# EVALUATION OF SOIL DIFFUSE CONTAMINATION IN VENICE REGION (ITALY)

# ÉVALUATION DE LA CONTAMINATION DIFFUSE DU SOL DE LA VÉNÉTIE (ITALIE)

# VALUTAZIONE DELLA CONTAMINAZIONE DIFFUSA DEI SUOLI DEL VENETO (ITALIA)

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## Abstract

A survey on the concentration of some metals and metalloids in soils of Veneto conducted on 2393 samples, of which 1363 topsoil (0-40 cm) and 1030 subsoil (70-100 cm), allowed to define the background values for the metals considered. Particularly for some metals and in areas of volcanic substrata these values were above certain threshold concentrations of contamination defined by the Italian environmental legislation. Some results of persistent organic pollutants monitoring in the soils are reported and available.
**Keywords:** *soil; organic pollutants; metals; Veneto*

## Resumé

Une investigation sur la concentration de certains métaux et métalloïdes dans les sols de la Vénétie menées sur 2393 échantillons, dont 1363 dans la couche arable (0-40 cm) et 1030 dans le sous-sol (70-100 cm), a permis de définir les valeurs de fond pour les métaux considérés. En particulier pour certains métaux et dans les zones de substrats volcaniques les concentrations valeurs sont au-dessus des seuils de contamination définis par la législation italienne sur la protection de l'environnement. Certains résultats de la surveillance des polluants organiques persistants dans le sol sont rapportés et disponibles.
**Mots-clés:** *sol; polluants organiques; métaux; Vénétie*

## Riassunto

Un monitoraggio della concentrazione di metalli e metalloidi in alcuni terreni del Veneto è stato condotto mediante l'analisi di 2393 campioni, 1363 superficiali (0-40 cm) e 1030 profondi (70-100 cm); i risultati sono stati utilizzati per definire i valori di fondo per i metalli considerati. In particolare per alcuni metalli e nei suoli formatisi su substrati vulcanici tali valori sono al di sopra delle concentrazioni soglia di contaminazione definite dal Testo Unico Ambientale. Analogo monitoraggio è in corso sulla concentrazione nei suoli dei microinquinanti organici.
**Parole chiave:** *suolo; inquinanti organici; metalli*

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## Introduction

Contaminants that more frequently are detected in the environment, due to the dispersion of substances caused by human activities, are metals and some persistent organic pollutants (POPs) such as PCDD/Fs, PAHs and PCBs.
Evaluation of soil contamination by metals needs to know natural background values due to pedogeochemical characteristics of soil, mainly soil mineral composition that could vary widely depending on materials on which soil is developed (Alloway, 1999; Kabata-Pendias e Pendias, 1984).
Since first monitoring activities conducted (1995) for soil survey, before by ESAV and then by ARPAV, aimed to build up a soil information database for Veneto Region – particularly within the realization of regional soil map at 1:250.000 scale (ARPAV, 2005) and the soil maps at 1:50.000 scale of Treviso (ARPAV, 2008), Venice (ARPAV, 2008) and Padua (printing) provinces – to determination of basic characteristics needed for soil classification detection of metals concentration was associated in order to define a regional framework.
Regulatory reference for pollution definition is the Italian Decree n. 152/2006 which states: "*If potentially polluted site is located in an area which is interested by natural or anthropic phenomena which determined the overcome of one or more threshold limits, these area assumed as background level existing for all parameters exceeding law limits*".
For application of the last part of this definition it is very important to determine natural background level for metals in soil to focus what is really polluted by external causes by what is due to natural concentration in soil.
In studies conducted in neighboring regions (Sartori et al., 2004) natural values of some metals certainly higher than the limit set by the standard for residential areas had already been identified. A similar approach also applies to organic micropollutants although in this case there is no "endogenous" but only "exogenous" source of substances in soil, mainly due to the atmospheric deposition of volatile organic substances emissions from combustion processes (APAT, 2006). The knowledge on organic pollutants content in soils can provide, therefore, useful information about the level of diffuse pollution and new elements to assess any risks associated to management of urban and agricultural land. Just agricultural soils should represent an especially "healthy" situation free from human impacts and may allow the definition of reference values (natural-anthropogenic background) that can be compared to situations interested to greater impact (urban land, industrial areas, areas near incinerators, etc.).

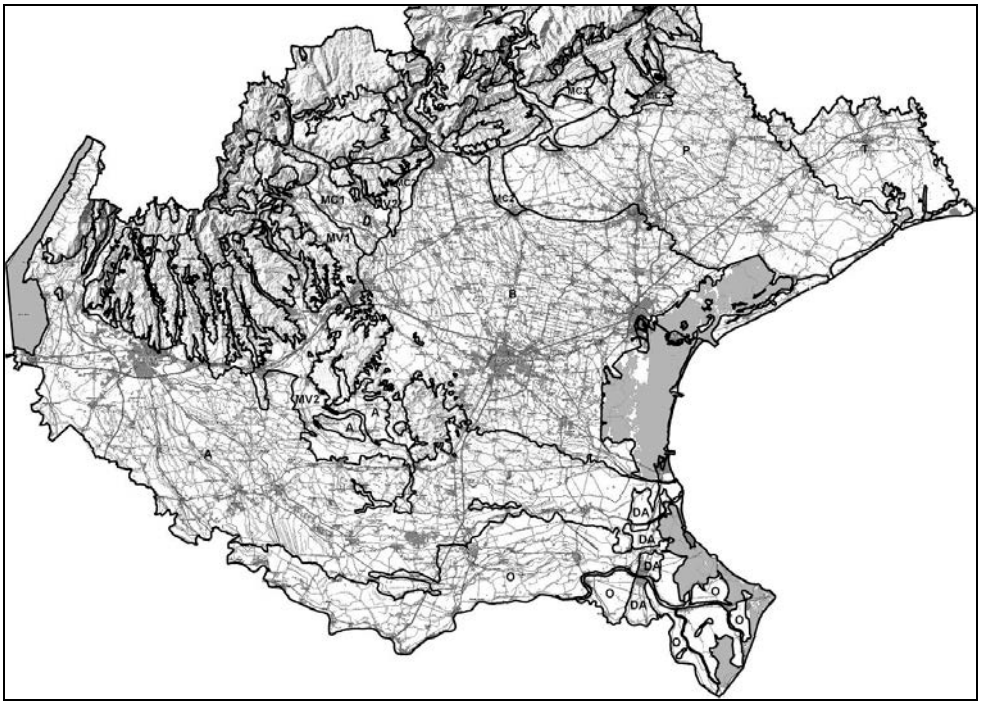
## Materials and methods

### *Heavy metals*

Determination of metal background values in soil was carried out as specified by ISO 19258:2005 (Soil Quality - Guidance on the determination of background values) that is the international reference for samplyng, analysis and data elaboration.

According with it pedo-geochemical background content represents the concentration of elements generated by the characteristic features of pedogenesis, such as the composition and alteration of the rock and any subsequent movements in soil. On the other hand background content refers to the concentration of an element in a specific type of soil, located in an area or region, resulting from both natural, geological and pedological processes and including diffuse source inputs, such as atmospheric deposition and agricultural practices.

Figure 1- *Depositional Units of the Plain: T= Tagliamento river deposit; P= Piave river deposit; B= Brenta river deposit; A= Adige river deposit; O= Po river deposit; MC1= Astico river fan; MC2= Prealpine rivers fan; MV1= Leogra-Timonchio rivers fan; MV2= Agno-Guà rivers fan; DP= north-eastern coastal deposit; DA= southern coastal deposit.*




The choice of sampling sites was carried out following the "typological approach" of ISO 19258:2005, i.e. depending on the parent material, soil types and land use. Homogeneous areas were defined by parent material composition. For the plain, where soils have been formed from alluvial deposits areas were defined by means of the origin of the sediments from which the soil was formed, and these were called "depositional units" (Fig. 1).

For the mountain area, where soils have been formed from materials on site areas were defined by means of the prevalent rocks from which the soil was formed together with the type of pedogenetical processes, and these were called "physiograpic units".

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In the selection of the sampling sites also land use was taken into consideration, in order to consider only sites with agricultural use, taking care to avoid contaminated areas or sites too close to potential sources of pollutants or showing signs of human intervention.

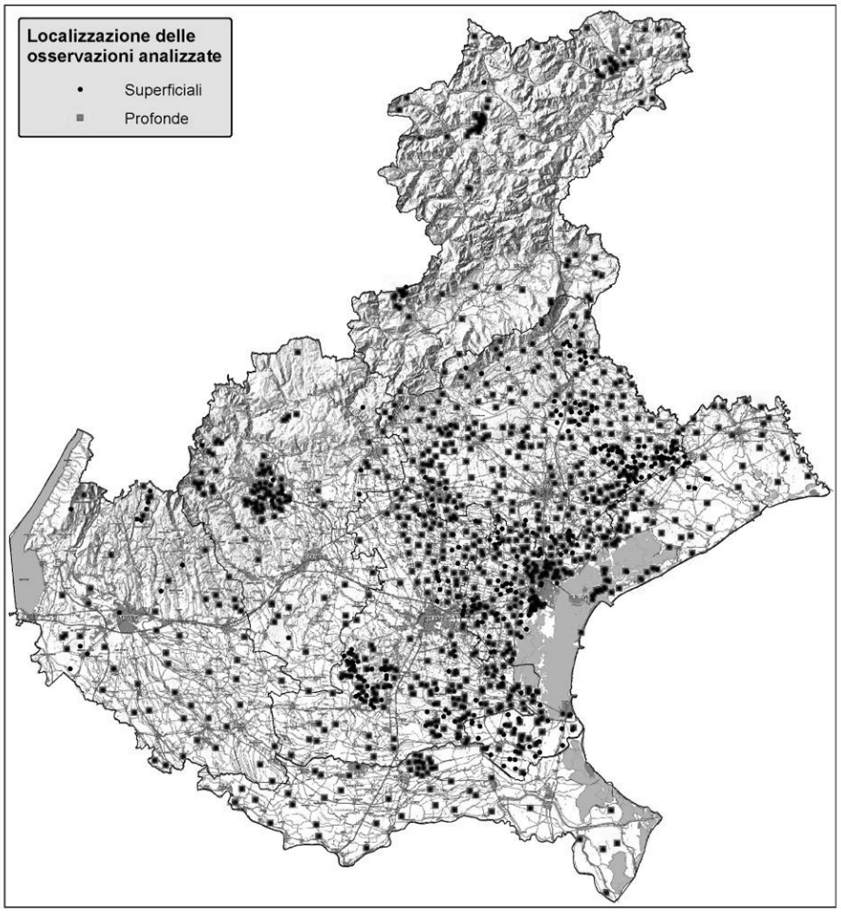


**Figure 2**

*Sampling sites of heavy metals monitoring plan*

Two sampling depth was chosen depending on soil horizons following different strategies for plain and mountain areas: in plain the first sample was taken within upper horizon, up to a maximum depth of 40-50 cm and the second in the subsoil within the first soil horizon or layer below 70 cm, that usually excludes a possible anthropogenic contribution. In mountain areas the first sample was taken within upper horizon, that has variable size, and the second in the subsoil within the first soil horizon or layer below 70 cm, or, when than soil was thinner, within the deeper layer. 2393 samples were totally analyzed, of which 1363 topsoil and 1030 deep. In the plain 1119 topsoil samples and 835 deep, while in mountain areas 244 topsoil and 195 deep.

The analytical determinations were performed at the ARPAV Laboratories of Treviso, through aqua regia extraction and ICP-AES detection, on the size fraction

less than 2 mm. Antimony, arsenic, beryllium, cadmium, cobalt, chromium, copper, mercury, nickel, lead, selenium, tin, vanadium, zinc, were determined in an aqua regia extractable fraction to measure the "pseudo-total" fraction.
Statistical analysis of data was worked out for the whole dataset for a first evaluation of concentration trends, and then for each depositional/physiographic unit. Some descriptive statistics were performed for each item, keeping separate values of the surface from deeper horizons; for each variable many parameters were determined mean, median, minimum, maximum, percentiles (5th, 25th, 75th, 90th and 95th), standard deviation, standard error, skewness and kurtosis, normality tests. Once outliers were removed, background value for each metal was determined by means of 95th percentile value within each depositional/physiographic units. Background values were then compared to threshold limits for residential sites stated by Italian environmental code (D. Lgs. 152/2006).

### *Persistent organic pollutants*

First step of monitoring went through the collection of all data already available within the region, even if carried out by different parties, to establish a database on which to perform the initial processing (Della Sala et al., 1999). Data were collected from 627 sites corresponding to 648 soil horizons analyzed. Specifically it was collected, for dioxins and furans, 171 analyzes from 151 sites, 527 analysis, of which 388 only in the province of Verona, from 516 sites for PCBs and 105 analyzes from 91 sites for PAH.
With the support of technicians from ARPAV Provincial Departments some sites were selected to perform sampling in the nearby of specific environmental pressure sources such as foundries, industrial areas, incinerators, cement plants but also sensitive sites such as public green areas.
Until December 2011 (48 collected and analyzed samples) sampling has focused on sites with no clear anthropogenic pressures, with the exception of 2 samples, in order to be able to perform the initial processing of a discrete number of sites with low human impact and therefore representative of diffuse contamination phenomena. In addition to the organic pollutants concentration measurement, all samples were analyzed for pH, texture, organic carbon, total lime, cation exchange capacity and heavy metals, parameters that can provide useful elements to establish the natural origin of the material collected and to understand the behavior of organic compounds in soil. Sampling, performed taking a representative sample of an area of about 4000 square meters, took place through the identification of areas as homogeneous as possible for pedological characteristics of the soil and land management, proceeding in a systematic scheme (ISO 10381-5/2005).
Sampling depth in investigated sites was different in relation to land use and the possible mixing of the horizon surface by the agricultural processing; plowed land the topsoil corresponds to the processed layer, while the deep horizon to a layer of depth between 70 and 100 cm; natural soils or surfaces not plowed for a long time (meadows, public parks, green vineyards) the topsoil sample has affected the first

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few centimeters of soil (usually 0-5 cm), while the deep was collected at depths between 15 and 25 cm, to evaluate the possible effect of atmospheric deposition and mobility of micropollutants within the soil.
All samples were analyzed by ARPAV Laboratories Service both for organic parameters and for the descriptive parameters of the soil.

## Results

In table 1 the background value for each metal and metalloid is reported for each depositional unit. This value was determined taking the higher between the upper and lower horizon values.

**Table 1** - *Background values in depositional units of Veneto, in bold values exceeding limits for residential sites.*

| | **Depositional Unit** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tagliamento river deposit (T) | Piave river deposit (P) | Brenta river deposit (B) | Adige river deposit (A) | Po river deposit (O) | Astico river fan (MC1) | Prealpine river fan (MC2) | Leogra-Timonchio river fan (MV1) | Agno-Guà river fan (MV2) | North-eastern coastal dep. (DA) | Southern coastal dep. (DS) |
| **As** | 14* | 13 | **45** | **50** | **31** | **21*** | **23** | **26** | **41*** | 12* | **23*** |
| **Be** | nd | 1.7 | **2.3** | 1.4 | 1.6 | **2.1*** | 1.6* | 1.7* | 1.5* | 0.2* | 0.9* |
| **Cd** | 0.62* | 0.64 | 0.95 | 1.17 | 0.60 | 0.66* | 0.86 | 0.86 | 0.59* | 0.25* | 0.25* |
| **Co** | 12* | 15 | 16 | **20** | **20** | **23*** | 16 | **35** | **51*** | 5* | 14* |
| **Cr** | 67* | 61 | 64 | 141 | **153** | 83* | 76 | **153** | **190*** | 19* | 89* |
| **Cu** | 44* | **186** | 110 | 79 | 63 | 103* | 114 | 86 | 66* | 58* | 54* |
| **Hg** | 0.09* | 0.26 | 0.67 | 0.32 | 0.08 | 0.31* | 0.26 | 0.16* | 0.10* | 0.85* | 0.13* |
| **Ni** | 42* | 52 | 38 | **125** | **130** | 64* | 56 | **120** | **161*** | 8* | 83* |
| **Pb** | 33* | 36 | 54 | 46 | 35 | 61* | 45 | **106** | 56* | 51* | 56* |
| **Sb** | nd | 1.0 | 2.4 | 1.5 | 1.4 | 2.0* | 0.8* | 2.8* | 1.6* | 0.8* | 1.2* |
| **Se** | nd | 0.50 | 0.31 | 1.00 | 0.90 | 0.40* | 0.40* | 0.44* | 0.72* | 0.10* | 0.68* |
| **Sn** | nd | **4.0** | **7.8** | **3.7** | **3.4** | **4.4*** | **3.4*** | **6.4*** | **2.9*** | **5.7*** | **5.8*** |
| **V** | nd | 87 | **96** | 89 | 80 | **203*** | 81* | **157*** | **146*** | 20* | 61* |
| **Zn** | 86* | 113 | 144 | **155** | 111 | 137* | 110 | **200** | **164*** | 67* | **181*** |

* number of samples for background level determination lower than 30 (suggested number according to ISO 19258-2005).

For antimony, cadmium, mercury, lead and selenium no exceeding of threshold concentrations for residential sites in any depositional units occurs.
In the Piave river unit high concentration of copper occurs due to the widespread cultivation of vineyards that requires repeated treatments with copper products for plant protection.
Also for lead values exceeding limits occur only in piedmont fans of Leogra-Timonchio river system.

Arsenic, beryllium, cobalt, chromium, nickel, vanadium and zinc values exceed the threshold concentration in many units, involving a significant area within the region.
In all the depositional units of the Veneto region a particular situation is pointed out for tin which everywhere has background values above threshold limit, with maximum values of more than 7 times higher than the limit in Brenta river unit. Anyway, the tin threshold limit stated by the Italian environmental code for residential sites has revealed inadequate if compared to the background values.
The unit with the highest number of background values exceeding the threshold limits is the Agno-Guà river fan in the plain, which receive alluvial deposits from the alteration of basalts, in which concentration of zinc, nickel, chromium, cobalt, arsenic, tin and vanadium is significantly higher than in sedimentary rocks (Alloway, 1995; Kabata Pendias, 2001).
Po, Adige and Brenta river units show many background values exceeding the limits, Piave river unit, only for copper and tin, while in the Tagliamento river unit no exceeding occurs (although data are not available for tin, beryllium, and vanadium).
Arsenic exceeding values occurring in Adige, Po and Brenta deposits are very significant as the area is very wide and toxicological characteristics of element lead to special warning.
Results of the monitoring of organic micropollutants show that for dioxins and furans were not no value exceeding the law limits (column A, 10 ng TE/kg) was detected, and only slightly more than 10% of the population have concentrations between 2 and 10 ng TE/kg (table 2), with a mean value equal to 0.77 ng TE/kg and the median equal to 0.31 ng TE/kg.

**Table 2** - *Main statistics of the results of the monitoring of organic micropollutants (48 samples).*

| Compounds | PCDD/F (ng I-TE/kg) | PCB (µg/kg) | IPA (mg/kg) |
|---|---|---|---|
| Mean | 0,77 | 2,3 | 0,03 |
| Median | 0,31 | 1,4 | 0,00 |
| 75° percentile | 0,91 | 2,7 | 0,03 |
| 95° percentile | 3,32 | 5,9 | 0,11 |
| Maximum | 5,06 | 16,1 | 0,22 |
| Decree n. 152/06 | 10 | 60 | 10 |

The highest values were found in three soils with natural vegetation in the foothills of the Alps; these values refer to the first few centimeters of soil and are between 1.8 and 5.1 ng TE / kg. This could be explained by the lack of effect of dilution related to the processes of the soil, which results in a greater concentration of atmospheric deposition in the first few centimeters of soil.
In remaining samples high concentrations are not observed. Only in two samples from plain concentration is greater than 2 ng TE/kg but, as they refer to a thicker horizon, they can be due to external sources.

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As regards PCBs no value exceeding the limit (column A, 60 mg / kg) were found; data distribution presents a clear prevalence of samples with concentrations below 0,01 mg/kg; the maximum value found is equal to 0,016 mg/kg in a sample of topsoil (0-3 cm) collected on the slopes of Monte Grappa under natural vegetation.
With regard to PCBs different congeners it can be observed that the dioxin-like PCBs are present in concentrations significantly lower than non dioxine-like.
As for dioxins, high values are observed in non-cultivated soils with values ranging between 3 and 16 µg/kg, due to the accumulation in a very small thickness; in the only sample of litter (humus), the observed values for PCBs are comparable to those of the underlying mineral soil, something that suggests that the rate of atmospheric deposition is constant even in more recent times.
As for PAHs, the concentrations found in the soil are quite lower than the thresholds set by the Legislative Decree 152/06. In fact, the median of total PAH is equal to 0.11 mg/kg compared to a legal limit of 10 mg/kg.
The sample collected near the A4 highway in the province of Verona has PAHs concentration no significantly different from the population: the topsoil sample which corresponds to a thickness of 5 cm, collected in a grassy vineyard and not plowed from several years (0.08 mg/kg at the surface and 0.07 mg/kg between 15 and 30 cm in total PAHs).

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