Status, sources and contamination levels of organochlorine pesticides residues in urban and agricultural areas: A preliminary review in central-southern Italian soils

Matar Thiombane[1*], Attila Petrik[1], Marcello Di Bonito[2], Stefano Albanese[1], Daniela Zuzolo[3], Domenico Cicchella[3], Annamaria Lima[1], Chengkai Qu[1], Shihua Qi[4], Benedetto De Vivo[5]

[1]. Department of Earth, Environment and Resources Sciences (DiSTAR), University of Naples "Federico II", Complesso Universitario di Monte Sant' Angelo, Via Cintia snc, 80126 Naples, Italy.

[2]. School of Animal, Rural and Environmental Sciences, Brackenhurst Campus Southwell NG25 0QF Nottingham Trent University, United Kingdom.

[3]. Department of Science and Technology, University of Sannio, via dei Mulini 59/A, 82100 Benevento, Italy.

[4]. State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 430074 Wuhan, People's Republic of China.

[5]. Pegaso University, Piazza Trieste e Trento 48, 80132 Naples & Benecon Scarl, Dip. Ambiente e Territorio, Via S. Maria di Costantinopoli 104, 80138 Naples, Italy

* Corresponding author: Matar Thiombane, thiombane.matar@unina.it

Abstract

Organochlorine pesticides (OCPs) are synthetic chemicals commonly used in agricultural activities to kill pests and are persistent organic pollutants (POPs). They can be detected in different environmental media but soil is considered an important reservoir due to its retention capacity. Many different types of OCPs exist, which can have different origins and pathways in the environment. It is therefore important to study their distribution and behaviour in the environment, starting to build a picture of the potential human health risk in different contexts. This study aimed at investigating the regional distribution, possible sources and contamination levels of 24 OCPs compounds in urban and rural soils from central and southern Italy. One hundred forty-eight topsoil samples (0–20 cm top layer) from 78 urban and 70 rural areas in 11 administrative regions were collected and analysed by gas chromatography–electron (GC-ECD).

Total OCPs residues in soils ranged from nd (no detected) to 1043 ng/g with a mean of 29.91 ng/g, and from nd to 1914 ng/g with a mean of 60.16 ng/g in urban and rural area, respectively. Endosulfan was the prevailing OCP in urban areas, followed by DDTs, Drins, Methoxychlor, HCHs, Chlordanes related-compounds and HCB. In rural areas the order of concentrations was: Drins > DDTs > Methoxychlor > Endosulfans > HCHs > Chlordanes > HCB. Diagnostic ratios and robust multivariate analyses revealed

that DDT in soils could be related to historical application, whilst (illegal) use of technical DDT or dicofol may still occur in some urban areas. HCH residues could be related to both historical use and recent application, whilst there was evidence that modest (yet significant) application of commercial technical HCH may still be happening in urban areas. Drins and Chlordanes compounds appeared to be mostly related to historical application, whilst Endosulfan presented a complex mix of results, indicating mainly historical origin in rural areas as well as potential recent applications on urban areas. Contamination levels were quantified by Soil Quality Index (SoQI), identifying high levels in rural areas of Campania and Apulia, possibly due to the intensive nature of some agricultural practices in those regions (e.g., vineyards and olive plantations). The results from this study (which is in progress in the remaining regions of Italy) will provide an invaluable baseline for OCP distribution in Italy and a powerful argument for follow-up studies in contaminated areas. It is also hoped that similar studies will eventually constitute enough evidence to push towards an institutional response for more adequate regulation as well as a full ratification of the Stockholm Convention.

Keywords: Organochlorine pesticides; Italian soils; diagnostic ratios; multivariate analysis; Soil Quality Index; Contamination

1. Introduction

The Stockholm Convention (2005) banned the use of Persistent Organic Pollutants (POPs), with the aim of protecting human health and the environment. The initial list prepared in 2003 included Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, Hexachlorobenzene (HCB) and Dichlorodiphenyltrichloroethane (DDT). This list was then expanded with other potential POPs in 2011: Hexachlorocyclohexane (HCH, including Lindane), Methoxychlor, and Endosulfan (Stockholm Convention, 2005, 2011). These organic pollutants are considered long-range transport compounds based on their ubiquity, persistence, and bioaccumulation potential in different environmental media (Weinberg, 1998, Szeto et al., 1991; Fang et al., 2017), as well their high toxicity to humans and non-target organisms (WHO, 2003; Nizzetto et al., 2006; Moeckel et al., 2008; Kim et al., 2017). They sink in different environmental matrices such as air, water, and soils, and further accumulate in the food chain (Prapamontol and Stevenson, 1991; Suchan et al., 2004; Qu et al., 2016). Soil continues to be a potential medium of exposure of OCPs and its biofilms and physico-chemical properties may influence fate and behaviours of OCPs metabolites through different degradation phenomena (Weinberg, 1998; WHO, 2003).

Since agricultural practices are a very important economic resource for Italy, this makes it the third OCPs user among European Union countries (Eurostat, 2014). In Italy, OCPs are used in most agricultural activities, in forestry as well as ornamental plants in urban gardens preservation against insects, fungal or animal pests. It is well known that Italy is the only European Union (EU) country that has not ratified the Stockholm Conventions, though the production and use of Aldrin, Chlordane, Dieldrin, Endrin, DDT, Heptachlor, HCB and HCH in its territory have been strictly restricted in harmony with several other regulatory schemes via the Rotterdam Convention in 1998, the European Directive in 2000 (Persistent organic pollutants amending Directive 79/117/EEC), the United Nations Economic Commission for Europe POPs Protocol (UNECE, 2010). Moreover, Italian environmental law (D. Lgs. 152/2006) established guideline threshold values that regulate the mitigation of OCPs in soils. This regulation guided a recent evaluation of the levels (for DDT) and residues (for HCH) in the Campania plain (Arienzo et al., 2015; Qu et al., 2016), and in agricultural soils in the province of Latina (Latium) (Donnarumma et al., 2009). However, this legislation does not involve OCPs such as Endosulfan and Methoxychlor: these compounds have been associated to both environmental and human health risk due to concerns that they are carcinogen, teratogen and male reproductive toxicants (PANNA, 2008; USEPA, 2007; Silva and Carr, 2009; Jayaraj et al., 2016). Whilst recent studies have started to investigate and define the level of OCPs in Italian soils (e.g., Donnarumma et al., 2009; Arienzo et al., 2015; Qu et al., 2016, 2017), there has been no systematic attempt to evaluate their wider distribution and variations across rural and urban areas in Italy. The aim of this study was to begin to establish a regional (and eventually national) baseline based on a large survey carried out in 11 regions of central and southern Italy. The main objectives of this study were:

(1) to identify the regional distribution of OCPs compounds in Italian soils,

(2) to evaluate their potential sources by using OCPs diagnostic ratios as well as robust compositional biplot and factor analysis, and

(3) to quantify OCPs contamination levels by using Soil Quality index (SoQI) in urban and rural soils.

This study is important because it will represent a fundamental stepping stone to build a long-overdue national picture of OCPs status in Italy. It is envisaged that the results of this study should trigger more detailed surveys in contaminated areas as well as ad-hoc risk-based studies, which in the long-term will constitute a strong-enough argument to cause an adequate institutional response by the Italian regulating authorities.

2. Materials and methods

2.1. Study area

The survey area included 4 administrative regions (Latium, Marches, Tuscany, and Umbria) from central and 7 (Abruzzo, Apulia, Basilicata, Calabria, Campania, Molise, and Sicily) from southern Italy (Fig. 1).

[Figure 1 about here]

The total survey area (considering administrative regional boundaries) extended to 157,716 km^2 with 31.26 million of inhabitants, mostly grouped in main urban areas (ISTAT, 2016). Most of the land is used for agricultural and forestry activities. Agriculture occupies one-fourth of the land available, which includes cultivation of hilly areas where agriculture results in modifying the natural landscape and resources through terracing, irrigation, and soil management (Corona et al., 2012; ISTAT, 2013; ISPRA, 2014a). Favourable meteorological conditions, dominated by a Mediterranean climate, allow intensive agriculture activities such as vineyards and olive plantations - mostly in hilly areas – as well as greenhouse production (tomatoes, potatoes, aubergines, peppers, peas, and citrus fruits) in coastal areas in Campania, Apulia, and Sicily (Costantini and Dazzi, 2013). The predominant crops in inland territory are seasonal ones like wheat, maize, potatoes, rice, and sugar beet. Most of forestry lands are composed of broad-leaved trees, with conifers and chestnut making up about one-fifth of the total (ISTAT, 2013).

Large urban areas such as Rome (Latium), Naples (Campania), Bari (Apulia) and Palermo (Sicily), are densely populated and surrounded by metropolitan areas where both industrials activities, manufactories and intensive agriculture occur (ISTAT, 2016).

2.2. Soil sampling procedure and preparation

The sampling campaign took place from early April to end of September 2016, with the aim to select the most representative topsoil samples in urban and rural areas throughout 11 regions (Latium, Marches, Tuscany, Umbria, Abruzzo, Apulia, Basilicata, Calabria, Campania, Molise, and Sicily) from the centre to southern Italy. In each region, the main urban areas and the nearest rural areas where most of the land is devoted to agricultural activities, were selected. Site selection was carried out by interpreting, using Geographical Information Systems (ArcGIS, 2012), information on land use/land cover of the study area (ISPRA, 2014b; Corine land cover, 2012) together with satellite imagery (Google Earth® professional, 2016). A total of 148 soil samples were collected with a nominal density of 2 samples/ 2500 km^2 (in urban and rural areas) (Fig. 1). Samples have been collected from public gardens in urban areas, and from agricultural land (farmlands/cropland) in rural areas. All the samples were collected using a stainless steel scoop, kept in labelled glass bottles and directly stored in ice boxes to minimize the losses caused by volatilization and initial degradation of the organic compounds. Each topsoil sample

(from 0-20 cm) was made by homogenizing 5 subsamples at the corners and the centre of a 100m^2 square, collecting approximately 1.5 kg in total. The sampling procedure followed the Geochemical Mapping of Agricultural and Grazing Land Soil (GEMAS) sampling procedure described by Reimann et al. 2014). Soil samples were homogenized and sieved using a <2mm mesh sieve after removing stones, detritus and residual roots. Finally, composite samples were stored at −4 °C in the environmental geochemistry laboratory of the University of Naples Federico II (Italy) until instrumental analysis. Geographical coordinates were recorded by geospatial positioning systems (WGS84, GPS) at each sample site.

2.3. Extraction procedure and analysis OCPs

Analyses were carried out by an Agilent 7890A gas chromatograph with a 63Ni electron capture detector (GC-ECD) equipped with a DB-5 capillary column (30.0 m length, 0.32 mm diameter, 0.25 mm film thickness), in the Key Laboratory of Biogeology and Environmental Geology of Ministry of Education at the University of Geosciences in Wuhan, China (Yang et al. 2008; Qu et al., 2016).

Gas chromatography-mass spectrometry (GC-MS) and gas chromatography-electron capture detector (GC-ECD) are the most common and appropriate systems to investigate organic contaminants in different environmental media. Many authors (Aramendia et al., 2007; Alves et al., 2012) showed the high sensitivity of GC-ECD for organophosphorus and organochlorine pesticides. In this study, the rationale of working with GC-ECD analyser was based on the excellent sensitivity and satisfactory quantification limits, allowing the identification and quantification of pesticides at low levels. A 10 g of dried soil samples were spiked with 20 ng of 2,4,5,6-tetrachoro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) as recovery surrogates and were Soxhlet-extracted with dichloromethane for 24 h. Activated copper granules were added to the collection flask to remove elemental sulphur. The extraction of OCPs was concentrated and solvent-exchanged to n-hexane and further reduced to 2–3mL by rotary evaporation. The alumina/silica (1:2) gel column (450°C muffle drying for 4 h, both deactivated with three percent water) was used to purify the extract and OCPs were eluted with 30mL of dichloromethane/hexane (2/3). Then the eluate was concentrated to 0.2 mL under a gentle nitrogen stream and a known quantity of penta-chloronitrobenzene (PCNB) was added as an internal standard prior to gas chromatography–electron (GC–ECD) analysis.

Nitrogen was used as carrier gas at 2.5 mL/min under constant-flow mode. Injector and detector temperatures were maintained at 290°C and 300°C, respectively. The oven temperature started from 100°C (with an equilibration time of 1 min), and rose to 200°C at a rate of 4°C/min, then to 230°C at 2°C/min, and finally reached 280°C at 8°C/min, and was held for 15 min. 2 µL of each sample was injected into the GC-µECD system for the analysis. Concentration of the individual target OCPs were

identified by comparison of their retention times (previously confirmed with GC/MS) and quantified using an internal standard. The gas chromatograph (GC-MS) parameters of the Agilent 6890GC-5975MSD system were the same as those of the Agilent 6890 GC equipped with 63Ni micro-electron capture detector (GC-μECD). The mass spectrometer (MS) was operated in electron impact ionization mode with electron energy of 70 eV. The ion source, quadruple and transfer line temperatures were held at 230, 150 and 280° C, respectively. Target compounds were monitored in selected ion monitoring (SIM) mode.

Procedure types used for quality assurance and quality/control (QA/QC) were as follows: method blank control (procedural blank samples), parallel sample control (duplicate samples), solvent blank control, and basic matter control (US EPA, 2000). The spiked samples containing internal standard compounds were analysed simultaneously with soil samples. A procedural blank and a replicate sample were run with every set of 12 samples analyzed to check for contamination from solvents and glassware. The limits of detection (LODs) were based on 3:1 S/N ratio. TCmX and PCB 209 were spiked as surrogate standards to judge procedural performance. The surrogate recoveries for TCmX and PCB 209 were 77.8 ± 19.0 % and 89.3 ± 20.3 %, respectively. The relative standard deviation (RSD) was less than 10%. All OCPs concentrations were expressed on an air-dried weight basis.

2.4. Geostatistical and multivariate analysis

OCPs associations and possible sources were identified by univariate and multivariate statistical analyses as well as diagnostic ratios, compositional biplot and robust factor analysis. Compositional biplot and robust factor analysis allowed to minimize and/or eliminate the presence of outliers and spurious correlation (Pawlowsky-Glahn and Buccianti, 2011; Filzmoser et al., 2012). DDT and HCH compounds were chosen for the multivariate computation both for their high toxicity levels, and for their proven predominance in Italian soils and air (e.g., Estellano et al., 2012; Pozo et al., 2016; Qu et al., 2016). Biplot statistical analysis (Gabriel, 1971) was used to display both samples and variables of the data matrix in terms of the resulting scores and loading (Pison et al., 2003; Otero et al., 2005). For a full description of compositional biplot, several examples are available in the literature (e.g., Maronna et al., 2006; Filzmoser et al., 2008, 2009; Hron et al., 2010; Thiombane et al., 2018). Factor analysis (FA) was used to explain the correlation structure of the variables through a reduced number of factors (Reimann et al., 2002). This has been successfully employed to evaluate the potential origins of the compounds in relation to their main hypothetical sources (Reimann et al., 2002; Jiang et al., 2009). Isometric logratio transformation (ilr) was applied on raw data prior to multivariate analysis (Filzmoser et al., 2009). R-

mode factor analysis was also performed, and the different factors obtained studied and interpreted in accordance with their presumed sources (Reimann et al., 2002, Albanese et al., 2007).

Two main open-source R packages for statistical software were used: "Compositions" (Van Den Boogaart et al., 2011) and "Robcompositions" (Templ et al., 2011). OCPs concentrations and factor score values were mapped for image-patterns recognition using GeoDAS (Cheng et al., 2001) and ArcGIS (ESRI, 2012) software. GeoDAS™ was used to produce dots and interpolated geochemical maps using the multifractal inverse distance weighted (MIDW) algorithm (Cheng et al., 1994; Lima et al., 2003). The concentration–area (C–A) fractal method was applied to classify OCPs concentration and factor score ranges in interpolated images.

2.5. Assessment of contamination level

Assessment of contaminated sites is a preliminary requirement to reveal potential impact of OCPs pesticides on public and ecosystem health (USEPA, 1991; CCME, 1992; Doe, 1995; APAT, 2008; DEFRA, 2011). The "Soil Quality Index" (SoQI) elaborated by the Canadian Soil Quality Guidelines for Protection of Environment and Human Health Agency (CCME, 2007) was implemented to define, classify and prioritize contamination level for each region. Advantages of the SoQI include that it a robust computation based on three factors for its calculations, namely: 1) scope (% of contaminants that do not meet their respective guidelines), 2) frequency (% of individual tests of contaminants that do not meet their respective guidelines), and 3) amplitude (the amount by which the contaminants do not meet their respective guidelines) and it is relatively simple to use. The SoQI was computed using thresholds values for residential areas established by Italian environmental law (D. Lgs. 152/2006) (Table 1) as reference guidelines.

[Table 1 about here]

SoQI index provides a quantitative index based on the amalgamation of the three factors (F_1, F_2 and F_3):

$$\mathrm{F1} = \frac{\sum fx}{\sum Cx} \mathrm{x}100 \qquad (1)$$

F1 (scope) represents the percentage of contaminants that do not meet their respective guideline values, where *fx* is the number of failed contaminants, and Cx is the total number of contaminants

$$\mathrm{F2} = \frac{\sum ftx}{\sum tx} \text{ x } 100 \qquad (2)$$

F2 (frequency) corresponds to the percentage of individual tests that do not meet their respective guidelines values, *ftx* represents the number of failed tests and *tx* symbolizes the number of tests.

$$\mathrm{Ex}_i = \frac{Zt_i}{Gv_i} - 1 \qquad (3)$$

Ex_i or Excursion is the magnitude by which the contaminant is over/below the respective guideline value. This is calculated as a ratio of the failed test value (Zti) and its respective guideline value (Gvi)

$$\mathrm{Ase} = \frac{\sum_{i=1}^{n} Exi}{\sum ftx} \qquad (4)$$

The average amount by which individual tests are out of compliance corresponds to Ase.

$$\mathrm{F3} = \frac{Ase}{0.01Ase + 0.01} \qquad (5)$$

F3 or amplitude represents the amount by which failed test values do not meet their guidelines.

$$\mathrm{SoQI} = 100 - \frac{\sqrt{\mathrm{F1}^2 + \mathrm{F2}^2 + \mathrm{F3}^2}}{1.732} \qquad (6)$$

And finally, SoQI is calculated by taking the square root of the sum of squared factors divided by 1.732 and extracting it from 100. The 1.732 normalizes the SoQI to a range between 0 and 100. The proposed classes are: very low contamination (90-100), low contamination (70-90), medium contamination (50-70), high (30-50) and very high contamination (0-30).

3. Results and discussion

3.1. Residues and pollution sources of OCPs

3.1.1. OCPs

Total OCPs residues in soils ranged from “no detected” (nd) to 1043.98 ng/g with a mean of 29.91 ng/g, and from nd to 1914.1 ng/g with a mean of 60.16 ng/g in urban and rural area, respectively (Table 2).

[Table 2 about here]

The coefficient of variation (CV) ranged from 0.27 to 8.72, and from 1.87 to 6.47 in urban and rural areas, respectively, reflecting a significant spatial variation.

Endosulfan was the most dominant group accounting for 44.42% of the total OCPs, followed by DDTs with 17.60%, Drins (15.75%), methoxychlor (12.17%), HCHs (6.08%), Chlordane related-compounds (3.53%) and HCB (0.55%) in urban areas (Fig. 2). In agricultural areas abundances were in the order: Drins (39.46%) > DDTs (29.94%) > methoxychlor (18.22%) > Endosulfan (5.12%) > HCHs (5.06%) > Chlordanes (1.40) > HCB (0.79%).

[Figure 2 about here]

3.1.2. Total DDT and derived metabolites

The total concentration of DDTs ranged from nd to 56.97 ng/g (mean = 5.26 ng/g - urban), and from nd to 632.95 ng/g (mean = 18.01 ng/g - rural). The highest DDTs concentrations in urban area, ranging from 24.82 to 56.97 ng/g, were found in the Sarno Basin (Campania), Apulia (Bari and Foggia) and Abruzzo (Fig. 3A). In contrast, the highest DDTs concentrations of rural areas, ranging from 400 to 628 ng/g, were found around Naples (Campania) where the vast majority of intensive agricultural land is located (Fig. 3B). In particular, total DDTs concentration presented a significantly skewed distributions as well as clear “outliers” (Figs. 3C and 3D). The latter, observed in rural areas around Naples (Campania – Fig 3D), can be considered as anomaly concentrations, which could be linked to the input of DDT through agricultural activities. Campania and Apulia are well known for their large vineyards and olives plantations on their hills and along coastal areas (Costantini and Dazzi, 2013; ISPRA, 2014a), and high DDTs residues may originate from agricultural activities in these areas. As a general observation, urban areas for this study showed lower DDTs residues compared to those reported in similar studies such as that on Beijing urban park soils (Li et al., 2008). On the other hand, some rural areas revealed much higher DDTs residues compared to those reported in counterparts studies (Table 3).

[Table 3 about here]

Technical DDT is made up of six congeners compounds such as p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD and o,p'-DDD. Moreover, it contains 65-80% of p,p'-DDT, 15-21% of o,p'-DDT, up to 4% of p,p'-DDD and impurities (Metcaft, 1995). In nature, p,p'-DDE and p,p'-DDD are the two main products of dechlorination of p,p'-DDT by microorganisms and/or physico-chemical properties of soil (Pfaender and Alexander, 1972; Mackay et al., 1992). More recently, dicofol has been introduced, which is structurally similar to DDT and contains high impurity of DDT-related compounds (25% of o,p'-DDT) (Qiu et al. 2005). The ratios between the parent compound and its metabolite can provide useful information on the DDT sources. For example, a survey on the formulated dicofol in China found that the ratio of o,p'-DDT/p,p′-DDT in air (Qiu et al., 2005) and soil (Yang et al., 2008) was as high as 7.

In this study, of the various compounds, the p,p'-DDT isomer was predominant, with 34.44% (urban) and 49.43% (rural). Its ranges went from nd to 16.98 ng/g (urban) and from nd to 418 ng/g (rural) (Table 2). The p, p'-DDE isomer had the second highest percentage (34.38%) and ranged from nd to 38.58 ng/g (mean = 1.81 ng/g). This was followed by o,p'-DDD (13.18%), o,p'-DDT (6.39%), o,p'-DDE (6.36%), and p,p'-DDD (5.24%) in urban areas. On the other hand, agricultural areas presented a higher dominance of p,p'-DDT (49.43%) followed by p,p'-DDE (29.96%) > o,p'-DDT (9.32%) > p,p'-DDD (6.17%) > (o,p'-DDD (3.64%) > o,p'-DDE (1.49%).

[Figure 3 about here]

When using the o,p'-DDT/p,p′-DDT ratio (Fig. 4A), this survey highlighted a broad range of values, from 0.0002 to 214 (mean = 3.46 – urban), and from 0.008 to 16.06 (mean = 0.74 – rural). In general, the vast majority (92.51%) of the urban and rural sampling sites displayed a o,p'-DDT/p,p′-DDT ratio below 7. However, high o,p'-DDT/p,p′-DDT ratio (above 7.0) were found in some locations, mainly within urban areas. Therefore, results point towards a predominance of historical application of technical DDT with the exception of some potential recent use of dicofol for the above highlighted urban areas.

Using the assumption that all p,p'-DDE and p,p'-DDD are degraded products of p,p'-DDT metabolite, the ratio of p,p'-DDT/(p,p'-DDE + p,p'-DDD) can be used to discern between historic applications of technical DDT (ratio < 1), compared to fresh or more recent applications (with ratio > 1) (Jiang et al., 2009). Results for this diagnostic ratio are again showing a significant range (Fig. 4B), from 0.0014 to 55.02 (mean = 4.02 - urban), and from 0.006 to 40.42 (mean = 2.55 – rural). In this case, less than half of the sites (47.2%) presented a ratio below 1. When using a value of 10 as arbitrary threshold for this ratio, a large number of urban areas resulted above it. It can be derived that residues of DDT for this study can be linked to a mixed contribution from historical and recent (illegal) application. The latter

was mostly highlighted in urban areas, similarly to the findings of Estellano et al. (2012), which emphasised the possible use of illegal technical DDT or dicofol in urban areas of the Tuscany region.

[Figure 4 about here]

Total HCHs concentrations (sum of α-HCH, β-HCH, γ-HCH and δ-HCH) ranged from nd to 25.08 ng/g (mean = 1.82 ng/g – urban), and from nd to 47.27 ng/g (mean = 3.04 ng/g – rural) (Table 2). The highest values of HCHs (18.67 to 25.07 ng/g) were found in the urban areas of Bari (Apulia) (with γ-HCH isomer = 14.18 ng/g), and in the agricultural areas in the Frosinone (Latium) and Lecce (Apulia), (from 23.69 to 47.11 ng/g, with β-HCH the predominant metabolite - 20.37 ng/g) (Figs. 5A, B). Low HCHs concentrations (from nd to 2.49) were found in several areas in Tuscany, Umbria, and Marches as well as in Calabria and Sicily, whilst higher values (from 2.49 to 25.07) were found in Latium, Campania and Apulia. These HCHs spatial variations were well captured by the bimodal distributions (Figs. 4C, D) indicating the existence of two different inputs or processes controlling the patterns of HCH in the study area. No outliers were recorded, but significant departure from the mean were instead highlighted (Figs 5C, D).

The β-HCH accounted for 60.25% and 48.31% of the total HCHs, ranging from nd to 5.49 ng/g (urban), and from nd to 20.37ng/g (rural). These values are followed by γ-HCH (21.60%) > α-HCH (12.24%) > δ-HCH (5.91%) in urban, and γ-HCH (21.29%) > α-HCH (18.62%) > δ-HCH (11.78%) in rural soils. The dominance of β-HCH among HCHs isomers may be related to its resistance to degradation, and its persistence for several years in soils (Mackay et al., 1992; Calvelo Pereira et al., 2006). High residue of β-HCH isomer in rural soils of the Frosinone district (Latium) could be linked to the high contamination level of β-HCH found in the sediments of the Sacco River valley (Latium), polluted by a nearby industrial landfill percolations containing by-products of Lindane (Bianconi et al., 2010; Battisti et al., 2013).

When compared to HCHs concentrations in European soils such as those found in natural areas from northern France (Villanneau et al., 2011), in agricultural soils from central Germany (Manz et al., 2001) and rural soils from southern Poland (Falandysz et al., 2001), the findings of this study reveal higher levels in comparison. On the other hand, this study presents lower levels compared to other studies, such as those related to agricultural soils of the Nagaon District (Mishra et al., 2012) and urban park of Beijing (Li et al., 2008), which highlighted HCHs concentrations ranging from 98 to 1945 ng/g, and 0.25 to 197 ng/g, respectively.

[Figure 5 about here]

Technical HCHs (60-70% α-HCH, 5-12% β-HCH, 10-12% γ-HCH, 6-10% δ-HCH and impurities) and Lindane (99% γ-HCH) are two commercial pesticides compounds that are restricted for application in Italy through European Directive in 2000 (Persistent organic pollutants amending Directive 79/117/EEC). HCH isomers have different fate and behaviour in environment. In particular, α- and γ-HCH isomers can be transformed by sunlight and through biodegradation into β-HCH, which is easily absorbed and more difficult to be evaporated from soil (Mackay et al., 1992; Calvelo Pereira et al., 2006). Studies revealed that the spatial arrangement of chlorine atoms in the β-HCH molecule protects the compound from a microbial degradation (e.g., Walker, 1999). To distinguish application of technical HCH from a use of Lindane, the diagnostic ratio of α/γ-HCH has been successfully used (Zhang et al., 2004), with ratios from 4.64 to 5.83 being related to application of technical HCH and nearly zero for Lindane applications (Zhang et al., 2004). Results for this study highlighted α/γ-HCH ratios ranging from 0.06 to 568 (mean = 12.96 – urban), and from 0.09 to 78.19 (mean = 4.19 – rural) (Fig. 6A). A proportion of 35.2% of the samples sites presented α/γ-HCH ratio below 1, 32.9% between 1 to 4.64, 12.2 % between 4.64 and 5.83, and 9.2% a ratio above 5.83, mostly in urban areas. The 22% of the sampling sites showing a ratio of α/γ-HCH above 4.64 can possibly be linked to applications of technical DDT.

The ratios of α/-β-HCH ranged from 0.002 to 822 (mean = 19.3 – urban), and from 0.005 to 180 (mean = 8.21 – rural) (Fig. 6B). Here a proportion of 52.6% of the sampling sites presented α/β-HCH ratio below 1.0. The findings seem to indicate both historical application and (illegal) recent use of technical HCH in soils of the survey area. Assessment of OCPs in air samples from the Tuscany region (Estellano et al., 2012) revealed possible illegal use of technical HCH or Lindane in some urban areas.

[Figure 6 about here]

3.1.3. Drins

Dieldrin, Aldrin and Endrins are collectively called Drins or Drin pesticides and were synthesized from pentadiens obtained as secondary products of petro-chemistry through the Diels-Alder reaction (Oppolzer, 1991). They were primarily used as an insecticide, as well as a rodenticide and piscicide. Total Drins (sum of Dieldrin, Aldrin, Endrin, Endrin aldehyde, and Endrin Ketone) for this study ranged from nd to 82.5 ng/g (urban) and from nd to 1212 ng/g (rural). The highest urban concentrations, ranging from 31.85 to 82.5 ng/g, were found in Apulia (Bari and Foggia) and Abruzzo, whereas rural areas in the Sarno Basin (Campania) and Lecce (Apulia) presented high Drins values, ranging from 120.2 to 1212 ng/g (Figs. 7A, B). Statistically abnormal distributions and outliers were observed both in urban areas and in rural areas (Figs 7C and D).

Among Drins, Endrin Ketone was the predominant compound accounting for 80.28% (urban) and 93.71% (rural), ranging from nd to 82.16 ng/g (urban), and from nd to 1199 ng/g (rural) (Table 2). Endrin Ketone is the final photodegradation product of Endrin and Endrin Aldehyde, and is difficult to further degrade (Fan and Alexeeff, 1999). These results may indicate that the Drins residues in soils are mainly the result of historical application across the study area. In comparison with other studies, for example with reported values from northern France (Villanneau et al., 2001), the present survey showed higher concentrations of Drins in urban and rural areas.

[Figure 7 about here]

3.1.4. Chlordanes related-compounds

Technical Chlordane is generally used for insecticides, herbicide and termicides, and is a mixture of more than 140 related compounds (Dearth and Hites, 1991). Sixty to 85% of technical chlordane is made up by stereoisomers cis- and trans-chlordane with a mixture of minor compounds such as Heptachlor, Heptachlor epoxide, cis and trans-nonachlor (Parlar et al., 1979). In this study, total concentrations of Chlordane related compounds (sum of cis-chlordane, trans-chlordane, Heptachlor and Heptachlor-epoxide) ranged from nd to 12.46 ng/g (mean = 1.05 ng/g – urban), and from nd to 14.68 ng/g (mean = 0.84 ng/g – rural). High urban concentrations of Chlordanes were found in Campania and Bari (Apulia), Palermo (Sicily), Grosseto (Tuscany), ranging from 10.03 to 12.46 ng/g, whilst large rural Chlordanes values were found in Tuscany, Campania (Naples) and Sicily showed, ranging from 6.11 to 14.68 ng/g (Figs. 8A, B). These results were confirmed by the presence of statistically abnormal distributions of Chlordane related compounds and, by one outlier (anomaly - Figs. 8C, D).

Among Chlordane related compounds, Heptachlor epoxide was the prevalent with 58.37% (urban) and 67.56% (rural). Heptachlor epoxide is explained as an oxidation and biodegradation product of Heptachlor which has been used in the past for killing insects in households, buildings, and on food crops, especially corn (Pornomo et al., 2013). Chlordane related compounds have been banned in 1988 (ATSDR, 1995). Thus, large Heptachlor epoxide concentration, and mean values of Heptachlor/Heptachlor epoxide ratio equal to 0.23 (urban) and 0.14 (rural) point towards historical application of the commercial Chlordane. However, when compared to similar studies, such as that conducted by Bidleman et al. (2004) in farmland of the Southern of USA (Chlordane related compounds concentration ranging from 0.05 to 5.1 ng/g), the results from this study seem to suggest extremely extensive applications made in some parts of the studied area.

425 [Figure 8 about here]

426

427 3.1.5. Endosulfans

428 Endosulfan is a cyclodiene pesticide used worldwide to control pests in non-food crops (cotton, tobacco,
429 timber, and ornamental plants), food crops such as vegetables, fruits, corn, and cereals and a control a
430 wide variety of insects and mites (ATSDR, 2000). Italy is the second consumer of Endosulfan in
431 European Union with 20% of the total volume, after Spain (Endosulfan Preliminary Dossier, 2003).
432 Technical endosulfan was globally banned under the Stockholm Convention (2011) because of its
433 threats to human health and the environment. Endosulfan is made up α- and β-endosulfan isomers that
434 are fairly resistant to degradation and persistent in the environment. Endosulfan sulfate is the
435 degradation product of Endosulfan, and it is a more hydro-soluble metabolite and susceptible to
436 photolysis (Cerrillo et al., 2005).

437 In this survey, total Endosulfan (sum of α-endosulfan, β-endosulfan, and endosulfan sulfate) ranged
438 from nd to 904.21 ng/g (mean = 13.25 ng/g) accounting for 44.32% of the total OCPs in urban areas,
439 and from nd to 92.99 ng/g (mean = 3.08 ng/g) accounting for 5.12% of total OCPs in rural area. High
440 Endosulfan concentrations were found in the urban area of Bari (Apulia), ranging from 71 to 904.21ng/g
441 and in rural areas of Lecce (Apulia) from 55.32 to 92.99 ng/g (Figs. 9A, B). These values are extremely
442 large if compared to those found in natural areas of the Northern France (ranging from nd to 1.84 ng/g -
443 Villanneau et al., 2001). Statistical distributions showed both outliers as well as abnormal behaviour of
444 Endosulfans concentrations (Fig. 9C, D), which could be associated with the diverse chemical
445 processes that may affect endosulfan compound behaviour in soils medium. Since α-endosulfan
446 decomposes more easily than β-endosulfan in soil, the ratio of α/β-endosulfan < 2.33 may be used to
447 judge the age of their residues in soil (Jennings and Li., 2014; Jia et al., 2010). In urban areas, α-
448 endosulfan isomer constituted 69.59% of the total endosulfan followed by β-endosulfan with 19.36%
449 and endosulfan sulphate (11.05%), and the ratio of α/β-endosulfan ranged from 0.05 to 312.9 (mean =
450 22.44). Endosulfan sulphate was the predominant compound in rural areas (84.58%), followed by β-
451 endosulfan and α-endosulfan, and the ratio of α/β-endosulfan ranged from nd to 40 (mean = 1.59).
452 These results strongly suggest a recent (illegal) use of technical endosulfan in urban areas, especially in
453 Apulia. In contrast, results for rural areas seem to point to historical application. The relatively recent
454 restriction of technical endosulfan (Stockholm Convention, 2011) and its uses in Italy until December
455 2007 may explain why it was still found in high proportion in the soils of the survey area (Pozo et al.,
456 2016; Qu et al., 2017).

457

[Figure 9 about here]

3.1.6. HCB and methoxychlor

HCB was listed among the first group of persistent OCPs compounds in the Stockholm Convention (Stockholm Convention, 2005), even though it has been restricted since 1985 in the European Union countries (Barber et al., 2005). It has been used as fungicide to control bunt on wheat, and seed treatment of onions and sorghum (Courtney, 1979). The values of HCB in this survey ranged from 0.01 to 2.39 ng/g (mean = 0.16 ng/g – urban), and from nd to 13.37 ng/g (mean = 0.47 ng/g – rural). HCB made up 0.55% (urban) and 0.79% (rural) of the total OCPs concentrations. Several studies reported that HCB is still used as a by-product or impurity in several chemical compounds, including chlorinated pesticides such as Lindane (Pacyna et al., 2003; Barber et al., 2005). Pearson correlation coefficient between HCB and γ-HCH compounds showed a slight correlation (r=0.44), which may suggest that HCB could be partially related to input of technical HCH or Lindane in the study area.

Most methoxychlor enters the environment when it is applied to forests, agricultural crops, and farm animals as insecticide (US EPA, 1991). It is one of the few organochlorine pesticides that has undergone an increase in its use since the ban on DDT, but methoxychlor was finally listed as banned OCPs pesticides by the United Nations Environmental Program (UNEP) (Stockholm Convention, 2011). In this study, the concentrations of methoxychlor ranged from nd to 53 ng/g (mean = 3.64 ng/g – urban) and from nd to 521 ng/g (mean of 10.96 ng/g – rural). When compared to other studies, the mean concentration of the methoxychlor (10.96) found in rural areas is comparable to that from agricultural soils of central China (Zhou et al., 2013), but bigger than that found in southern Mexico (Cantu-Soto et al., 2011) and soils from the hilly areas of Nepal (Yadav et al., 2017).

3.2. Compositional Biplot and robust Factor analysis

Compositional biplots explained 66.9% (PC1-PC2) and 61.5% (PC1-PC3) of the variability (Fig. 10).

[Figure 10 about here]

The sum of DDTs (DDTs) p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD may be considered a variables association (A), due to the vicinity of their vertices and their rays pointing to the same direction. Among the associations, DDTs and p,p'-DDE displayed the highest vector length (communality - Fig. 10A). It was possible to discriminate DDTs variables and highlights two sub-groups based to their chemical structures (Fig. 10B):

- $A_{1,}$ formed by o,p'-DDT and o,p'-DDD (superimposition of vertices and low communalities, and
- A_2, formed by p,p'-DDT, p,p'-DDE, p,p'-DDD (proximity and high communality).

Furthermore, the o,p'-DDE variable presented a high length vector and it was separated from other DDTs metabolites. These findings point towards a significant interrelationship between DDT isomers. High lengths of p,p'-DDTs metabolites could be associated with a dominant input of technical DDT in soils of the study area (Qu et al. 2016). Low communalities and superimposition of the o,p'-DDT and o,p'-DDD variables may also be associated with the use of dicofol which contains more o,p'-DDTs metabolites (Qi et al., 2005). Moreover, the high length of the o,p'-DDE vector and its disassociation to others DDTs isomers may illustrate its specific behaviour in soil based on its specific physico-chemical properties (Solubility, partition coefficient, and vapour pressure) (Pfaender and Alexander, 1972).

Another variables association (B) made by α-HCH, γ-HCH and δ-HCH was highlighted (Fig. 10A). This was also characterized by the vicinity of their vertices with their vectors being superimposed to one another. This configuration can be associated to a similar behaviour of these three isomers in the soils of the study area. In fact, α-HCH, γ-HCH and δ-HCH metabolites are the main compounds related to the commercial technical HCH (Senthil Kumar et al., 2001), which is reflected by how α-HCH and δ-HCH vectors are geometrically symmetric respect to the HCHs vector (Fig. 10B). This spatial configuration illustrates their similar behaviour in the soils of the study area. The β-HCH variable is marked by a high communality, and its vector forms 90° with the (B) variables association (Fig. 10A). These results seem to suggest that the β-HCH compound has a different fate and behaviour in soils compared to other HCH metabolites. Moreover, the high communality and disassociation of β-HCH respect to other HCH metabolites could explain its persistence to degradation and its accumulation in soil of the study area (Jiang et al., 2009).

Factor analysis was performed to determine the correlation between DDT and HCH isomers which further revealed the possible sources of these compounds. Factor loadings and total variances of individual OCPs were computed to facilitate the interpretation (Table 4). DDT and HCH metabolites of the three-factor model were separated by positive and negative loadings and sorted in descending order:

[Table 4 about here]

- Urban sites

F_1: o,p'-DDT, p,p'-DDD, - (γ-HCH, α-HCH)

F_2: p,p'-DDD, - (δ-HCH, β-HCH)

F_3: p,p'-DDT, - (o,p'-DDE)

- Rural sites

F_1: p,p'-DDD, o,p'-DDT, o,p'-DDD, - (γ-HCH, α-HCH)

F_2: p,p'-DDE, o,p'-DDE, - (β-HCH)

F_3: o,p'-DDD, - (p,p'-DDT)

Factor scores values for F1, ranging from –3.78 to 1.64 (urban), and –2.75 to 2.94 (rural), were plotted to represent their spatial distribution (Fig. 11). High urban factor score values (ranging from 1.26 to 1.62), associated mainly with o,p'-DDT (0.84) and p,p'-DDD (0.76) compounds, were found in Frosinone (Latium), in Foggia (Apulia), in southeastern coastal area of Calabria and in the Sicily region (Palermo and Gela) (Fig. 11A). High factor loading of the o,p'-DDT isomer (0.84), explained by its dominance in urban soils, may be attributed to the application of dicofol, containing high o,p'-DDT residue. Further increase of p,p'-DDD (0.76) isomer in these areas was relatively significant and might be related to degradation processes of DDT compounds. Low urban factor scores (< to -1.60), tied to α-HCH (-0.69) and γ-HCH (-0.68), were mainly observed in Calabria and Marches. These are potentially related to application of technical HCH. The physico-chemical properties of α-HCH and γ-HCH are similar, showing a relatively easy degradation in soils (Mackay et al., 1992; Calvelo Pereira et al., 2006). The highest rural factor score values (ranging from 1.52 to 2.94), associated with p,p'-DDD (0.81), o,p'-DDT (0.79) and o,p'-DDD (0.64) compounds, were found mainly along the coasts (Latium, Campania - Naples,- Calabria, and southern Sicily – Fig. 11B), where intensive agriculture activities such as those carried out in vineyards and olive plantations occur (Corona et al., 2012; ISPRA, 2014a). The higher loading of p,p'-DDD compound can be associated to historical applications of DDT together with a more recent application of dicofol, illustrated by occurrence of o,p'-DDT, and o,p'-DDD isomers in these areas. This is partially in line with the results of Qu et al. (2016) which have indicated that DDT residues in the Campania plain are mainly the result of historical application.

[Figure 11 about here]

F2 factor score values ranged from -2.56 to 2.26 (urban), and -2.16 to 1.92 (rural) (Fig. 12). The urban areas of Grosseto (Tuscany), northern Campania and Taranto (Apulia) displayed the highest factor scores (> 1.90) corresponding to the p,p'-DDE (0.81) isomer (Fig. 12A). These results can be associated to historical application of technical DDT because p,p'-DDE is a degradation product of p,p'-DDT isomer.

The highest F_2 factor scores (ranging from 1.77 to 2.75) were related to p,p'-DDE (0.81) and o,p'-DDE (0.53), and were found in most rural sites in the northern part of the study area and in Naples

(Campania). This may be attributed to historical application of technical DDT, because high factor scores of DDE metabolites are matching their degradations and fate in situ. Low factor scores values (ranging from -2.16 to -1.39) corresponded to β-HCH (-0.77) and were found in rural sites of Frosinone (Latium) (Fig. 12B). This might be related to the dominance or specific behaviour of the β-HCH metabolite in soils of this area. As previously mentioned, high level of the β-HCH isomer was found in soils and sediments from the Sacco River valley (Frosinone), which are polluted by the release of industrial landfill percolations containing by-product of Lindane.

[Figure 12 about here]

Values for the F_3 factor score, ranged from -2.83 to 2.05 (urban) and –3.93 to 2.66 (rural) (Fig. 13). The highest urban factor score values (> 1.23) corresponded to p,p'-DDT (0.79) and were found in Palermo (Sicily), Naples (Campania) and Tuscany (Fig. 13A). This is likely to be related to recent illegal application of technical DDT, which is confirmed by the dominance of the p,p'-DDT isomer in soils of these areas, similarly to what Qu et al. (2016) have found in soils of the Campania plain. Pozo et al. (2016) also highlighted recent use of technical DDT in Palermo (Sicily), whilst an assessment of OCPs pollution sources in urban air of Tuscany revealed possible illegal use of commercial technical DDT (Estellano et al., 2012). Low factor score values (ranging from -2.83 to -1.85) were found in Tuscany, and corresponded to o,p'-DDE. We might preclude that the occurrence o,p'-DDE isomer in Tuscany may related to unknown synthetic chemicals. A follow up study in this region may give reasons of the occurrence of this metabolite in Tuscany soils.

The highest rural factor score values (ranging from 2.09 to 2.66) corresponded to o,p'-DDD in Calabria (Cosenza) and Tuscany (Fig. 13). Low values (ranging from -3.93 to -1.67) were found in rural areas in Basilicata, revealing dominance of p,p'-DDT. These results point towards a mixed input of DDT residues through recent use and historical application in rural areas of Calabria.

[Figure 13 about here]

3.3. Contamination assessment

The SoQI index was used to represent the degree of contamination, and therefore concern, of the studied area (Fig. 14).

[Figure 14 about here]

SoQI values in soils of urban and rural areas of the Tuscany, Umbria, Marches, and Molise are equal to 100 (Fig. 14A, B). This is associated to very low contamination levels, where none of the sampling sites (both in urban and rural soils) presented concentration beyond the threshold values established by Italian environmental legislation (D. Lgs. 152/2006). Similarly, low levels of concern were observed for urban and rural area of Basilicata and Calabria (Fig.14A, B).

Urban soils in Campania (Naples, Sarno Basin), Abruzzo, and Apulia (Foggia and Bari) presented SoQI ranging from 50 to 70, corresponding to a medium contamination level. In addition, rural soils in Latium (Frosinone and Civitavecchia), Abruzzo, and Apulia (Taranto and Manfredonia) also showed the same SoQI (50 – 70).

The lowest urban SoQI value (46.2), associated to a high contamination level, was found in urban soils of the metropolitan area of Foggia. This could be related to the use of OCPs pesticides against pests in urban gardens. For rural areas, instead, the lowest SoQI values (ranging from 30 to 50) were found in soils of Campania (Naples metropolitan area and Sarno Basin) and Apulia (Lecce). This further confirms the observations made previously which linked high contamination levels with intensive agricultural activities such as those occurring in vineyards and olive plantation along the coastal areas.

4. Conclusion

This study presented the results of a regional survey of OCPs compounds conducted in urban and rural soils of 11 administrative regions from central and southern Italy, as part of an on-going project aiming to cover the entire Italian territory. The main findings revealed the concentration of 24 OCPs, ranging from nd to 1043 ng/g (mean = 29.91 ng/g – urban), and from nd to 1914 ng/g (mean of 60.16 ng/g – rural). In particular, high DDTs concentrations were mostly shown in urban and rural soils of Campania and Apulia. Enrichment of HCH was also highlighted in the central regions of the study area, with relatively lower values in the north and southern parts. Furthermore, Endosulfan related compounds and Methoxychlor were found to be 42.32% and 12.17% of the total OCPs in urban areas, respectively, which are likely to be related to recent applications, particularly in Apulia.

Diagnostic ratios of DDTs residues clearly unveiled a dominance of historical application of these compounds in soil, but also a minor (yet significant) more recent illegal use of technical DDT or dicofol mainly in urban areas. A mixed application of HCH was also highlighted, with residues both from historical and recent applications. On the other hand, the different compositions of Drins and Chlordanes related compounds emphasized that the residues of these compounds are mainly related to a historical application. At the same time, recent applications of Endosulfan residues in urban areas

were suggested, together with an historical use of this compound in agricultural soils. Unfortunately, the Italian environmental legislation has not established to date any guideline (threshold) values with regards to Endosulfan residues in soil (see D. Lgs. 152/2006), failing to recognise their potential threat to human health.

These results were also backed up by the findings of the multivariate computations performed on HHT and HCHs residues, pointing out that (1) DDT and HCHs residues could be mainly related to historical but also more recent (illegal) application; (2) occurrence of DDTs residues in soils of the Campania region could be related to historical application of technical DDT; (3) indirect evidence of illegal 'fresh' application of DDT were identified in urban areas of Tuscany, Sicily and Campania; (4) HCH levels in Latium (Frosinone) rural areas could be related to β-HCH metabolite to the anomalous sediments in the Sacco River valley, affected by nearby industrial landfill percolations.

This study should be considered as a first stepping stone (as a regional survey) towards a major investigation on the main sources and levels of OCPs throughout the Italian territory. As such, it is envisaged that the findings will contribute to build OCPs baseline and drive towards an entire coverage of the Italian territory. The survey, which is currently progressing in the remaining 9 regions of northern Italy, has highlighted areas with high concentrations of some OCPs, which can be in part explained by recent (illegal) applications. Even though it was not the scope of this study, this study highlighted some potential human health concerns, which need addressing urgently. Given the associated human health risks and the potential wider implications for the environment, these results strongly point towards follow-up studies to be held in areas of higher contamination levels (Naples and Sarno Basin as well as Foggia and Lecce regions), with a larger number and higher density of soil and air samples. It is also hoped that similar studies will build science-based evidence to be fed back at institutional level for more adequate and comprehensive regulations and, in the long-term, for a full ratification of the Stockholm Convention.

Acknowledgments

This work was sustained by the financial support of the MIUR through two industrial projects: 1) "*Integrated agro-industrial chains with high energy efficiency for the development of eco-compatible processes of energy and biochemicals production from renewable sources and for the land valorisation (EnerbioChem)*" PON01_01966, funded in the framework of Operative National Program Research and Competitiveness 2007–2013 D. D. Prot. n. 01/Ric. 18.1.2010; and 2) "*Development of green technologies for production of BIOchemicals and their use in preparation and industrial application of POLImeric materials from agricultural biomasses cultivated in a sustainable way in Campania Region (BioPoliS)*" PON03PE_00107_1, funded in the framework of Operative National Program Research and

Competitiveness 2007–2013 D. D. Prot. N. 713/Ric. 29/10/2010" (Research Units Responsible: Prof. B. De Vivo).

Reference

Albanese, S., De Vivo, B., Lima, A., Cicchella, D., (2007). Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy). J. Geochem. Explor. 93 (1), 21–34.

Alves, Andréa A. R. et al. (2012). Comparison between GC-MS-SIM and GC-ECD for the determination of residues of organochlorine and organophosphorus pesticides in Brazilian citrus essential oils. J. Braz. Chem. Soc. [online]. 2012, vol.23, n.2, pp.306-314. ISSN 0103-5053. http://dx.doi.org/10.1590/S0103-50532012000200017.ATSDR (Agency for Toxic Substances and Disease Registry) 1995. Chlordane (CAS#12789-03-6). http://www.atsdr.cdc.gov/toxfaqs/tfacts31.pdf (Feb. 26, 2014).

ATSDR (Agency for Toxic Substances and Disease Registry, USA), (2000). Toxicological Profile for Endosulfan. ATSDR, Atlanta, GA,USA.

APAT (Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici), (2008). Criteri metodologici per l'applicazione dell'analisi assoluta di rischio ai siti contaminati. Revisione 2 APAT, Roma,156 pp. http://www.isprambiente.gov.it/ files/temi/siti-contaminati-02marzo08.pdf.

Aramendia, M. A.; Borau, V.; Lafont, F.; Marinas, A.; Marinas, J. M.; Moreno, J. M.; Urbano, F. J. (2007). Determination of herbicide residues in olive oil by gas chromatography–tandem mass spectrometry. Food Chem. 105 (2), 855-861.

Arienzo, M., Albanese, S., Lima, A., Cannatelli, C., Aliberti, F., Cicotti, F., Qi, S., De Vivo, B., (2015). Assessment of the concentrations of polycyclic aromatic hydrocarbons and organochlorine pesticides in soils from the Sarno River basin, Italy, and ecotoxicological survey by Daphnia magna. Environ. Monit. Assess. 187,1-14.

Barber J.L., Sweetman, A.J., Van Wijk, D., Jones, K.C., (2005). Hexachlorobenzene in the global environment: emissions, levels, distribution, trends and processes. Sci. Total Environ. 349, 1-44.

Battisti, S., A. Caminiti, G. Ciotoli et al. (2013). 'A spatial, statistical approach to map the risk of milk contamination by beta-hexachlorocyclohexane in dairy farms'. Geospatial Health 8(1): 77–86.

Bianconi D., De Paolis M.R., Agnello M.C., Lippi D, Pietrini F, Zacchini M, Polcaro C, Donati E, Paris P, Spina S, Massacci A. (2010). Field-scale rhyzoremediation of contaminated soil with hexachlorocyclohexane (HCH) isomers: the potential of poplars for environmental restoration and economical sustainability. In: Golubev IA (ed) Handbook of phytoremediation. Nova Science. Publishers Inc, Hauppauge, pp. 783-794.

688 Bidleman, T.F., Leone, A.D., (2004). Soil-air exchange of organochlorine pesticides in the Southern
689 United States (US). Environmental Pollution 128, 49–57.
690 Calvelo Pereira, R., Camps-Arbestain, M., Rodríguez Garrido, B., Macías, F., Monterroso, C., 2006.
691 Behaviour of α-, β-, γ- and δ-hexachlorocyclohexane in the soil-plant system of a contaminated
692 site. Environmental Pollution, 144, 210-217.
693 Cantu-Soto, E. U., Meza-Montenegro, M. M., Valenzuela-Quintanar, A. I., Felix-Fuentes, A., Grajeda-
694 Cota, P., Balderas-Cortes, J. J., et al. (2011). Residues of organochlorine pesticides in soils
695 from the Southern Sonora, Mexico. Bulletin of Environmental Contamination and Toxicology,
696 87(5), 556–560.
697 CCME. (1992). National classification system for contaminated sites. Report # CCME EPC-CS39E.
698 Canadian Council of Ministers of the Environment, Winnipeg.
699 CCME Canadian Council of Ministers of the Environment. (2007). Soil Quality Index 1.0: Technical
700 Report. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the
701 Environment, Winnipeg.
702 Cerrillo I., Granada A., Lopez-Espinosa M.J., Olmos B., Jimenez M., Cano A., Olea N., Olea-Serrano
703 MF. (2005). Endosulfan and its metabolites in fertile women, placenta, cord blood, and human
704 milk. Environ Res. 98, 233–239.
705 Cheng, Q., Agterberg, F.P., Ballantyne, S.B., (1994). The separation of geochemical anomalies from
706 background by fractal methods. J. Geochem. Explor. 51, 109–130.
707 Cheng, Q., Bonham-Carter, G.F., Raines, G.L., (2001). GeoDAS: A new GIS system for spatial analysis
708 of geochemical data sets for mineral exploration and environmental assessment. The 20th Intern.
709 Geochem. Explor. Symposium (IGES). Santiago de Chile, 6/5-10/5, pp. 42-43.
710 Corona, P., Barbati, A., Tomao, A., Bertani, R., Valentini, R., Marchetti, M., Perugini, L., (2012). Land
711 use inventory as framework for environmental accounting: an application in Italy. IForest-
712 Biogeosciences and Forestry 5 (4), 204. http://dx.doi.org/10.3832/ifor0625-005.
713 Costantini, E.A.C., Dazzi, C., (2013).The Soils of Italy. Springer. pp 354.
714 Coordination de l'information sur l'Environnement Land Cover (Corine Land Cover, Italy) (2012).
715 http://www.pcn.minambiente.it/geoportal/catalog/search/resource/details.page?uuid=%7BA016A8
716 35-D5D8-4089-A9AE-2CC2D74B0C81%7D.
717 Courtney K.D. 1979. Hexachlorobenzene (HCB): a review. Environ Res. 20, 225–66.
718 Dearth, M.A., Hites, R.A., (1991). Complete analysis of technical chlordane using negative ionization
719 mass spectrometry. Environ. Sci. Technol. 25, 245–254.
720 DEFRA (Department for Environment, Food and Rural Affairs), (2011). Guidelines for Environmental
721 Risk Assessment and Management: Green Leaves III. Defra and the Collaborative Centre of

722 Excellence in Understanding and Managing Natural and Environmental Risks, Cranfield
723 University, U.K. 84 pp.
724 DoE (Department of Environment), (1995). A Guide to Risk Assessment and Risk Management for
725 Environmental Protection. HSMO, London.
726 Donnarumma L., Pompi, V., Faraci, A., Conte, E. (2009). Dieldrin uptake by vegetable crops grown in
727 contaminated soils, J. Environ. Sci. Health, Part B. 44, 449-454.
728 Endosulfan Preliminary Dossier, (2003). Umweltbundesamt, Berlin, pp 55.
729 Eurostat. (2014). http://ec.europa.eu/eurostat/statistics-explained/index.php/Pesticide_sales_statistics.
730 explained/index.php/Pesticide_sales_statistics#Data_sources_and_availability
731 ESRI (Environmental Systems Research Institute), (2012). ArcGIS Desktop: Release 10. Redlands, CA:
732 Environmental Systems Research Institute.
733 Estellano V.H., Pozo, K., Harner, T., Corsolini, S., Focardi, S., (2012). Using PUF disk passive samplers
734 to simultaneously measure air concentrations of persistent organic pollutants (POPs) across the
735 Tuscany. Region, Italy. Atmos Pollut Res. 3, 88-94.
736 Falandysz, J., Brudnowska, B., Kawano, M., Wakimoto, T., (2001). Polychlorinated biphenyls and
737 organochlorine pesticides in soils from the southern part of Poland. Arch. Environ. Contam.
738 Toxicol. 40, 173-178.
739 Fan, M.A., and G.V. Alexeeff, (1999). Public Health Goal for Endrin in Drinking Water. Office of
740 Environmental Health and Hazard Assessment. Environmental Protection Agency,
741 California, pp: 5-6.
742 Fang, Y., Nie, Z., Die, Q., Tian, Y., Liu, F., He, J., Huang, Q., (2017). Organochlorine pesticides in soil,
743 air, and vegetation at and around a contaminated site in southwestern China: concentration,
744 transmission, and risk evaluation. Chemosphere. 178, 340-349.
745 https://doi.org/10.1016/j.chemosphere.2017.02.151.
746 Filzmoser, P., Hron, K., (2008). Outlier detection for compositional data using robust methods. Math.
747 Geosci. 40 (3), 233–248.
748 Filzmoser, P., Hron, K., Reimann, C., (2009). Principal component analysis for compositional data with
749 outliers. Environmetrics, 20 (6), 621–632.
750 Filzmoser, P., Hron, K., Tolosana-Delgado, R., (2012). Interpretation of multivariate outliers for
751 compositional data. Computers & Geosciences. 39, 77-85.
752 Gabriel, K.R., 1971. The biplot graphic display of matrices with application to principal component
753 analysis. Biometrika 58 (3), 453-467.
754 Hron, K., Templ, M., Filzmoser, P., (2010). Imputation of missing values for compositional data using
755 classical and robust methods. Comput. Stat. Data Anal. 54 (12), 3095–3107.

ISPRA (2014a), Audizione dell'Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA) presso la Commissione Agricoltura, congiuntamente con la Commissione Ambiente, della Camera sul consumo di suolo, Audizione, Roma, 27/2/2014. [Italian]

ISPRA, (2014b). Il consumo di suolo in Italia. Retrieved from http://www.isprambiente.gov.it/it/pubblicazioni/rapporti/il-consumo-di-suolo-in-italia [in Italian]

ISTAT (2013) indicatori ambientali urbani, Anno 2011. ISTAT, Roma [Italian].

ISTAT (2016). Resident Population on 1st January, 2017. https://www.istat.it/en/population-and households.

Jayaraj, R.; Megha, P.; Sreedev, P. (2016). Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdisciplinary Toxicology. 9(3-4): 90–100, doi:10.1515/intox-2016-0012.

Jennings, A., Li, Z., (2014). Scope of the worldwide effort to regulate pesticide contamination in surface soils. J. Environ. Manag. 146, 420-443.

Jia, H., Liu, L., Sun, Y., Sun, B., Wang, D., Su, Y., Kannan, K., Li, Y.-F., (2010). Monitoring and modelling endosulfan in Chinese surface soil. Environ. Sci. Technol. 44, 9279–9284.

Jiang, Y.F., Wang, X.T., Jia, Y., Wang, F., Wu, M.H., Sheng, G.Y., Fu, J.M., (2009). Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. J. Hazard Matter 170, 989-997.

Kim, K. H., Kabir, E. and Jahan, S. A. (2017). Exposure to pesticides and the associated human health effects. Sci. Total Environ. 575, 525–535.

Legislative Decree 152/2006 Decreto Legislativo 3 aprile (2006). n. 152, "Norme in materia ambientale". Gazzetta Ufficiale n. 88 14-4-2006, Suppl Ord n. 96.

Li X.H., Wang, W., Wang, J., Cao, X.L., Wang, X.F., Liu, J.C., (2008). Contamination of soils with organochlorine pesticides in urban parks in Beijing, China. Chemosphere. 70, 1660–1668.

Lima, A., De Vivo, B., Cicchella, D., Cortini, M., Albanese, S., (2003). Multifractal IDW interpolation and fractal filtering method in environmental studies: an application on regional stream sediments of Campania Region (Italy). Appl. Geochem. 18 (12), 1853-1865. Doi: 10.1016/S0883-2927(03)00083-0.

Mackay, D., Shiu, W.Y., Ma, K.C., (1992). Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Compounds, Lewis Publishers, Chelsea, MI.

Manz, M., Wenze, K.D., Dietze,U., 2001.Persistent organic pollutants in agricultural soils of central Germany. Sci. Total Environ. 277,187–198.

Maronna, R., Martin, R., Yohai, V., (2006). Robust Statistics: Theory and Methods. John Wiley pp. 436. ISBN: 978-0-470-01092-1.

790 Metcalf, R.L. (1995). Insect Control Technology. In: Kroschwitz, J. and Howe-Grant, M. (eds.). Kirk-
791 Othmer Encyclopedia of Chemical Technology. Volume 14. New York, NY: John Wiley and Sons,
792 Inc. pp. 524-602.
793 Mishra, K., Sharma, R.C., Kumar, S., (2012). Contamination levels and spatial distribution of
794 organochlorine pesticides in soils from India. Ecotoxicol. Environ. Saf. 76, 215–225.
795 Moeckel, C., Macleod, M., Hungerbuhler, K., Jones, K.C., (2008). Measurement and modelling of diel
796 variability of polybrominated diphenyl ethers and Chlordanes in air. Environmental Science &
797 Technology 42, 3219–3225.
798 Nizzetto, L., Cassani, C., Di Guardo, A., (2006). Deposition of PCBs in mountains: the forest filters effect
799 of different forest ecosystem types. Ecotoxicology and Environmental Safety 63, 75-83.
800 Oppolzer W. (1991) Intermolecular Diels-Alder Reactions. In: Trost BM, Fleming I (eds) Comprehensive
801 Organic Synthesis. Pergamon Press, Oxford, vol 5 chap 4.1.
802 Otero, N., Tolosana-Delgado, R., Solera., A., Pawlowsky-Glahn, V., Canals, A., (2005). Relative vs.
803 absolute statistical analysis of compositions: A comparative study of surface waters of a
804 Mediterranean river. Water Res. 39, 1404–1414.
805 Pacyna J.M., Breivik, K., Munch, J., Fudala, J., (2003). European atmospheric emissions of selected
806 persistent organic pollutants, 1970–1995. Atmos Environ. 37(1), 19–31.
807 PANNA, (2008). Endosulfan Monograph http://www.panna.org/
808 files/PAN%20Int%20Endosulfan%20Monograph.pdf>.
809 Parlar, H., Hustert, K., Gab,S., Korte, F., (1979). Isolation, identification, and chromatographic
810 characterization of some chlorinated Cl0 hydrocarbons in technical chlordane. J Agric Food
811 Chem 27, 278-283.
812 Pawlowsky-Glahn, V., Buccianti, A., (2011). Compositional Data Analysis: Theory and Applications.
813 John Wiley & Sons. pp. 400.
814 Pfaender, F. K., and M. Alexander. (1972). Extensive microbial degradation of DDT in vitro and DDT
815 metabolism by natural communities. J. Agr. Food Chem. 20, 842-846.
816 Pison, G., Rousseeuw, P.J., Filzmoser, P., Croux, C. (2003). Robust factor analysis. J. Multivar. Anal.
817 84, 145-172.
818 Pozo, K., Palmeri, M., Palmeri, V., Estellano, V.H., Mulder, M.D., Efstathiou, C.I., Sara, G.L., Romeo, T.,
819 Lammel, G., Focardi, S., (2016). Assessing persistent organic pollutants (POPs) in the Sicily
820 Island atmosphere, Mediterranean, using PUF disk passive air samplers. Environ. Sci. Pollut. R.
821 23(20), 796-804.
822 Prapamontol, T., Stevenson, D. (1991). Rapid method for the determination of organochlorine pesticides
823 in milk. J. Chromatogr. 552, 249-257

824 Qiu, X., Zhu, T., Yao, B., Hu, J., Hu, S., (2005). Contribution of dicofol to the current DDT pollution in
825 China. Environ. Sci. Technol. 39, 4385-4390.
826 Qu, C., Albanese, S., Chen, W., Lima, A., Doherty, A.L., Piccolo, A., Arienzo, M., Qi, S., De Vivo, B.,
827 (2016). The status of organochlorine pesticide contamination in the soils of the Campanian Plain,
828 southern Italy, and correlations with soil properties and cancer risk. Environ. Pollut. 216, 500-511.
829 Qu, C., Albanese, S., Lima, A., Li, J., Doherty, A.L. Qi, S., De Vivo, B., (2017). Residues of
830 hexachlorobenzene and chlorinated cyclodiene pesticides in the soils of the Campanian Plain,
831 southern Italy, Environmental Pollution, 231(2), 1497-1506.
832 https://doi.org/10.1016/j.envpol.2017.08.100.
833 Reimann, C., Filzmoser, P., Garrett, R., (2002). Factor analysis applied to regional geochemical data:
834 problems and possibilities. Appl. Geochem. 17 (3), 185–206.
835 Reimann C., Birke M., Demetriades A., Filzmoser P., O'Connor P. (Editors) and GEMAS Team, (2014).
836 Chemistry of Europe's agricultural soils — part A: methodology and interpretation of the GEMAS
837 data set. Geologisches Jahrbuch (Reihe B), Schweizerbarth: Hannover, pp. 528.
838 Senthil Kumar, K., Kannan, K., Subramanian, A.N., Tanabe, S., (2001). Accumulation of organochlorine
839 pesticides and polychlorinated biphenyls in sediments, aquatic organisms, birds and bird eggs
840 and bat collected from South India. Environmental Science and Pollution Research. 8, 35-47.
841 Silva, M.H., Carr Jr., W.C., (2009). Human health risk assessment of endosulfan. II: Dietary exposure
842 assessment. Regul. Toxicol. Pharmacol. 56, 18–27.
843 Stockholm Convention on Persistent Organic Pollutants (POPs), (2011). http://chm.pops.int/.
844 Stockholm Convention on Persistent Organic Pollutants (POPs) UNEP: persistent organic pollutants
845 (2001). http://www.pops.int/documents/convtext/ convtext_en.pdf.
846 Stockholm Convention on Persistent Organic Pollutants (POPs). (2005). World Wide Found, Stockholm
847 Convention “New POPs”: screening additional POPs candidates, April 2005, pp. 38.
848 Suchan, P., Pulkrabová, J., Hajslová, J., Kocourek, V., (2004). Pressurized liquid extraction in
849 determination of polychlorinated biphenyls and organochlorine pesticides in fish samples. Anal.
850 Chim. Acta. 520,193–200.
851 Szeto, S.Y., Price, P.M., (1991). Persistence of pesticide residues in mineral and organic soils in the
852 Fraser valley of British Columbia. J. Agric. Food Chem. 39, 1679–1684.
853 Templ, M., Hron, K., Filzmoser, P., (2011). Robcompositions: Robust Estimation for Compositional
854 Data. Manual and Package, Version 1.4.4.
855 Thiombane, M., Zuzolo, D., Cicchella, D., Albanese, S., Lima, A., Cavaliere, M., De Vivo, B., (2018). Soil
856 geochemical follow-up in the Cilento World Heritage Park (Campania, Italy) through exploratory
857 compositional data analysis and C-A fractal model. J. Geochem. Explor. 189, 85–99.

858 UNECE (United Nation Economic Commission for Europe). 2010. Convention on long–range
859 transboundary air pollution. http://www.unece.org/env/lrtap/pops_h1.htm.
860 US EPA, 1991. Risk Assessment Guidance for Superfund: Volume I — Human Health Evaluation
861 Manual (Part B, Development of Risk-Based Preliminary Remediation Goals). U.S. Environmental
862 Protection Agency, Washington, DC. [EPA/540/R-92/003]
863 US EPA, 2000. Ultrasonic Extraction, Test Methods for Evaluating Solid Waste, Method 3550C,
864 Revision 3, US Environmental Protection Agency, Washington, DC.
865 USEPA, 2007. Endosulfan. Hazard Characterization and Endpoint SelectionReflecting Receipt of a
866 Developmental Neurotoxicity Study and Subchronic Neurotoxicity Study. PC Code: 079401. DP
867 Barcode D338576. Reaves, E.,Washington, DC: Office of Prevention, Pesticides a Toxic
868 Substances, U.S. Environmental Protection Agency. April 7, 2007.
869 http://www.epa.gov/pesticides/reregistration/endosulfan/.
870 Van Den Boogaart, K.G., Tolosana-Delgado, R., Bren, R., 2011. Compositions: Analysis. R Package
871 Version 1. pp. 10–12. Available at: http://CRAN.R-project.org/package=compositions.
872 Villanneau, E.J., Saby, N.P.A., Marchant, B.P., Jolivet, C., Boulonne, L., Caria, G., Barriuso, E., Bispo,
873 A., Briand, O., Arrouays, D., 2011. Which persistent organic pollutants can we map in soil using a
874 large spacing systematic soil monitoring design? A case study in Northern France. Science of
875 the Total Environment 409, 3719-3731.
876 Walker, K., Vallero, D.A., Lewis, R.G., 1999. Factors influencing the distribution of lindane and other
877 hexachlorocyclohexane in the environment. Environ. Sci. Technol. 33, 4373–4378.
878 Weinberg, J. 1998. Overview of POPs and need for a POPs treaty. Public forum on persistent organic
879 pollutants-the international POPs elimination network. 1998.
880 WHO, 2003. Health risks of persistent organic pollutants from long–range transboundary air pollution.
881 http://www.euro.who.int/data/assets/ pdf file/0009/78660/e78963.pdf. pp. 252.
882 Yadav, I. C., Devi, N. L., Li, J., Zhang, G., and Breivik, K.: Possible emissions of POPs
883 in plain and hilly areas of Nepal: Implications for source apportionment and health
884 risk assessment, Environ. Pollut., 220, 1289–1300.
885 https://doi.org/10.1016/j.envpol.2016.10.102,2017.
886 Yang, D., Qi, S.H., Zhang, J.Q., Tan, L.Z., Zhang, J.P., Zhang, Y., Xu, F., Xing, X.L., Hu, Y., Chen, W.,
887 Yang, J.H., Xu, M.H., 2012. Residues of organochlorine pesticides (OCPs) in agricultural soils of
888 Zhangzhou City, China. Pedosphere. 22, 178–189.
889 Yang, X. L.,Wang, S. S., Bian, Y. R., Chen, F., Yu, G. F., Gu, C. G., 2008. Dicofol application resulted in
890 high DDTs residue in cotton fields from Northern Jiangsu province, China. Journal of hazardous
891 materials. 150, 92-98.

Z.L. Zhang, J. Huang, G. Yu, et al., 2004. Occurrence of PAHs, PCBs and organochlorine pesticides in Tonghui River of Beijing, China, Environ. Pollut. 130, 249–261.

Zhou, Q., Wang, J., Meng, B., Cheng, J., Lin, G., Chen, J., Zheng, D., Yu, Y., 2013. Distribution and sources of organochlorine pesticides in agricultural soils from central China. Ecotoxicol. Environ. Saf. 93, 163-170.

Table and figure Captions

Figure 1. Land use/land cover of the study area (simplified from Corine Land Cover 2012). Urban (red dots) and rural (blue dots) sampling site locations are displayed.

Figure 2. Variation of individual and total (HCHs, DDTs, Drins, Chlordanes, Endosulfans, OCPs) OCPs concentrations in urban in areas and agricultural soils. Note the logarithmic scale applied on the Y axis.

Figure 3. Distribution of total DDTs in urban (A) and rural (B) areas. The concentration–area (C–A) fractal method was applied to set DDTs ranges. Edaplots (combination of histogram, density trace, one-dimensional scattergram and Box plot) of DDTs raw data in urban (C) and rural areas (D) are displayed.

Figure 4. Scatter diagrams of o,p'-DDT/p,p'-DDT (4A) and p,p'-DDT/(p,p'-DDE +p,p'-DDD) ratios (4B). The different symbology reflects whether the sites were urban (red dots) and rural nature (blue dots).

Figure 5. Spatial distribution of HCHs in urban (5A) and rural (5B) areas. C–A fractal method was applied to set HCHs ranges. Edaplots allow distinguishing occurrence of "outliers" observations in the survey (5C, D) areas.

Figure 6. Scatter diagrams of α/γ-HCH (Fig. 6A) and α/β-HCH (Fig. 6B) ratios.

Figure 7. Spatial distribution of Drins in urban (7A) and rural (7B) areas; the concentration–area (C–A) fractal method was applied to set concentration ranges. Edaplots (7C, D) allow distinguishing occurrence of outlier observations in urban and rural areas.

Figure 8. Distribution of total Chlordane related compounds in urban (8A) and rural (8B) areas. Edaplots (8C, D) reveal abnormal distribution of the dataset and occurrence of an outlier rural area.

Figure 9. Distribution of concentration Endosulfan in urban (A) and rural (B) areas. Edaplots (9C,D) reveal abnormal distribution of the dataset and occurrence of low and high outliers in urban and rural areas.

Figure 10. Robust biplots for the first and second principal components (A) and for the first and third principal components (B) based on DDTs and HCHs investigated compounds.

925 **Figure 11**. Dots and Interpolated factor score maps of the Factor 1 in urban areas (11A) and rural soils
926 (11B). Factor score values ranges are based on C-A (concentration-Area) fractal plot after a min-
927 max normalisation.
928 **Figure 12**. Dots and Interpolated factor score maps of the Factor 2 in urban areas (12A) and rural soils
929 (12B). Factor score values ranges are based on C-A fractal plot after a min-max normalisation.
930 **Figure 13**. Dots and Interpolated factor score maps of the Factor 3 in urban areas (13A) and rural soils
931 (13B). Factor score values ranges are based on C-A fractal plot after a min-max normalisation.
932 **Figure 14**. Spatial distribution of SoQI contamination levels in urban (14A) and rural areas (14B) in the
933 11 regions of the study area.
934 **Table 1**. Organochlorine pesticides guideline thresholds values in soils, fixed by the Italian
935 environmental law (D. Lgs. 152/2006) in residential areas (and/or park areas) and Industrial (or/or
936 commercial) sites.
937 **Table 2**. Descriptive statistics of the 24 OCPs compounds (ng/g) in 148 topsoil samples from urban and
938 rural areas of centre and southern Italy; min, max and CV indicate the minimum, maximum and
939 coefficient of variation of the dataset, respectively.

940 **Table 3**. Total OCPs concentrations (ng/g dry weight) in topsoil of the survey area compared to those
941 found in other studies in the recent literature.

942 **Table 4**. Varimax-rotated factor (three-factor model) using 78 topsoil samples from urban areas and 70
943 samples from agricultural soils; bold entries: loading values over |0.50|.

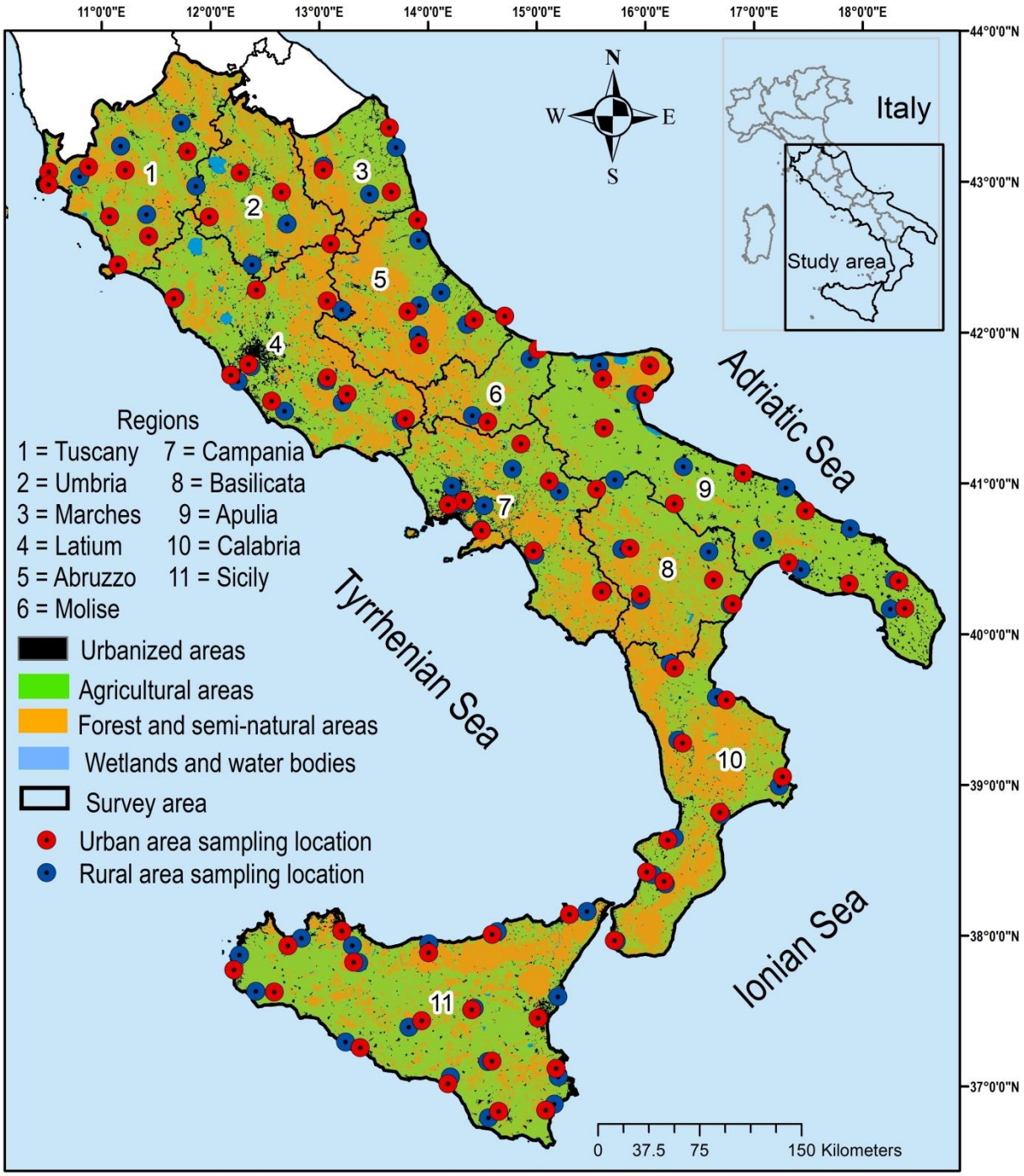
11°0'0"E
12°0'0"E
13°0'0"E
14°0'0"E
15°0'0"E
16°0'0"E
17°0'0"E
18°0'0"E
44°0'0"N
43°0'0"N
42°0'0"N
41°0'0"N
40°0'0"N
39°0'0"N
38°0'0"N
37°0'0"N
N
W
E
S
Italy
Study area
Regions
1 = Tuscany
2 = Umbria
3 = Marches
4 = Latium
5 = Abruzzo
6 = Molise
7 = Campania
8 = Basilicata
9 = Apulia
10 = Calabria
11 = Sicily
Urbanized areas
Agricultural areas
Forest and semi-natural areas
Wetlands and water bodies
Survey area
Urban area sampling location
Rural area sampling location
Adriatic Sea
Tyrrhenian Sea
Ionian Sea
0
37.5
75
150 Kilometers

Figure 1

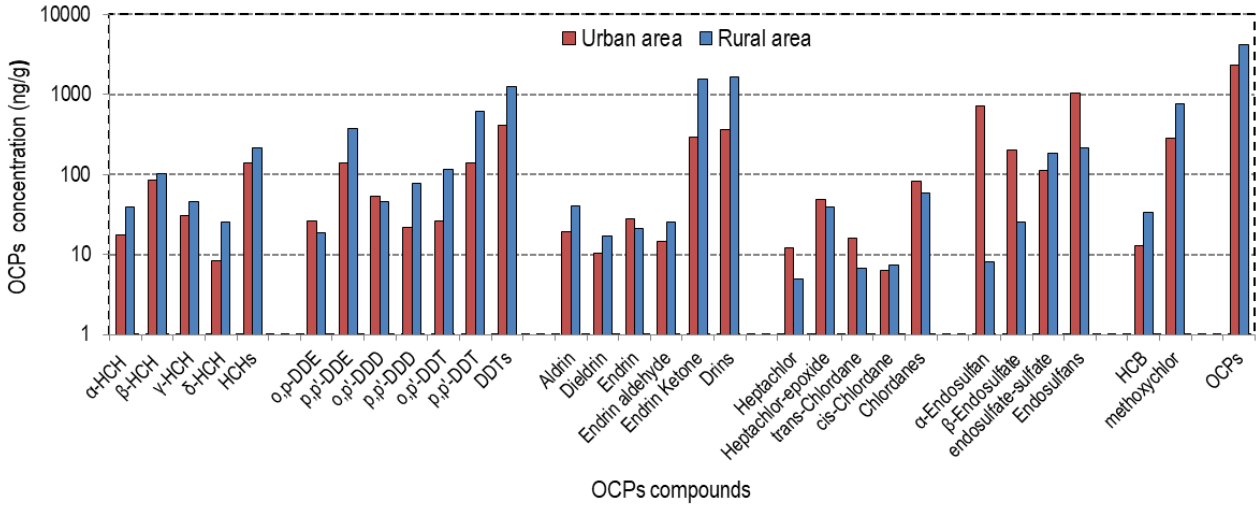
10000
1000
100
10
1
OCPs concentration (ng/g)
Urban area
Rural area
α-HCH
β-HCH
γ-HCH
δ-HCH
HCHs
o,p-DDE
p,p'-DDE
o,p'-DDD
p,p'-DDD
o,p'-DDT
p,p'-DDT
DDTs
Aldrin
Dieldrin
Endrin
Endrin aldehyde
Endrin Ketone
Drins
Heptachlor
Heptachlor-epoxide
trans-Chlordane
cis-Chlordane
Chlordanes
α-Endosulfan
β-Endosulfate
endosulfate-sulfate
Endosulfans
HCB
methoxychlor
OCPs
OCPs compounds

Figure 2

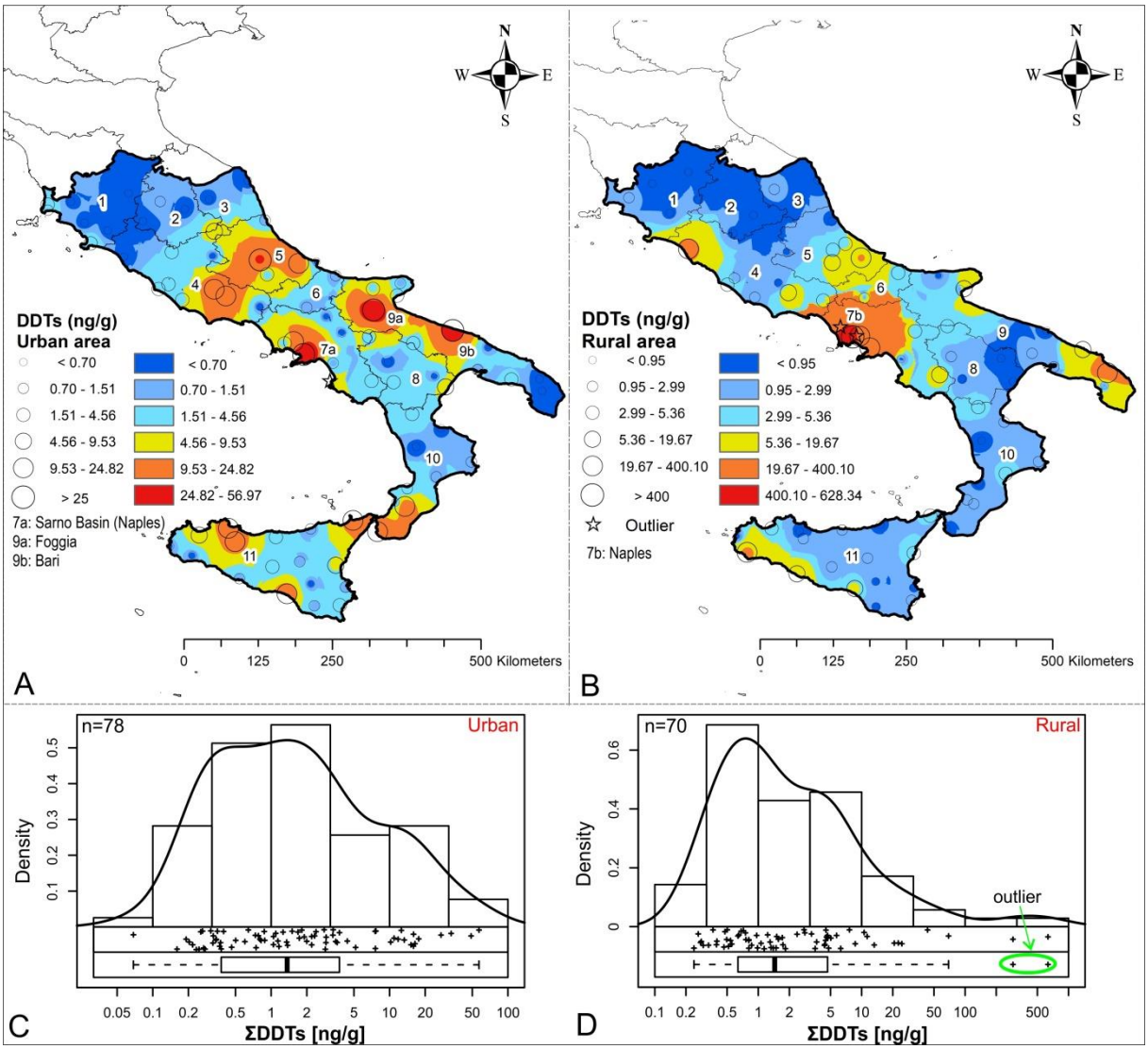
N
W
E
S
DDTs (ng/g)
Urban area
< 0.70
0.70 - 1.51
1.51 - 4.56
4.56 - 9.53
9.53 - 24.82
> 25
24.82 - 56.97
7a: Sarno Basin (Naples)
9a: Foggia
9b: Bari
0 125 250 500 Kilometers
A
DDTs (ng/g)
Rural area
< 0.95
0.95 - 2.99
2.99 - 5.36
5.36 - 19.67
19.67 - 400.10
> 400
400.10 - 628.34
Outlier
7b: Naples
0 125 250 500 Kilometers
B
n=78
Urban
Density
ΣDDTs [ng/g]
C
n=70
Rural
outlier
Density
ΣDDTs [ng/g]
D

Figure 3

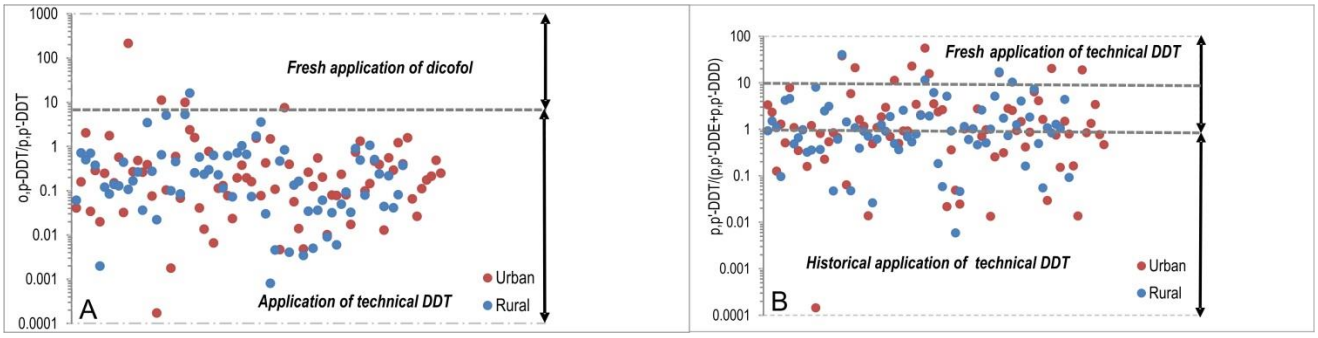
1000
100
10
1
0.1
0.01
0.001
0.0001
o,p-DDT/p,p'-DDT
Fresh application of dicofol
Application of technical DDT
Urban
Rural
A
100
10
1
0.1
0.01
0.001
0.0001
p,p'-DDT/(p,p'-DDE+p,p'-DDD)
Fresh application of technical DDT
Historical application of technical DDT
Urban
Rural
B

Figure 4

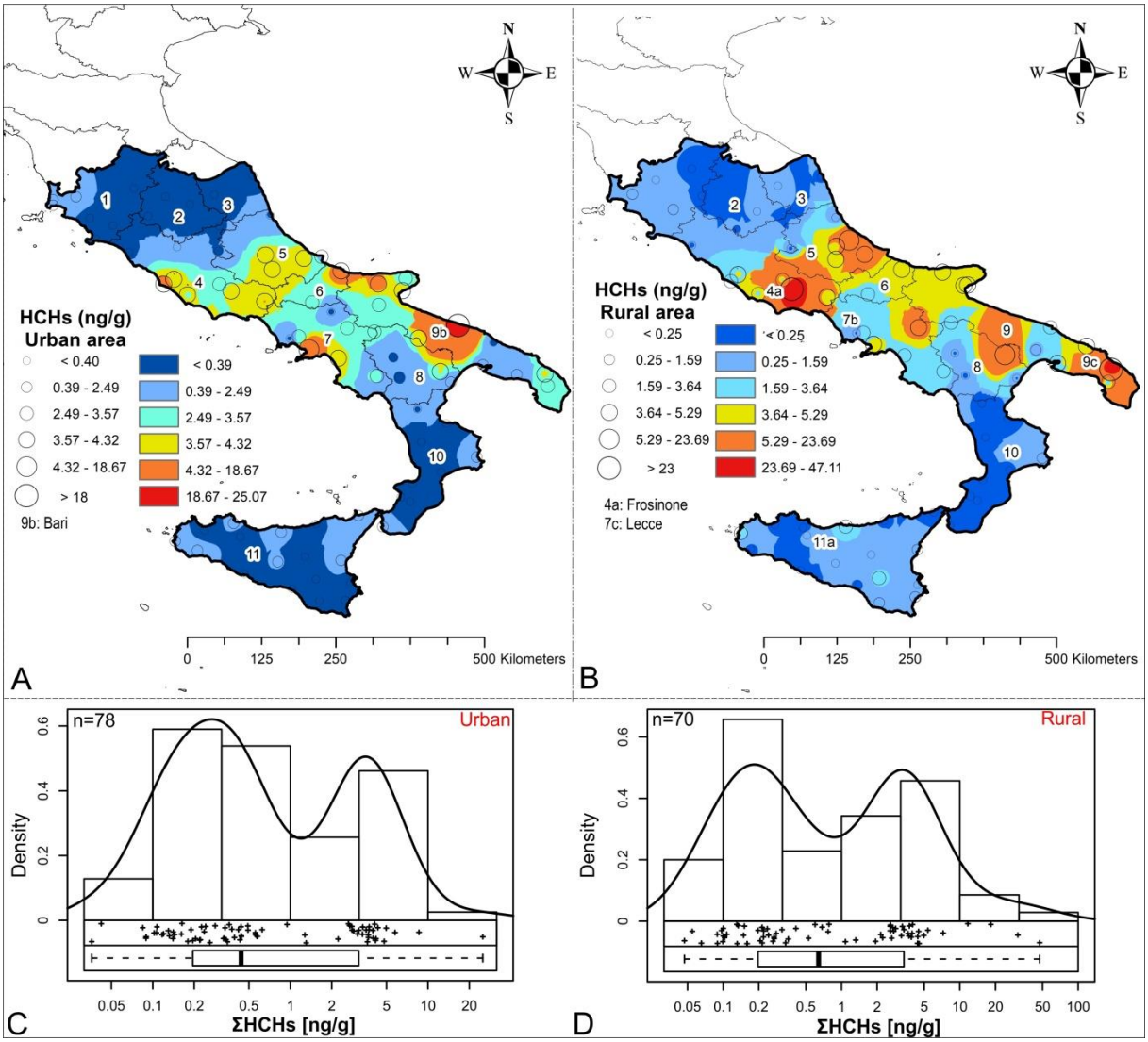
N
W
E
S
HCHs (ng/g)
Urban area
< 0.40
0.39 - 2.49
2.49 - 3.57
3.57 - 4.32
4.32 - 18.67
> 18
< 0.39
0.39 - 2.49
2.49 - 3.57
3.57 - 4.32
4.32 - 18.67
18.67 - 25.07
9b: Bari
0 125 250 500 Kilometers
A
HCHs (ng/g)
Rural area
< 0.25
0.25 - 1.59
1.59 - 3.64
3.64 - 5.29
5.29 - 23.69
> 23
< 0.25
0.25 - 1.59
1.59 - 3.64
3.64 - 5.29
5.29 - 23.69
23.69 - 47.11
4a: Frosinone
7c: Lecce
0 125 250 500 Kilometers
B
n=78
Urban
Density
ΣHCHs [ng/g]
C
n=70
Rural
Density
ΣHCHs [ng/g]
D

Figure 5

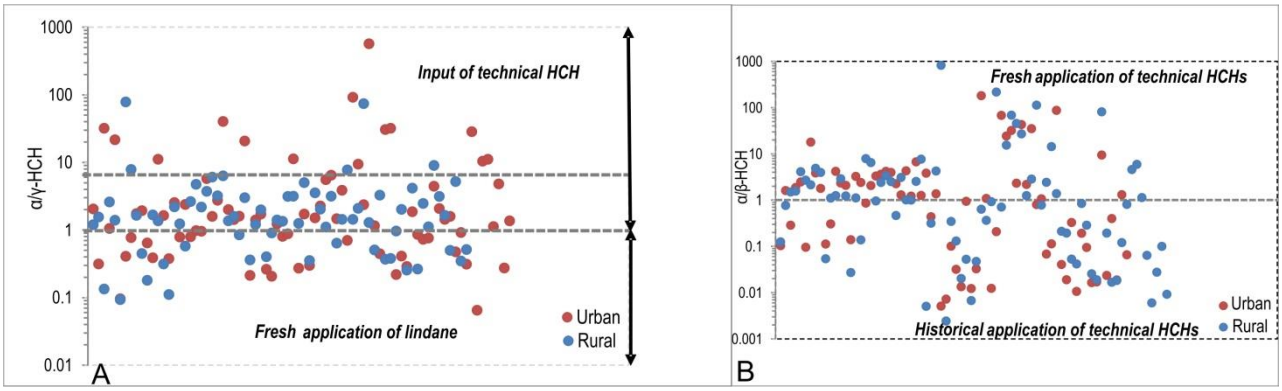
1000
100
10
1
0.1
0.01
α/γ-HCH
Input of technical HCH
Fresh application of lindane
Urban
Rural
A
1000
100
10
1
0.1
0.01
0.001
α/β-HCH
Fresh application of technical HCHs
Historical application of technical HCHs
Urban
Rural
B

Figure 6

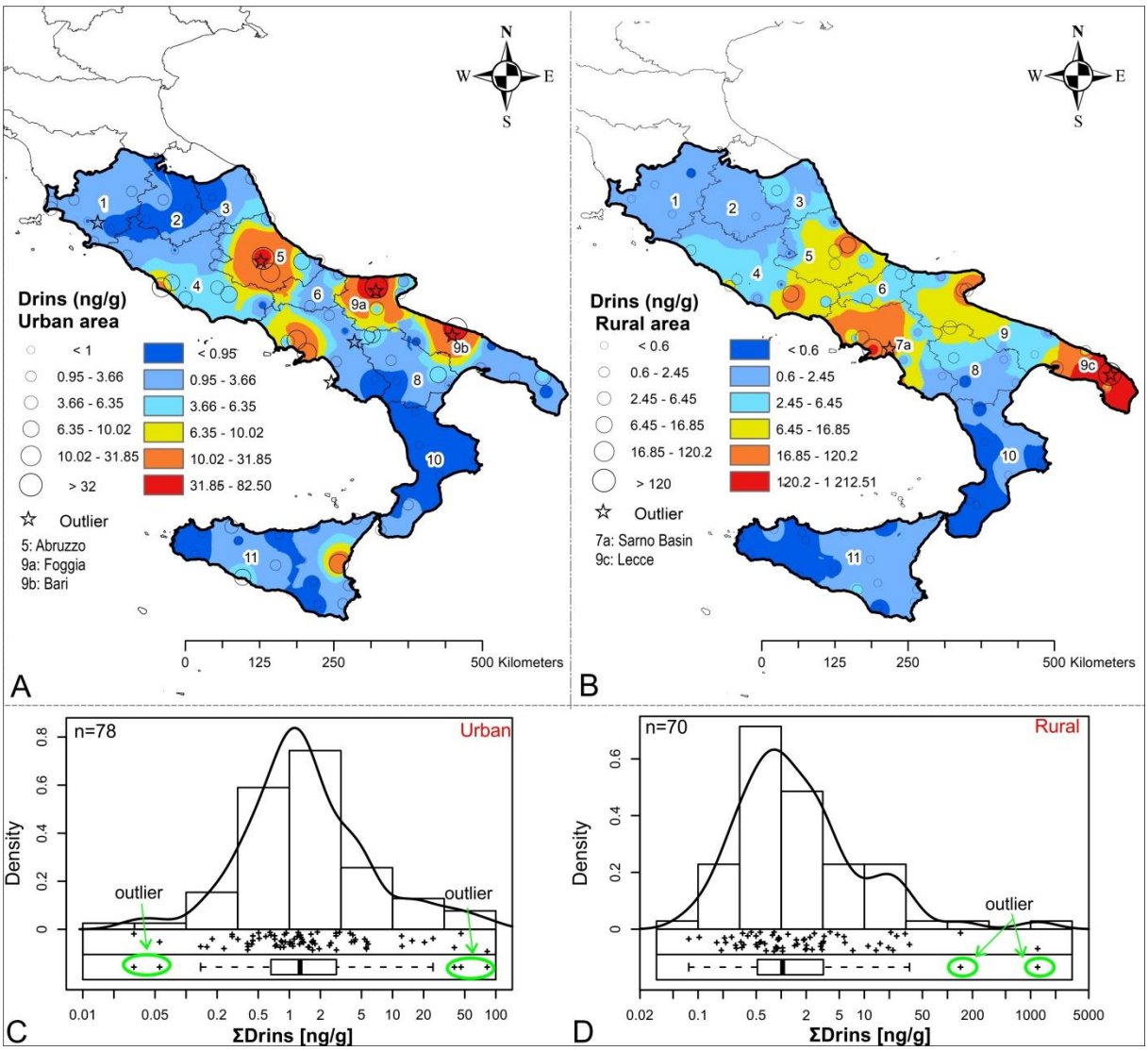
Drins (ng/g)
Urban area
< 1
0.95 - 3.66
3.66 - 6.35
6.35 - 10.02
10.02 - 31.85
> 32
< 0.95
0.95 - 3.66
3.66 - 6.35
6.35 - 10.02
10.02 - 31.85
31.85 - 82.50
Outlier
5: Abruzzo
9a: Foggia
9b: Bari
0 125 250 500 Kilometers
A
Drins (ng/g)
Rural area
< 0.6
0.6 - 2.45
2.45 - 6.45
6.45 - 16.85
16.85 - 120.2
> 120
< 0.6
0.6 - 2.45
2.45 - 6.45
6.45 - 16.85
16.85 - 120.2
120.2 - 1 212.51
Outlier
7a: Sarno Basin
9c: Lecce
0 125 250 500 Kilometers
B
n=78
Urban
Density
outlier
outlier
0.01 0.05 0.2 0.5 1 2 5 10 20 50 100
ΣDrins [ng/g]
C
n=70
Rural
Density
outlier
0.02 0.1 0.5 2 5 10 50 200 1000 5000
ΣDrins [ng/g]
D

Figure 7

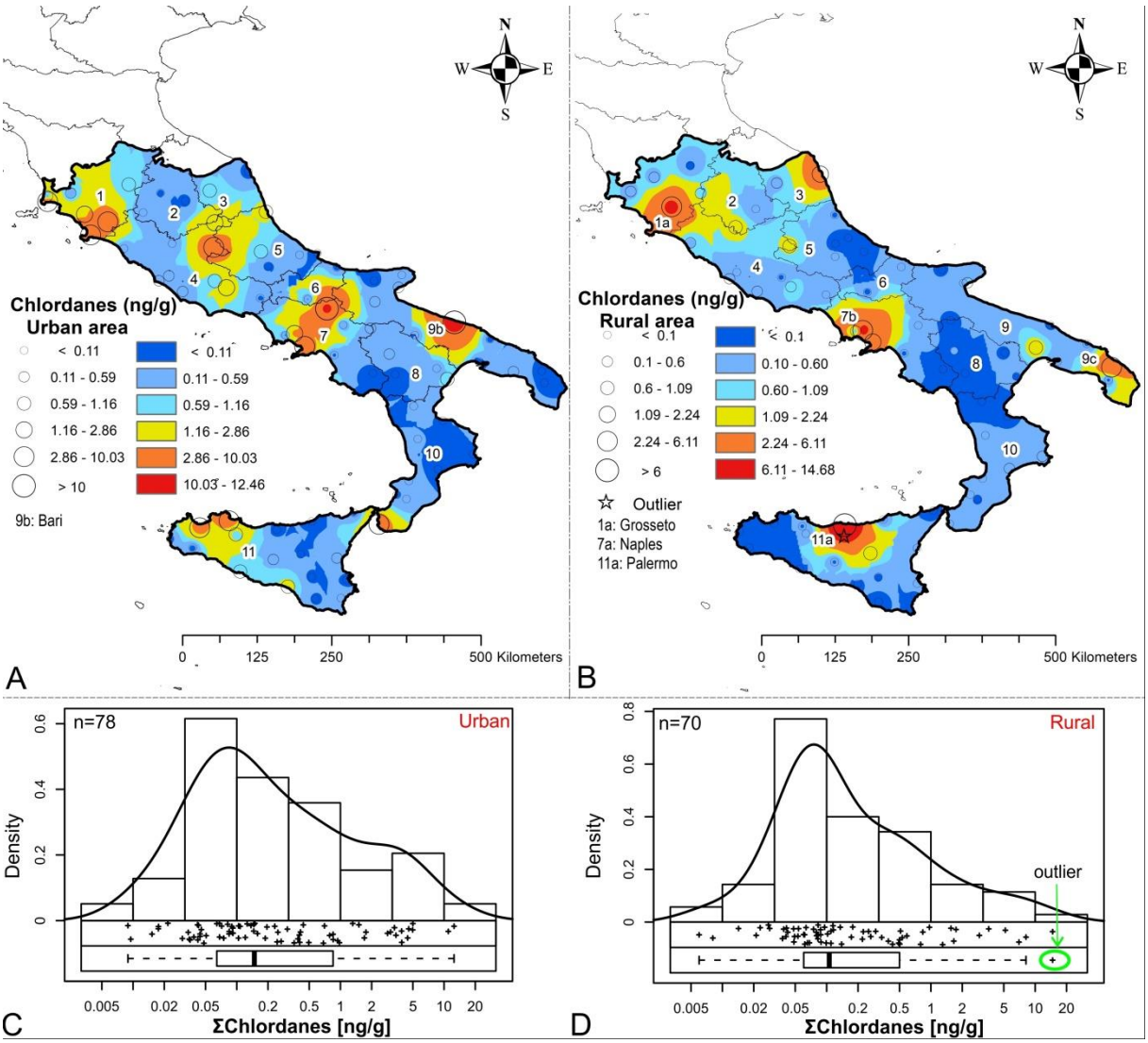
N
W
E
S
Chlordanes (ng/g)
Urban area
< 0.11
0.11 - 0.59
0.59 - 1.16
1.16 - 2.86
2.86 - 10.03
> 10
9b: Bari
0 125 250 500 Kilometers
A
Chlordanes (ng/g)
Rural area
< 0.1
0.1 - 0.6
0.6 - 1.09
1.09 - 2.24
2.24 - 6.11
> 6
Outlier
1a: Grosseto
7a: Naples
11a: Palermo
0 125 250 500 Kilometers
B
n=78
Urban
Density
ΣChlordanes [ng/g]
C
n=70
Rural
outlier
Density
ΣChlordanes [ng/g]
D

Figure 8

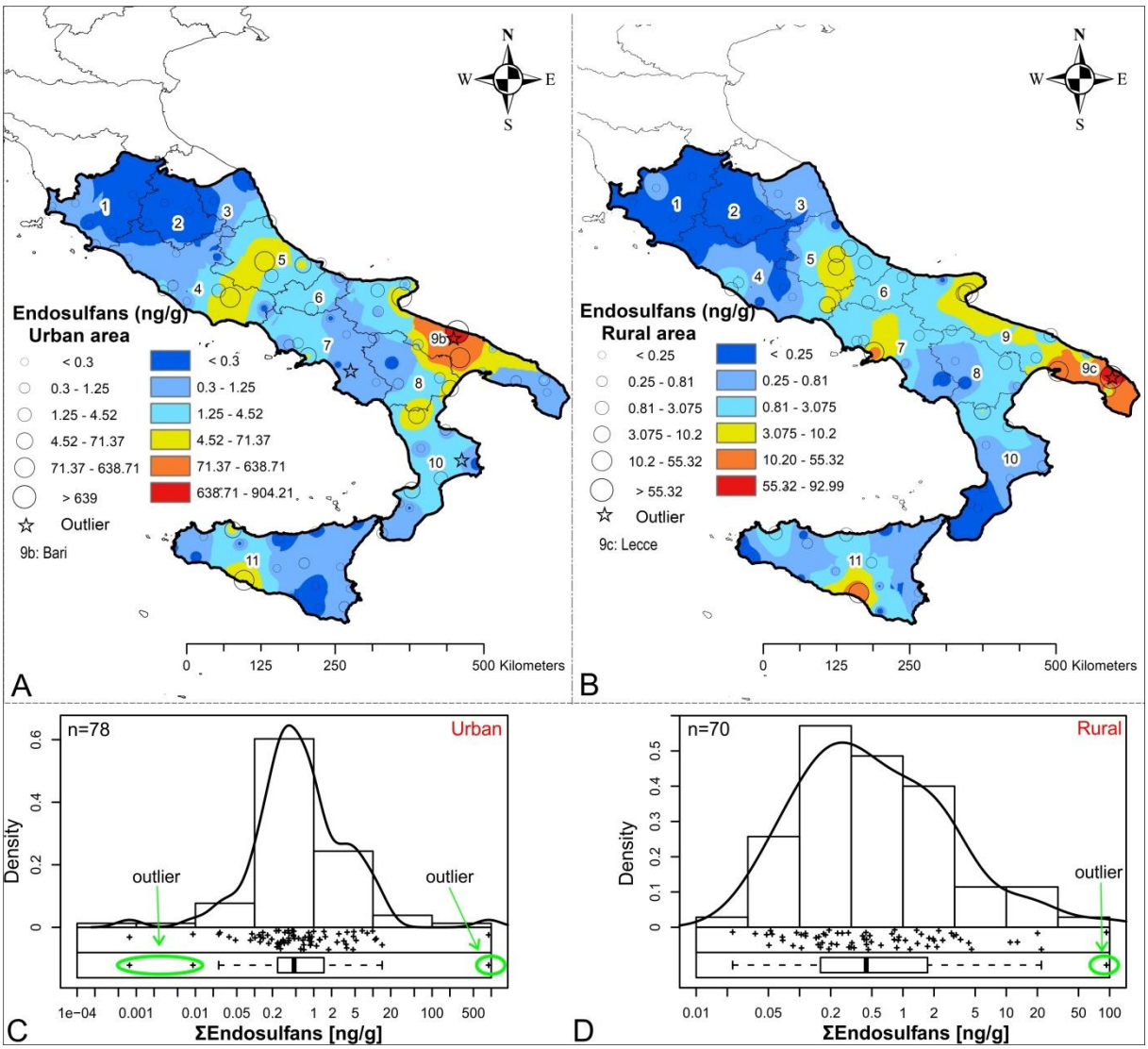
N
W
E
S
Endosulfans (ng/g)
Urban area
< 0.3
0.3 - 1.25
1.25 - 4.52
4.52 - 71.37
71.37 - 638.71
> 639
Outlier
9b: Bari
638.71 - 904.21
0
125
250
500 Kilometers
A
Endosulfans (ng/g)
Rural area
< 0.25
0.25 - 0.81
0.81 - 3.075
3.075 - 10.2
10.2 - 55.32
> 55.32
Outlier
9c: Lecce
0.25 - 0.81
0.81 - 3.075
3.075 - 10.2
10.20 - 55.32
55.32 - 92.99
B
n=78
Urban
outlier
outlier
Density
ΣEndosulfans [ng/g]
C
n=70
Rural
outlier
Density
ΣEndosulfans [ng/g]
D

Figure 9

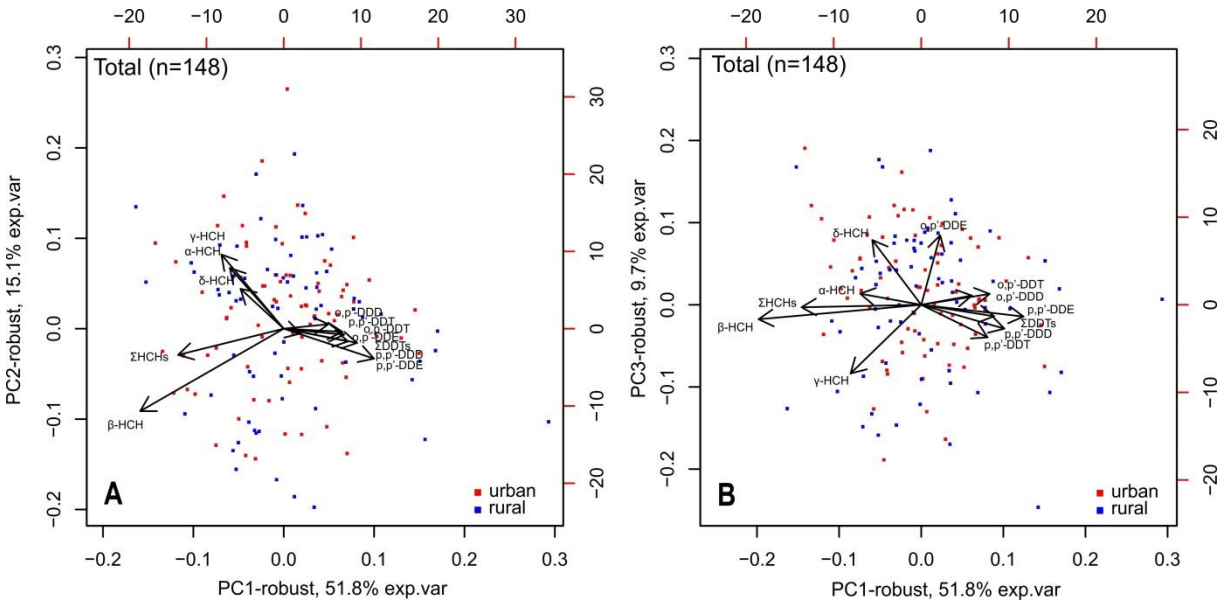
Total (n=148)
A
PC2-robust, 15.1% exp.var
PC1-robust, 51.8% exp.var
γ-HCH
α-HCH
δ-HCH
ΣHCHs
β-HCH
o,p'-DDD
p,p'-DDT
o,p'-DDT
o,p'-DDE
ΣDDTs
p,p'-DDD
p,p'-DDE
urban
rural
Total (n=148)
B
PC3-robust, 9.7% exp.var
PC1-robust, 51.8% exp.var
δ-HCH
o,p'-DDE
α-HCH
ΣHCHs
β-HCH
γ-HCH
o,p'-DDT
o,p'-DDD
p,p'-DDE
ΣDDTs
p,p'-DDD
p,p'-DDT
urban
rural

Figure 10

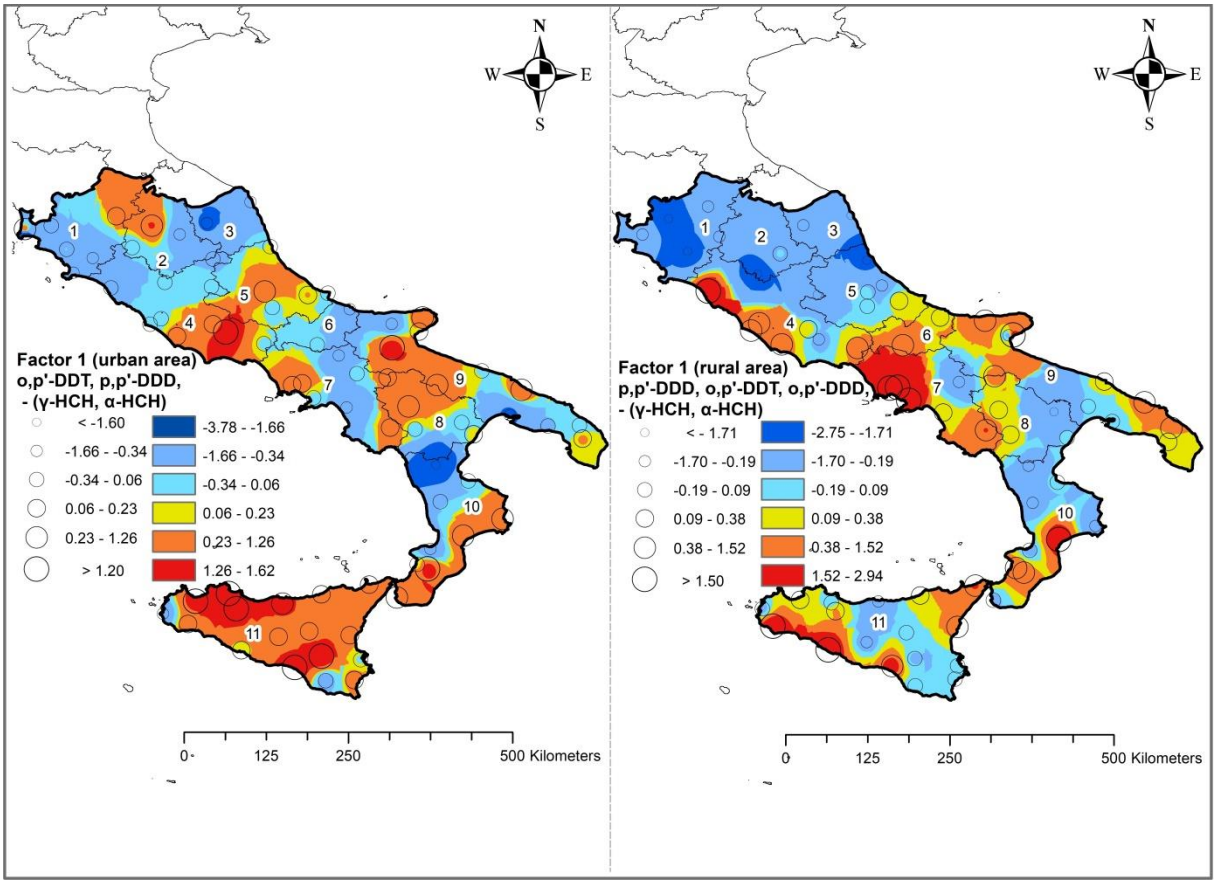
N
W
E
S
Factor 1 (urban area)
o,p'-DDT, p,p'-DDD,
- (γ-HCH, α-HCH)
< -1.60
-1.66 - -0.34
-0.34 - 0.06
0.06 - 0.23
0.23 - 1.26
> 1.20
-3.78 - -1.66
-1.66 - -0.34
-0.34 - 0.06
0.06 - 0.23
0.23 - 1.26
1.26 - 1.62
0
125
250
500 Kilometers
Factor 1 (rural area)
p,p'-DDD, o,p'-DDT, o,p'-DDD,
- (γ-HCH, α-HCH)
< - 1.71
-1.70 - -0.19
-0.19 - 0.09
0.09 - 0.38
0.38 - 1.52
> 1.50
-2.75 - -1.71
-1.70 - -0.19
-0.19 - 0.09
0.09 - 0.38
0.38 - 1.52
1.52 - 2.94
0
125
250
500 Kilometers

Figure 11

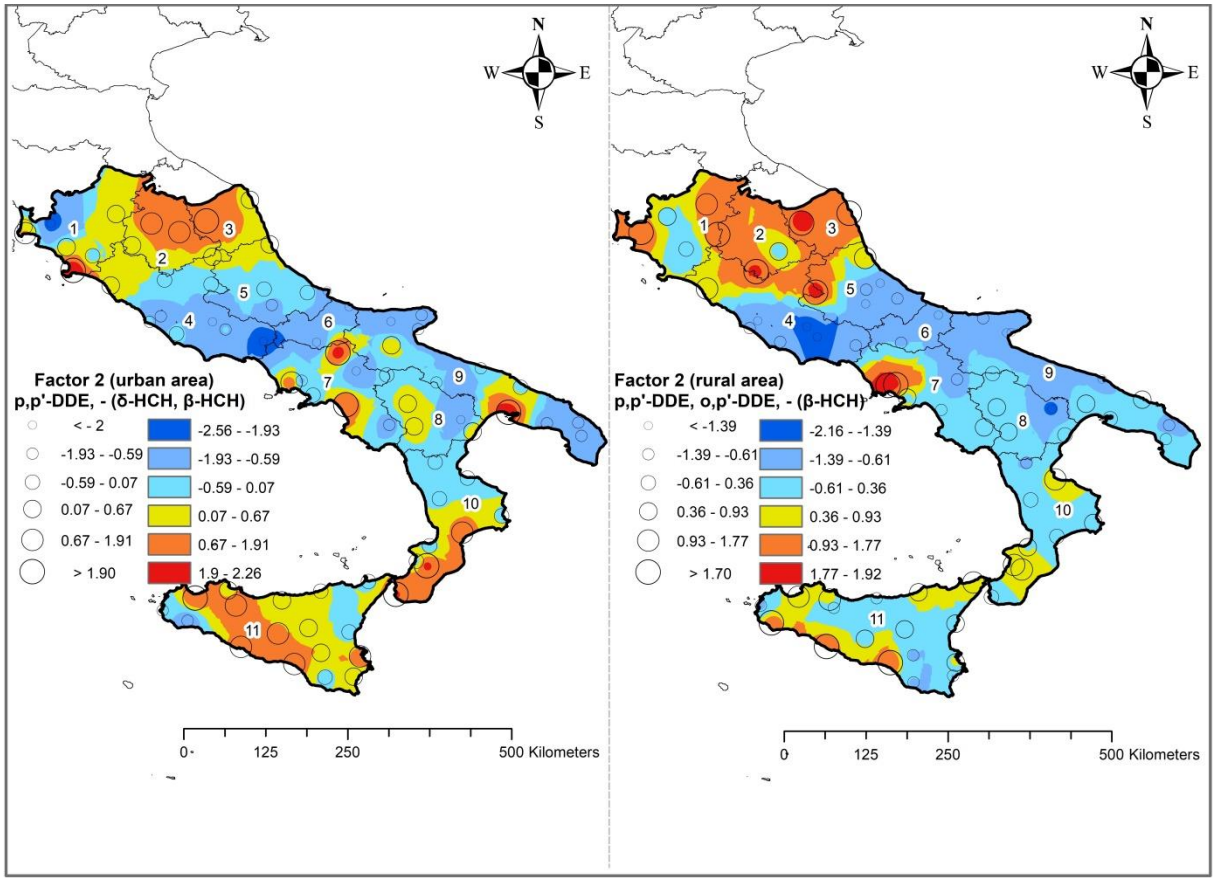
N
W
E
S
Factor 2 (urban area)
p,p'-DDE, - (δ-HCH, β-HCH)
< - 2
-1.93 - -0.59
-0.59 - 0.07
0.07 - 0.67
0.67 - 1.91
> 1.90
-2.56 - -1.93
-1.93 - -0.59
-0.59 - 0.07
0.07 - 0.67
0.67 - 1.91
1.9 - 2.26
0
125
250
500 Kilometers
Factor 2 (rural area)
p,p'-DDE, o,p'-DDE, - (β-HCH)
< -1.39
-1.39 - -0.61
-0.61 - 0.36
0.36 - 0.93
0.93 - 1.77
> 1.70
-2.16 - -1.39
-1.39 - -0.61
-0.61 - 0.36
0.36 - 0.93
0.93 - 1.77
1.77 - 1.92
0
125
250
500 Kilometers

Figure 12

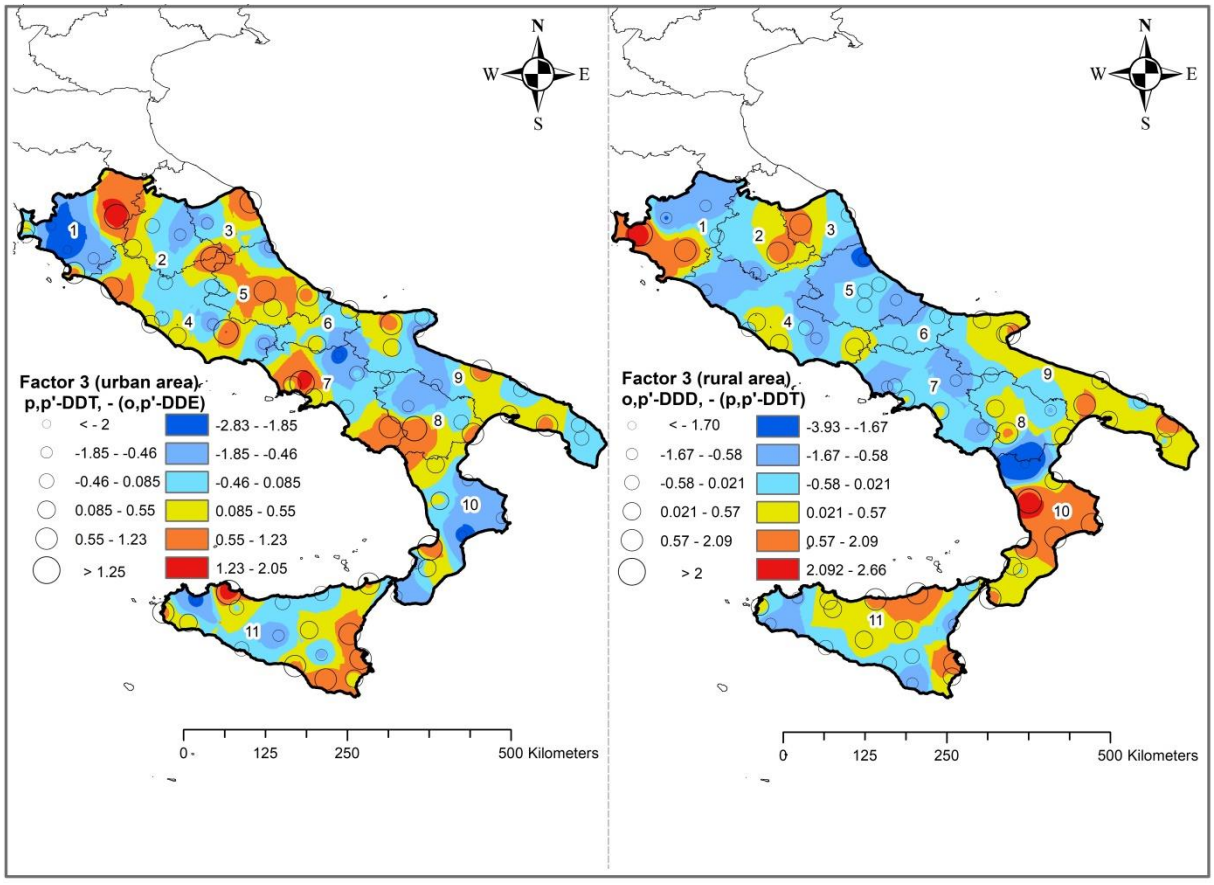
N
W
E
S
Factor 3 (urban area)
p,p'-DDT, - (o,p'-DDE)
< - 2
-1.85 - -0.46
-0.46 - 0.085
0.085 - 0.55
0.55 - 1.23
> 1.25
-2.83 - -1.85
-1.85 - -0.46
-0.46 - 0.085
0.085 - 0.55
0.55 - 1.23
1.23 - 2.05
1
2
3
4
5
6
7
8
9
10
11
0
125
250
500 Kilometers
N
W
E
S
Factor 3 (rural area)
o,p'-DDD, - (p,p'-DDT)
< - 1.70
-1.67 - -0.58
-0.58 - 0.021
0.021 - 0.57
0.57 - 2.09
> 2
-3.93 - -1.67
-1.67 - -0.58
-0.58 - 0.021
0.021 - 0.57
0.57 - 2.09
2.092 - 2.66
1
2
3
4
5
6
7
8
9
10
11
0
125
250
500 Kilometers

Figure 13

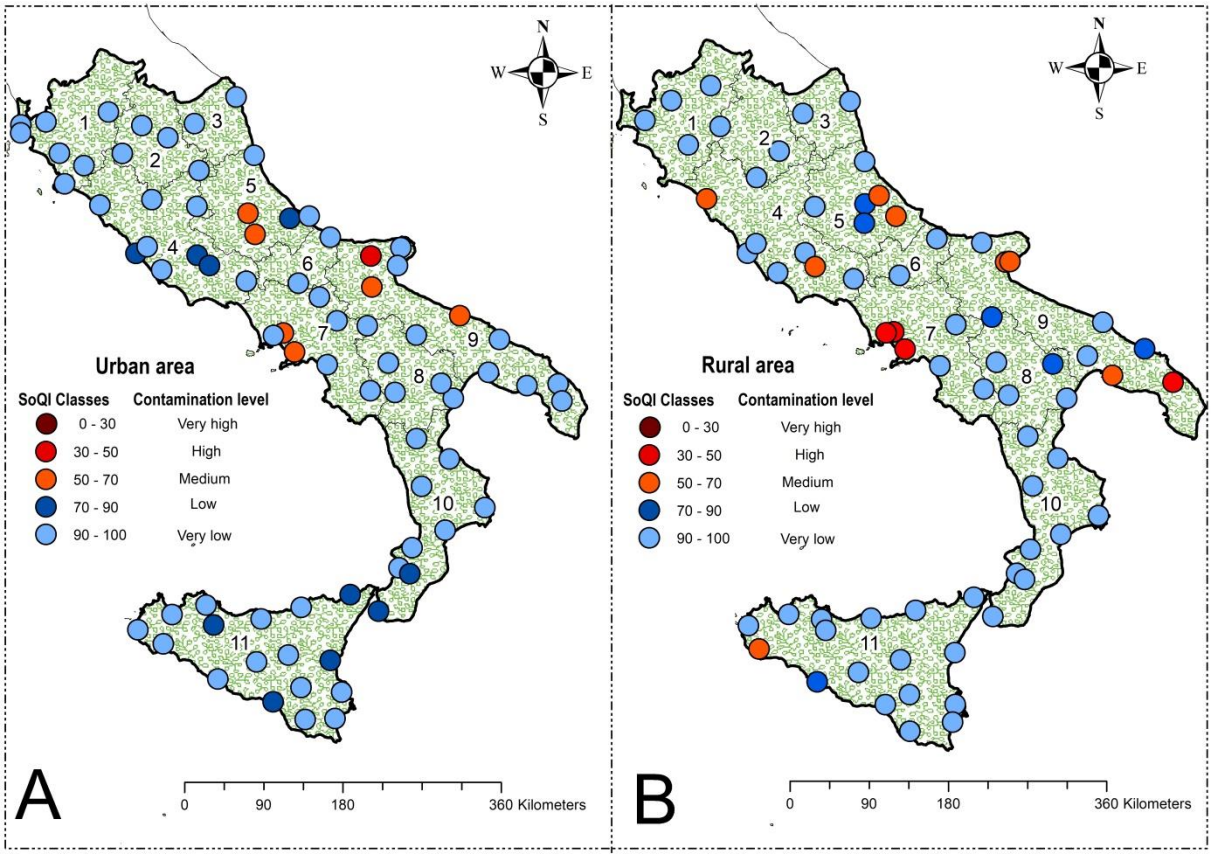
N
W
E
S
1
2
3
4
5
6
7
8
9
10
11
Urban area
SoQI Classes
Contamination level
0 - 30
Very high
30 - 50
High
50 - 70
Medium
70 - 90
Low
90 - 100
Very low
A
0
90
180
360 Kilometers
Rural area
B

Figure 14

Table 1. Organochlorine pesticides guideline thresholds values in soils, fixed by the Italian environmental law (D. Lgs. 152/2006) in residential areas (and/or park areas) and Industrial (or/or commercial) sites.

	Residential or recreation or park areas sites (ng/g)	Industrial or commercial sites (ng/g)
Aldrin	10	100
α-HCH	10	100
β-HCH	10	500
γ-HCH or Lindane	10	500
δ-HCH	10	100
Chlordane	10	100
DDT, DDE, DDD	10	100
Dieldrin	10	100
Endrin	10	2000

Table 2. Descriptive statistics of the 24 OCPs compounds (ng/g) in 148 topsoil samples from urban and rural areas of centre and southern Italy; min, max and CV indicate the minimum, maximum and coefficient of variation of the dataset, respectively.

		Urban area				Rural area			
Compounds (ng/g)	DL	Min.	mean	Max.	CV	Min.	Mean	Max.	CV
α-HCH	0.011	n.d	0.22	4.43	2.40	n.d	0.57	19.21	4.15
β-HCH	0.006	n.d	1.10	5.50	1.36	n.d	1.47	20.38	1.87
γ-HCH	0.011	n.d	0.39	14.19	4.19	n.d	0.65	11.29	2.73
δ-HCH	0.01	n.d	0.11	2.72	3.06	n.d	0.36	18.18	6.05
HCHs	-	n.d	1.82	25.08	1.78	n.d	3.05	47.27	2.30
p,p'-DDT	0.025	n.d	1.81	16.99	1.73	n.d	8.90	418.46	5.68
o,p'-DDT	0.02	n.d	0.34	5.04	2.24	n.d	1.68	48.27	4.80
p,p'-DDE	0.019	n.d	1.81	38.59	3.20	n.d	5.40	139.93	4.19
o,p'-DDE	0.021	n.d	0.33	7.56	2.99	n.d	0.27	4.34	2.26
p,p'-DDD	0.006	n.d	0.28	3.05	2.19	n.d	1.11	36.22	4.24
o,p'-DDD	0.025	n.d	0.34	5.04	2.24	n.d	1.68	48.27	4.80
DDTs	-	n.d	5.26	56.98	1.90	n.d	18.01	632.95	4.59
cis-Chlordane	0.018	n.d	0.08	1.77	2.93	n.d	0.11	3.40	4.07
trans-Chlordane	0.021	n.d	0.20	7.71	4.47	n.d	0.10	1.97	3.33
Heptachlor	0.021	n.d	0.15	3.72	3.41	n.d	0.07	1.20	2.33
Heptachlor-epoxide	0.014	n.d	0.62	10.95	2.64	n.d	0.57	13.73	3.43
Aldrin	0.046	n.d	0.25	2.69	1.75	n.d	0.59	13.37	3.27
Dieldrin	0.036	n.d	0.13	1.16	1.75	n.d	0.24	9.80	4.87
Endrin	0.030	n.d	0.36	10.70	3.49	n.d	0.30	6.65	2.94
Endrin aldehyde	0.030	n.d	0.19	1.30	1.26	n.d	0.36	4.79	2.42
Endrin Ketone	0.032	n.d	3.78	82.17	2.95	n.d	22.24	1199.97	6.47
α-Endosulfan	0.017	n.d	9.22	710.34	8.72	n.d	0.12	3.02	3.25
β-Endosulfan	0.017	n.d	2.57	176.79	7.81	n.d	0.36	10.36	4.18
endosulfan-sulfate	0.064	n.d	1.46	17.43	1.92	n.d	2.61	79.74	3.84
HCB	0.009	0.011	0.17	2.39	2.25	n.d	0.48	13.37	3.53
methoxychlor	0.025	n.d	3.64	53.23	2.23	n.d	10.96	521.79	5.80
OCPs	-	0.0011	29.91	1043.98	0.27	n.d	60.16	1914.10	4.02

Table 3. Total OCPs concentrations (ng/g dry weight) in topsoil of the survey area compared to those found in other studies in the recent literature.

Locations	Characteristic	DDTs	HCHs	Drins	Endosulfans	Chlordanes	References
Southern Italy	Urban soils	nd – 56.97	nd – 25.08	nd – 82.58	nd – 904.2	nd – 12.47	This study
Southern Italy	Rural soils	nd – 632.95	nd – 47.27	nd – 1214.41	nd – 93.13	nd – 14.69	This study
Northern France	Natural areas	nd – 28.6	nd – 5.06	nd – 2.26	nd – 1.84	–	Villanneau et al. 2011
Central Germany	Agriculture fields	23.7–173	4.6–11.5	–	–	–	Manz et al. 2001
Southern of Poland	Urban and rural soils	23 – 260	1.1 – 11	–	–	–	Falandysz et al. 2001
Southern of USA	Farm lands	0.10 – 1490	0.1 – 0.71	–	–	0.05 – 5.1	Bidleman et al. 2004
Zhangzhou China	Agriculture soils	0.64 – 78.07	0.72 – 30.16	–	–	–	Yang et al. 2012
Beijing (China)	Urban soils park	0.942 – 1039	0.25 –197.0	–	–	–	Li et al. 2008
Nagaon distrcit (India)	Agriculture soils	166 – 2288	98 – 1945	–	–	–	Mishra et al. 2012

Table 4. Varimax-rotated factor (three-factor model) using 78 topsoil samples from urban areas and 70 samples from agricultural soils; bold entries: loading values over |0.50|.

Variables	**Urban areas** Factors			**Rural areas** Factors		
	F1	F2	F3	F1	F2	F3
α-HCH	**-0.69**	0.12	-0.36	**-0.80**	-0.08	0.19
β-HCH	0.10	**-0.83**	-0.12	-0.15	**-0.77**	-0.06
γ-HCH	**-0.68**	0.04	-0.19	**-0.71**	-0.26	0.03
δ-HCH	-0.25	**-0.64**	0.17	-0.24	-0.43	0.31
o,p-DDE	-0.33	0.04	**-0.75**	-0.45	**0.53**	0.33
p,p'-DDE	0.04	**0.81**	0.12	0.16	**0.81**	-0.30
o,p-DDD	0.45	0.33	0.47	**0.64**	0.15	**0.62**
p,p'-DDD	**0.76**	0.19	0.03	**0.81**	0.28	-0.10
o,p-DDT	**0.84**	0.13	-0.13	**0.79**	0.03	-0.09
p,p'-DDT	-0.08	0.07	**0.79**	0.30	0.25	**-0.81**
Eigenvalues	2.60	1.96	1.64	3.77	1.675	1.23
Total variance in %	26.04	19.58	16.45	33.31	19.6	13.81
Cum. of total variance	26.04	45.63	62.09	33.31	52.92	66.81