association was selected: Co-Fe-V-Tl-Be (F1); Pb-Zn-Sb-Sn (F2) and Cu-P (F3) accounting for the 36.1%, 28.13% and the 17.87% of the total variance, respectively.

Due to the fact that for a given source, an emission profile can be developed based on the values of the ratio among the concentrations of different PAH compounds (Tobiszewski and Namiesnik, 2011), some diagnostic ratios were used for the discrimination of some emission sources within the study area, as well.

Further, a Preliminary Quantitative Risk Assessment (PQRA) was carried out using the total concentrations of PAHs. The process allowed to estimate the carcinogenic risk for the resident population deriving from the exposure to these organic compounds. The calculation of the Incremental Lifetime Cancer Risk (ILCR) was carried outstarting from the total PAHs concentrations, expressed as benzo(a)pyrene-equivalent concentrations (BaP-equivalent), taking as reference a residential exposure scenario, three different exposure routes (contact, inhalation and ingestion) and, finally, two different receptors (adults and children).

4. Results and discussion

In general, the north-eastern sector of the study area appears to be characterized by low hazard, while the area south of Acerra is associated to a significant environmental hazard since, on the average, more than 7 contaminants, among the ones considered, show values exceeding the guidelines values established by IEL.

The obtained results show, in accordance with what highlighted in the Potential Hazard map, that the urban centers of Acerra, Pomigliano, Brusciano and Marigliano are the areas with the highest anthropogenic impact.

Regarding the source of metal pollution factor analysis suggested that the main control on local soil chemical composition is due to:

• volcanic origin of soils itself (Co-Fe-V-Tl-Be);

• motor vehicle mobility and other urban processes (Pb-Zn-Sb-Sn) (where Pb derives mainly from the entail of gasoline, Zn from the decay of tires, Sb from the consumption of brakes and Sn from other anthropic activities);

• agricultural activities (Cu-P) (where Cu is a component of fungicides and P is normally an additive of soil improvers and phosphated fertilizers).

For PAHs, obtained results showed that, in almost the whole area, these compounds mainly originate from pyrogenic processesrather than petrogenic processes; that is,they are formed when organic matter is exposed to high temperatures in anoxic conditions. Specifically, most of PAHs derive from combustion processes (Fig. 2), mainly of biomasses, potentially associated with bothan intense agricultural activity and the presence of a power plants fuelled bypalm oil (i.e. the Fri-el plant) in the area. A portion of the territory is, in addition, largely characterized by compounds mostly related with vehicular emissions (e.g. fuels in cars and trucks) and are, in fact, found at higher concentrations in correspondence with urban areas.

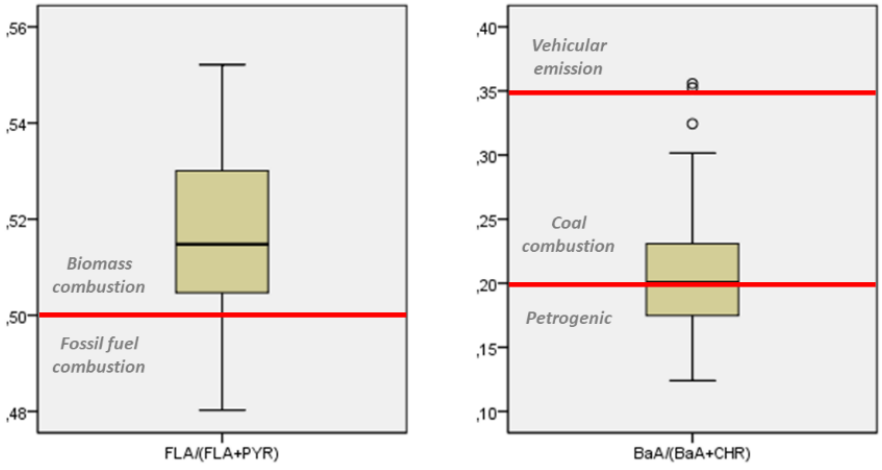

Fig. 2. Boxplots of some PAHs diagnostic ratios. The red lines highlight the reference ratio thresholds to discriminate among different sources

5. Conclusion

Given the large number of people living in the area, and the presence of numerous production activities, the obtained results are not surprising. The highest concentrations of many organic compounds were mostly found around the municipalities of Acerra and Brusciano, and to a lesser extent between Pomigliano and Casalnuovo. The distribution of metal concentrations is less clustered, with frequent high values throughout the area to the

south (i.e. the area between Casalnuovo and Marigliano) even though Acerra and Brusciano are still the most polluted centers.

Clearly it is necessary to implement new studies mainly towards health risk assessment in probabilistic terms also focused on the hazard deriving from metals and other substances, organic and non-organic, which have not been covered in this study.

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