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An appraisal of soil diffuse contamination in an industrial district in northern Italy

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Soil diffuse contamination from REEs, trace elements, and organic contamination in an Italian Province.

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Abstract

Soil diffuse contamination is one the major soil threats, especially in regions with a high population density and strong industrialization. In this work 70 monitoring sites in agricultural, natural, and periurban soils of an Italian Province (858 km²) were sampled and analysed. Overall, 140 samples were taken at two depths and analysed for 10 trace elements (As, Co, Cr, Cu, Ni, Pb, Sb, Sn, V and Zn), 13 Rare Earth Elements (REE - Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tm, Y, and Yb) and for organic contaminants (PCBs, PCDDs and PAHs). Aim of work was to give an appraisal of the degree of soil diffuse contamination in a large Italian Province and to apply and verify the suitability of available tools to quantify background values and evaluate the intensity of contamination.

Data were processed, background values estimated, and enrichment and contamination factors calculated. Results allowed a discrimination between natural or anthropic-derived contaminants. Some contaminants revealed clear trends of enrichment in function of the land use (in particular for peri-urban soils). REEs were found to mostly derive from parent material, with the exception of Tm and Eu.

The results obtained in this study show the importance of merging the quantification of contaminants with the elaboration of indices of contamination. These require an accurate quantification of background values to be able to discriminate the anthropic contribution.

Among the tools used in this study (Enrichment and Contamination factors), the first revealed to be more accurate, but as a drawback they cannot be applied to organic contaminants and need to carefully select the reference element to be adopted. This study revealed that some contaminants - i.e. Sb, Sn, Pb, and organic contaminants - can be identified as tracers of diffuse contamination, and should be therefore always included in similar studies.

Introduction

Soil pollution from diffuse sources is recognized as one of the major soil threats by the EU Soil Thematic Strategy (European Commission, 2006). In fact, some pollutants are nowadays widespread in the soil system due to their long-term airborne deposition, and they should be considered for the implementation of environmental legislation, the definition of clean-up values in remediation activities and, more generally, for a sustainable management of the soil resource. This is especially true in regions with a high population density and strong industrialization, where land is intensely used (Van Straalen, 2002). Even areas far from industrial centers may also show increased concentrations of contaminants due to long-range atmospheric transport (Al-Khashman, 2004; Loska et al., 2004; Steinnes et al., 1997; Wilson et al., 2005;).

In recent years, Rare Earth Elements (REEs) have been identified as “emerging contaminants”. REEs have neither been characterized as essential elements for life, nor as strongly toxic elements in the environment. In soils they mainly originate from parent materials, some of them occurring in granites or pegmatites as phosphates, carbonates, silicates or fluorides (Tyler, 2004). REEs have recently become widely used for industrial and agricultural activities like fertilization and sewage sludge re-use (Zhang et al., 2001) and have received therefore increasing attention as indicators of contamination. In particular, in the literature the ratio between the sum of light REEs and the sum of heavy ones (L/H) is proposed as indicator of depletion/enrichment of these elements. Light REE are distinguished from heavy REE for having atomic mass lower than 153 and an effective radius lower than 95 pm. In soils, HREEs are more likely to leach in soils than LREEs and as a consequence HREE are depleted and LREEs gradually enriched with time (Miao et al 2008). The analysis of changes in this relationship between surface and deep horizons can therefore be used to highlight the presence of anthropogenic REE.

When investigating soil diffuse contamination, one of key topics is how to differentiate the natural background levels from human-induced pollution (Hanesch et al., 2001; Rodriguez, 2008). The knowledge of a contaminant background value is crucial for the correct implementation of environmental legislation and to evaluate the intensity of contamination. Background values in soils can be defined as the concentration of contaminants without human influence (Salminen and Gregorauskiene, 2000). Therefore, in the case of potentially toxic elements, their usual concentration in soil consists of both a natural pedo-geochemical

fraction and an anthropogenic fraction (ISO, 2005). Because of the latter, it is often difficult to quantify the natural background concentrations of trace elements in soils.

Among the tools proposed in literature to evaluate the intensity of pollution and to differentiate between geogenic and anthropogenic element sources, are Contamination Factors and Enrichment Factors. They both imply the quantification of background concentration of contaminants. The Contamination Factor is the ratio between point-contaminant concentration and its average content in the earth crust or its local background value (Dantu et al., 2009; Krishna and Govil, 2008; Marcinkonis, 2008). Enrichment Factors (EFs) analyze data with respect to a background value and *reference* elements (RE) assumed to be immobile in the soil system.

The majority of the studies carried out so far on diffuse contamination by organic and inorganic contaminants in soils have focused on the quantification of concentrations of contaminants and on the description of the most likely sources. However, studies on the calculation of background values and evaluation of degree of contamination were rarely proposed.

Aim of the present work is to give an appraisal of the degree of soil diffuse contamination in a large Italian Province and to apply and verify the appropriateness of tools developed to establish background values and evaluate the intensity of soil contamination for a large dataset of organic and inorganic contaminants. To do this, the effect of different land uses was investigated, contaminant background concentrations determined, contamination and enrichment factors calculated for a large analytical set comprising 10 inorganic contaminants, 13 rare earth elements, and 3 classes of organic contaminants.

Materials and methods

Study area

The Province of Torino is located in the Piedmont region, NW Italy. It covers 6851 km², with a total population of 2251123. Land in the plains is heavily industrialised and intensively cultivated. The highest human pressure is found in the peri-urban area of the city of Torino, where 42% of the surface is covered by buildings or roads (ISTAT, 2001), population density is 182 000 inhabitants/ha (15 times higher than the surrounding areas) and the majority of industrial plants is located.

This area represents a typical example of European areas that experienced, post WWII, a strong industrial development and an increase of urbanization. As a consequence, a growing proportion of population moved to cities, with a consequent increased pressure on environmental compartments (air, water, soil, biota).

Soil sampling

The soil sampling scheme is based on a 9×9 km grid covering the whole province of Torino and on a 3×3 km grid located in the periurban zone of the city of Torino. In 2007, 70 monitoring sites were sampled, for details of sampling procedures see Fabietti et al. (2006).

Of the 70 sites, 29 were classified as natural (n), 17 as agricultural (a) and 24 as periurban (p) of the city of Torino.

The location of sampling sites and their distribution among distribution natural, agricultural and periurban can be observed in Figure 1.

Overall, 140 soil samples were analyzed for general soil properties, pseudo-total metal contents (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Sr, V and Zn), rare earth elements (REEs Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm Tm Y, and Yb), and for PAHs, PCBs, and PCDD/DFs.

Figure 1: Overview of sampling grid 9×9 km (whole Province of Torino) and 3x3 km (periurban area)

General soil properties

Samples were air-dried, gently crushed in ceramic mortars and sieved at < 2 mm. A portion of each sample was further ground at < 0.15 mm for *aqua regia* (HCl/HNO₃, 3:1 solution) digestion (ISO 11466, 1995). Particle size distribution was determined by the pipette method (Mipaf, 1999). The pH was determined in a KCl solution, 1:2.5 soil/solution ratio (Mipaf, 1999), organic carbon by dry combustion (ISO 10694, 1995), and cation exchange capacity with BaCl₂ at pH 8.1 (ISO 13536, 1995).

Inorganic contaminants and rare earth elements analysis

The *aqua regia* extracts were analysed for metals and REEs with an ICP-MS (Agilent, 7500CE). Duplicates were made for all samples and results accepted when the coefficient of variation was within 5%. A blank and the Certified Reference Material 141 R (Community Bureau of Reference, Geel, Belgium) were included in each batch of analyses for quality control. Results were satisfactory when within a range of ±10% from the certified value.

Organic contaminant analysis

Extraction of organic contaminants was carried out using an ASE 200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA). Extractions were conducted using dichloromethane for PAHs, and toluene for PCBs and PCDDs/DFs. Extracts were purified in an automated Powerprep system (FMS, Waltham, MA, USA) and analysed for PAHs after concentration to 1 ml (EPA 8270D, 1996). The concentrations and profiles of PAH compounds were determined using a high-resolution gas chromatograph Agilent 6890, interfaced with a high-resolution mass spectrometer Agilent 5973 (Agilent, CA, USA). Identification and quantification of 16 PAH compounds (the so-called EPA list) was based on matching their retention time with a mixture of PAH standards. The fractionation and purification of PCBs and PCDDs/DFs after ASE extraction was performed by an automated Powerprep system (FMS, Waltham, MA, USA). The identification and quantification of PCBs and PCDDs/DFs (EPA 1613B, 1994; EPA 1668A, 1999) was carried out with the same instrumentation used for PAHs. The capillary column was 30 m long, with a 0.25 mm i.d. and 0.25 mm stationary phase film thickness (HT8, SGE Analytical Science, Australia). Thirty-two PCBs and 17 PCDDs/DFs isomers and congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular-ion cluster standards. Known amounts of ¹³C-labelled PCBs and PCDDs/DFs were added as internal standards. Recoveries ranged 75–92%, and concentrations were corrected for the recoveries accordingly. Results of dioxin congeners were expressed as I-TE (toxicity equivalents), calculated using toxicity equivalency factors reported by the World Health Organization (Van den Berg et al., 1998).

Background values calculation

Contaminants' background values were calculated, following the ISO Guidance (ISO, 2005), as the value corresponding to the 90th percentile, after removal of outliers, the latter identified as those observations above the 75th percentile by at least 1.5 times the interquartile range.

For elements such as Co, Cr, Ni, V whose origin in soils from the Piedmont Region is mostly related to the parent material (Biasioli et al., 2006; Fabietti et al., 2010; Facchinelli et al., 2001), the natural background was determined using data from the deeper soil horizon, assumed as non affected by diffuse pollution (i.e. the B horizon).

For organic contaminants and elements such as Pb, Cu, Sb, Sn, and Zn, whose origin can be ascribed mostly to point or diffuse sources of contamination (Fabietti et al., 2010) the

“anthropic background” was determined using data from the top soil horizon investigated (i.e. the A horizon).

Contamination factor

Contamination Factors (Cf) are calculated with the following formula (Loska et al., 2004):

$$Cf = X_{\text{sample}} / X_{\text{bck}}$$

Where X_{sample} is the mean content of contaminant and X_{bck} is background level determined for individual contaminant calculated as previously described. A low contamination factor generally indicates a low degree of contamination. In the literature, it is assumed that there is evidence of an anthropogenic enrichment if Cf is > than 1.

Enrichment factors

Enrichment factors is based on the normalization of analytical data against “conservative” reference elements (RE). Among reference elements used in the literature and analysed in the present study Al, Fe, Mn, and Sr were tested and the following formula (Blaser et al., 2000) was applied:

$$Ef = (X_{\text{sample}} / RE_{\text{sample}}) / (X_{\text{bck}} / RE_{\text{bck}})$$

where X_{sample} and RE_{sample} are respectively the contents in mg/kg of the element considered and of the reference element selected in the topsoil of each monitoring site, and X_{bck} and RE_{bck} are the background value of the element considered calculated for the entire study area as previously described.

Reference elements are assumed to have had a uniform flux from crustal-rock sources over a long period of time (Sutherland, 2000). The most common RE used in literature are Al, Ca, Fe, Li, Mn, Sc, and Sr (Çevik et al., 2009; Dantu, 2009; Ghrefat and Yusuf, 2006; Loska et al., 2004; Marcinkonis, 2008; Rubio et al., 2000; Sterckeman et al., 2006; Sutherland, 2000).

A reference element should not be influenced by anthropic activities and should be little affected by weathering processes (Saur and Juste, 1994; Reimann and De Caritat, 2000; Sutherland, 2000). It is assumed that RE ratio stays constant and similar to the crustal value during natural processes, but will change if an element is added via anthropogenic input.

In general, an $EF < 1$ indicates depletion and an $EF > 1$ indicates enrichment of the element considered. Contamination categories can be identified on the basis of the enrichment factor.

Data handling

Statistical analysis was conducted using the software SPSS 13 (SPSS inc.) and Minitab 15 (MINITAB Inc.). Data were geographically managed and processed with the GIS software ArcGis 9.0 (ESRI Inc., California., USA).

Results and discussion

General soil properties

The descriptive statistics of topsoil general properties is reported in **Table 1** divided by land use (agricultural, natural and periurban).

Agricultural soils have a mean pH of 5.5, natural soils have a mean pH of 5.0, and periurban have a mean of 5.7. The mean organic matter content of agricultural and periurban soils (respectively 4.0 and 1.8 %) is lower than natural ones (7.5%) evidently as a consequence of the biomass removal brought about by agricultural practices and of the litter accumulation typical of natural soils.

Cation exchange capacity (CEC) in agricultural soils has a mean value of $31.9 \text{ cmol kg}^{-1}$, while natural soils show a higher value, $36.0 \text{ cmol kg}^{-1}$. Periurban soils show the lowest CEC ($11.3 \text{ cmol kg}^{-1}$) probably in relation to their low organic matter content.

Table 1

Inorganic contaminants

Trace elements

In **Table 2** the descriptive statistics of trace elements content in the 70 investigated sites is presented. Results are shown divided by land use, agricultural (a), natural (n), and periurban

(p), and by sampling depth (A or B horizon). For comparison, Italian legislative limits for soil contaminants in public green areas are also reported (no specific limits are currently adopted for agricultural soils).

Mean contents for A horizons of Pb, Cu, Zn, Sb and Sn are always below legislative limits in all the land uses (except for Sn, probably due an excessively low limit for this parameter). Mean concentrations for these pollutants tend to decrease with depth, reflecting an accumulation in surface layers probably caused by diffuse contamination. On average, concentration of these metals increase in the order $a < n < p$, with periurban soils showing higher concentrations than other soil uses, in particular for Cu, Sb, Sn and Zn. These elements are typically related to emissions from industrial plants, incinerators and traffic (Alloway, 1997) that contribute to a diffuse deposition.

Mean Cr, Ni and Co topsoil contents are in all land uses always above the legislative limits. Natural soils show Co, Cr and Ni content higher in subsoils than in topsoils, with the exception of Cr in periurban soils. This could be attributed to the presence in the area of several outcrops of ultramaphic rocks, enriched in these metals (Biasioli et al., 2006; Fabietti et al., 2010; Facchinelli et al., 2001). The enrichment of Cr and Ni in periurban soils may also derive from atmospheric deposition originated from traffic and industrial activity.

Mean topsoil contents of As are in all land uses below legislative limits, with a few hotspots in natural soils, slightly decreasing from A to B horizon suggesting - together with their low mean concentrations - a mainly natural origin.

Mean V topsoil contents are slightly below legislative limits, with various samples above the threshold. Almost no differences can be observed with depth and with the different land uses, suggesting its main natural origin.

Table 2

Rare earth elements

In **Table 3** data for REEs in the study area are shown. Results are presented as individual REE content, as the sum of all elements (Σ REE), as the the sum of Heavy Rare Earth Elements (HREE, i.e. Dy, Er, Gd, Ho, Tb, Tm and Yb), as the sum of Light Rare Earth Elements (LREE, i.e. Ce, Eu, La, Nd, Pr and Sm), and as the LREE/HREE ratio (L/H).

Data from the present study revealed a highly variable share of individual REEs, these elements decreasing in the following order: $Ce > La > Nd > Y > Pr > Sm > Gd > Dy > Er > Yb > Eu > Ho > Tm$. Similar trend was observed by Zhu and Xing (1992b).

When comparing results obtained with the different land uses, a trend can be observed with periurban soils (Σ REE: 1669 mg/kg) being more enriched than agricultural soils (Σ REE: 159 mg/kg) and natural ones (Σ REE: 134 mg/kg). A T-test conducted among individual topsoil REE did not allow to discriminate land uses except in the case of Tm, which showed an enrichment in periurban soils. **DISCUSSION??**

When the individual REE are considered, some hotspots could be detected for Eu in periurban soils (with concentrations up to 8.6 and 9.7 mg/kg), same soils resulted also enriched in other inorganic contaminants, suggesting point-contamination for this REE in periurban areas.

Results observed for Σ REE are in agreement with data presented by [Hu et al. \(2006\)](#) that found mean REE concentrations in China equal to 181 mg/kg (1225 soil samples); in Brazil equal to 77 mg/kg (1363 soil samples). Other authors have found slightly lower concentrations of REEs in Australia (105 mg/kg, [Diatloff et al., 1996](#)) and Japan (98 mg/kg, [Yoshida et al. 1998](#)). For EU, the FOREGS ([Salminen, R. et al., 2005.](#)) dataset reports (790 soil samples) mean topsoil content of Σ REE equal to 115 mg/kg.

In data from the present study, only weak differences could be observed between topsoil and subsoil for individual REEs, as well as for the sum and light/heavy REEs ratio, reflecting on average an absence of diffuse contamination and suggesting the main natural origin of these elements.

Table 3

Organic contaminants

Almost all the investigated soils presented contents of PAH with less than 4 rings (i.e. naphthalene, acenaphthene, fluorene, phenantrene and anthracene) below detection limit (<1 ng/g), reflecting the high degradability and volatility of these compounds. PAHs with a number of rings higher than 4 are more recalcitrant to degradation and have stronger affinity with soil organic matter, nevertheless these compounds could be detected only in 20% of the soil samples, showing concentrations far below legislative limits. The only PAHs that could be detected in the samples investigated are benzo[b]fluoranthene, chrysene, fluoranthene, and benzo[a]pyrene. Among these, benzo(a)pyrene (B[a]p) has been proposed in literature as a tracer of total PAHs concentration ([Wilcke, 2000](#)) and will be used in the following part of

the discussion as representative of the overall PAH contamination. In the investigated soils, PCBs, and PCDD/DFs were always detectable.

Results for organic contaminants (B[a]p, PCBs, and PCDD/DFs) divided by land use are shown in **Table 4**. Organic contaminants were always below legislative limits for green areas, revealing a moderate degree of pollution however, even if concentrations were low, some clear trends could be observed among land uses. Organic contaminants in fact were lower in agricultural and natural soils than in periurban soils. These latter showed for B[a]p and PCBs concentrations twice those observed in natural soils and three times those found in agricultural ones. PCDD/DFs were found to be more ubiquitous, with only a moderate enrichment in periurban soils. These trends can be attributed to the elevated degree of anthropic pressure of periurban soils and/or the proximity to sources. The higher content in organic contaminants observed in natural soils can be due to the strong affinity to soil organic matter of these compounds (Masih and Taneja, 2006).

Table 4

Correlations among contaminants

A correlation analysis after log-transformation conducted among As, Co, Cr, Cu, Ni, Pb, Sb, Sn, Zn, B[a]p, PCBs and PCDDs/DFs for all soils gave the results presented in Table 5.

Data show a strong correlation between Cr, Ni, and Co, substantiating their common lithological origin. Lead shows good correlations with Zn, Sb, PCDDs/DFs, PCBs and B[a]p in all soils, suggesting a common anthropic origin for these contaminants, regardless of the land use.

Table 5

Background levels calculation

Background levels for inorganic contaminants were calculated according to the ISO guidance previously described. Background was investigated to give an estimation of diffuse contamination and as a key parameter to further compute contamination factors and enrichment factors.

Calculated background values were above Italian legislative limits for Co (background: 23 mg/kg), Cr (275 mg/kg), Ni (137 mg/kg) and V (92 mg/kg). Background values lower than Italian limits were obtained for As (13 mg/kg), Cu (43 mg/kg), Pb (50 mg/kg), Sb (0.9 mg/kg), Sn (4.1 mg/kg), Zn (84 mg/kg).

For the sum of REEs the background was calculated to be 204 mg/kg.

Background values for organic contaminants were low, in agreement with the moderate contamination observed for these parameters (B[a]p: 31.5 ng/g, PCB: 8.9 ng/g, PCDD: 3.5 ng/kg I-TE).

Contamination factor

Cf in association with Ef, are one of the tools proposed in the literature to evaluate the intensity of soil pollution.

Cf were calculated for the investigated soils as previously described. The boxplots for Cf for inorganic and organic contaminants are shown in figure 2 divided by land use. Dashed lines in the figure represent limits between soils with evidence of anthropic contamination. Cf resulted effective in differentiating the effect of contamination in function of the different land uses, in particular for some contaminants and for periurban soils. In fact, these latter could be classified as having evidence of anthropic contamination for PCDD/DF, PCB, B[a]p, Cu, Sb, Sn and Zn. Also, elements whose origin was mostly attributed to parent material such as Cr and Ni, presented some anthropic contribution in periurban soils.

On the average, no anthropic contribution could be observed for As, Co, V, and REEs. For these elements, in fact, Cf were always low, and no significant differences could be observed between land uses. Maxima of Cf were always < 1 , reflecting minimal or no contamination.

Figure 2: Boxplots of Contamination factors divided by land uses: agricultural (a), natural (n) and periurban (p). Dashed lines are limits between classes of contamination as proposed by [Hakanson 1980](#).

Enrichment factors

Similarly to Cf, enrichment factors (Ef) are commonly used to evaluate the intensity of contamination on soils and can only be applied to inorganic contaminants. Ef allow to verify hypothesis of natural or anthropogenic origin for a contaminant, by comparing data with those of a conservative element and with the area background value.

For the calculation of enrichment factors (Ef), data have to be normalized against a reference element, assumed as immobile in soils and not affected by contamination. For the present study the suitability of Al, Fe, Mn and Sr to act as reference elements was explored. Descriptive statistic of these metals in the investigated soils is presented in **Table 6**.

To verify the appropriateness of these elements to be used as background, their raw data were processed to verify the absence of human influence on their origin and distribution. This was done through the calculation of their coefficient of variation (CV) and the application of the Anderson-Darling normality test. Differences among reference elements at the two sampling depths considered were tested with a paired T-test run under the assumptions of equal variances, as confirmed by a Levene test for homoscedasticity (not shown).

Coefficients of variation were low (ranging 26-36 %) and constant for both sampling depth for Fe, Al e Mn. Sr, on the contrary, showed a relatively high CV, being 52.4% in topsoils and 54.9% in subsoils.

T-test revealed no significant differences with depth for all four elements, confirming their main lithogenic origin. Al, Fe, and Mn were normally distributed, confirming their natural origin, while Sr distribution was found to be log-normal.

Background values for the four elements were calculated applying ISO protocol previously described.

Table 6

Following reference elements data processing, Enrichment factors were calculated for inorganic contaminants in all land uses (for REE only the Σ REE was used). Ef were calculated using Al, Fe, Mn, and Sr to account for differences in the suitability of these elements to act as reference. **Figure 3** shows boxplots of EFs calculated considering all land uses together using the four reference elements above mentioned. Dashed line represents limit for evidence of contamination ($Ef > 1$).

Overall, for all inorganic contaminants no statistically significant differences could be observed between Ef calculated using Al, Fe, and Mn as reference elements. On the other hand, Sr systematically overestimated Ef compared to the other reference elements. This can be justified by the number of outliers in Sr distribution, that determined a higher variability of this element compared to Al, Fe and Mn. As a result, Fe was selected as reference element for further data processing.

In **Figure 4** boxplots of Ef normalized against Fe for inorganic contaminants are shown, divided by land use. Dashed line represents limit for evidence of contamination ($Ef > 1$). Similarly to what presented for Contamination factor, the Ef allowed to highlight differences for land uses for some contaminants.

Some elements appeared to be independent of the land use, such as As, Co, V and, to a lesser extent, Cr and REE. For this latter, a minimal enrichment in agricultural soils appeared that could be related to the application of inorganic fertilizers. The trends in Cf for this first group of elements suggested their main natural origin.

Cu, Sb and Sn and to a lesser extent Ni and Zn, revealed an enrichment in periurban soils, as a consequence of their proximity to sources.

Pb compared to the other elements was the only contaminant with mean Cf > 1 in all land uses, suggesting its widespread diffusion in topsoils of the sampling area.

Figure 3

Figure 4

CONCLUSIONS

The investigation of 140 soil samples within the Province of Torino revealed some clear trends for organic and inorganic contaminants and provided useful information on the suitability of available tools for the description of soil diffuse contamination.

Trends and correlations among contaminants, together with the use of Contamination and Enrichment Factors (Cf and Ef) revealed the presence of a certain degree of diffuse pollution originated from traffic and industrial activities. Periurban areas appeared to suffer the most relevant contamination compared with natural and agricultural sites.

Copper, Sb, Sn, Pb, and to a lesser extent Zn presented mean and background values well below Italian legislative limits for green areas. However, contamination and enrichment factors for these elements showed for these elements values above 1, reflecting their dominant anthropic origin. The intensity of diffuse contamination was low these elements in agricultural and natural soils and became relevant for periurban ones.

Co, Cr, Ni, and V had high mean and background values, often above Italian limits for green areas. However, Cf and Ef for these metals were close or lower than 1, showing no indication of anthropic contribution (except for Ni in periurban areas) and confirming the prevailing natural origin of these elements in the study area. This was substantiated by the fact that no differences could be identified in function of the land uses.

Arsenic had low mean and background content, and did not revealed evidence of anthropic enrichment.

Rare Earth Elements gave results comparable with those observed in the literature. They seemed to mostly relate to parent material, only exceptions were Tm systematically higher in periurban soils. Eu also showed some hotspots in periurban areas, suggesting point-contamination for this element. Cf and Ef for REE confirmed their natural origin, with the exception of a slight enrichment in agricultural areas.

For organic contaminants, PAHs, PCB, and PCDD/DF had mean and background contents always very low, with agricultural and natural soils presenting Cf below 1, showing no evidence of anthropic enrichment. Instead, a clear anthropic enrichment was evident for periurban soils, especially for PCB and PCDD/DF, for which a Cf above 1 was observed.

The results obtained in this study show the importance of merging the quantification of contaminants with the elaboration of indices of contamination. These latter require an accurate quantification of background values to be able to discriminate the anthropic contribution. Among the tools used in this study (Enrichment and Contamination factors), the first revealed to be more accurate, but as a drawback it cannot be applied to organic contaminants and needs to carefully select the reference element to be adopted. Therefore, given the similar results produced, we suggest the adoption of Contamination factors as a reliable tool to evaluate intensity and origin of contamination for further studies related to diffuse soil pollution. This study revealed that some contaminants can be identified as tracers of diffuse contamination, and should be therefore always included in similar studies i.e. Sb, Sn, Pb, and organic contaminants.

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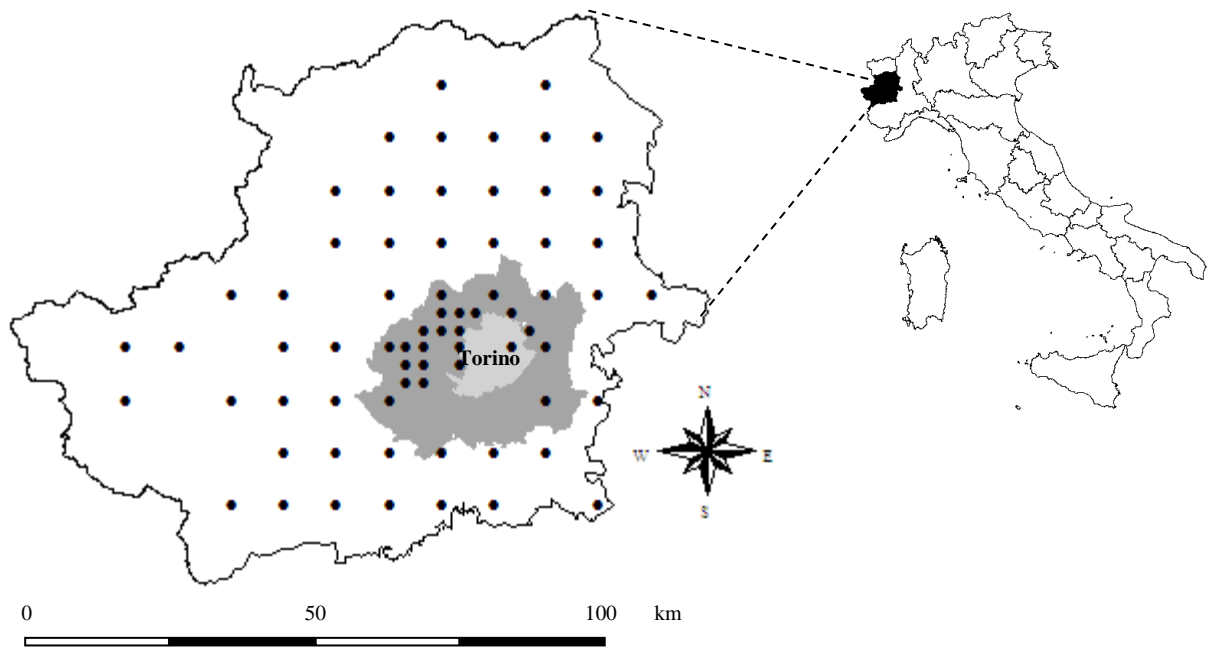


Figure 2: Overview of sampling grid 9×9 km (whole Province of Torino) and 3x3 km (periurban area)

Figure 2: Boxplots of Contamination factors divided by land uses: agricultural (a), natural (n) and periurban (p). Dashed line represent limit between contaminated (>1) and uncontaminated (<1) soils.

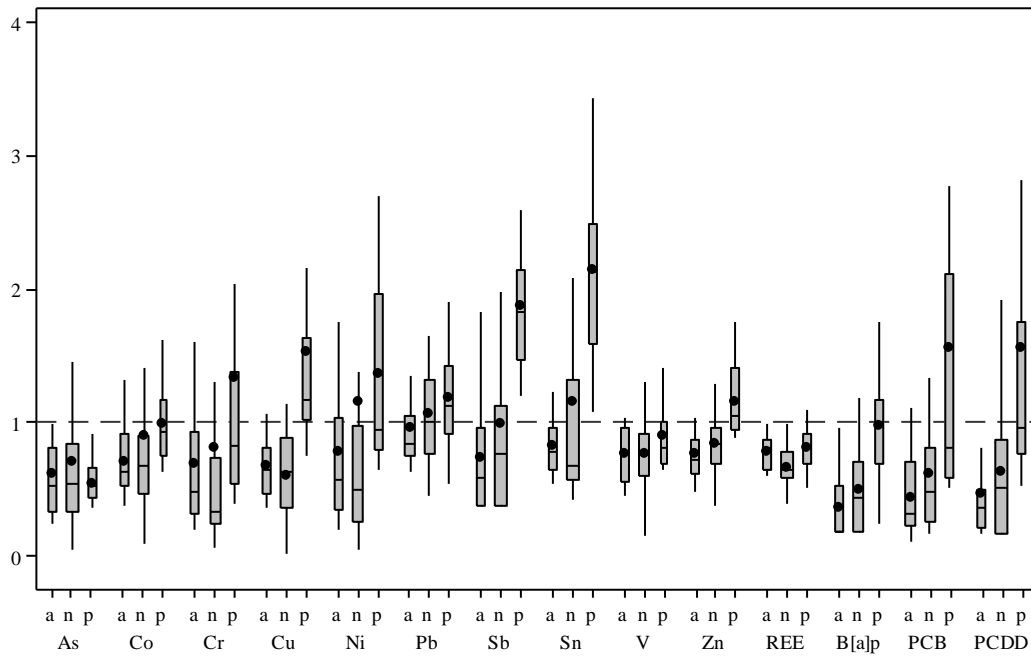


Figure 3: Box-plots of Topsoil Efs, normalized to Al, Fe, Mn and Sr. Dashed line represent limit between contaminated (>1) and uncontaminated (<1) soils.

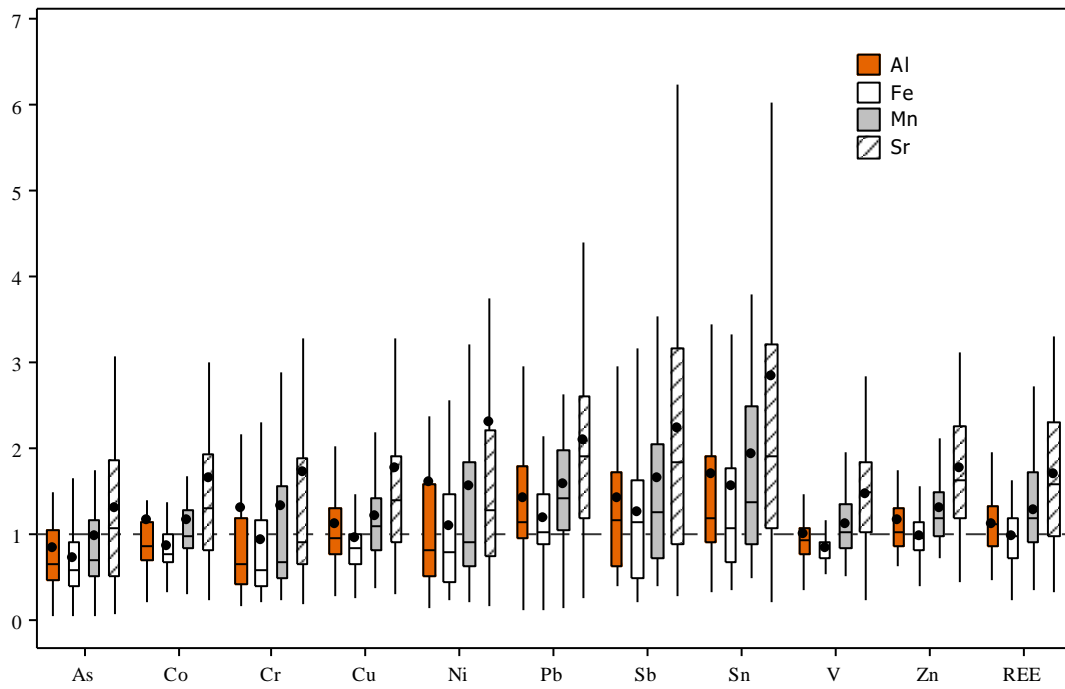


Figure 4: Box-plots of Topsoil Efs values normalized to Fe. Data are presented divided by agricultural (a), natural (n) and periurban (p) land use. Dashed line represent limit between contaminated (>1) and uncontaminated (<1) soils.

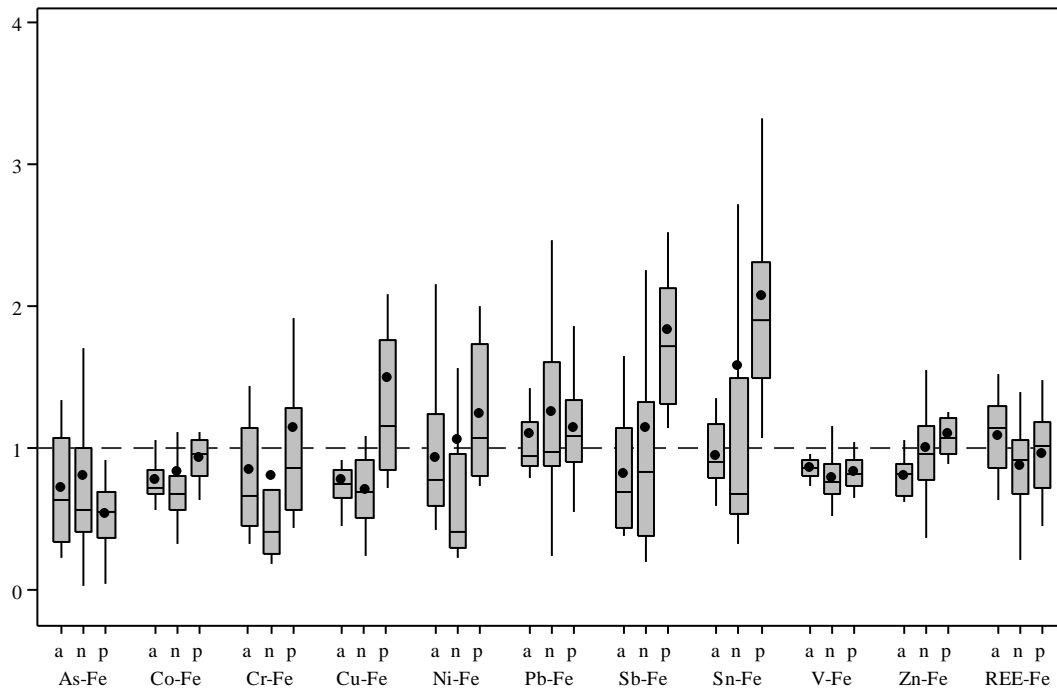


Table 1 - Descriptive statistics of main physical-chemical properties of topsoils. Results are presented divided by land use (agricultural, natural and periurban)

	Agricultural			Natural			Periurban		
	CEC	OM %	pH	CEC	OM %	pH	CEC	OM %	pH
	cmol kg ⁻¹	%		cmol kg ⁻¹	%		cmol kg ⁻¹	%	
Mean	31.9	4.0	5.5	36.0	7.4	5.0	11.3	1.8	5.7
Median	33.5	3.7	5.5	36.0	8.2	5.2	11.3	1.4	5.3
Std. dev.	6.4	2.1	0.9	5.5	3.2	1.2	4.0	0.9	1.1
Min	13.3	1.3	4.3	21.9	0.9	3.6	5.9	0.9	4.4
Max	39.7	9.9	7.8	49.9	15.1	7.1	19.5	3.4	7.4

Table 2: Descriptive statistics of inorganic contaminants. Results (mg/kg) are presented divided by land use (agricultural, natural, periurban) and depth, topsoil (A) – subsoil (B). Italian legislative limits for green/residential areas are also shown.

	As		Co		Cr		Cu		Ni		Pb		Sb		Sn		V		Zn	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
	Agricultural																			
Mean	8.0	7.9	17	17	192	186	30	28	107	107	33	29	0.5	0.4	3.2	3.0	70	70	65	66
Median	6.9	6.2	15	18	135	140	29	27	80	84	29	27	0.4	0.3	3.0	2.9	73	69	62	63
St Dev	4.6	5.3	6	6	141	118	12	12	78	76	13	11	0.3	0.3	0.8	0.9	18	17	19	17
Min	3.3	2.8	9	8	54	66	16	13	29	35	22	17	0.3	0.3	2.1	2.0	42	48	42	47
Max	21	22	31	29	550	470	65	59	330	350	74	58	1.2	1.1	4.7	5.0	96	97	127	120
	Natural																			
Mean	9.3	8.8	21	23	224	257	27	25	159	165	37	29	0.7	0.6	4.4	3.6	71	70	72	68
Median	7.0	6.4	16	15	94	100	28	25	69	65	35	28	0.5	0.3	2.6	2.5	72	70	72	65
St Dev	7.3	6.7	19	22	300	373	14	15	284	304	15	12	0.6	0.9	5.2	2.9	26	26	22	24
Min	0.7	1.4	2	2	19	17	1	1	7	7	16	7	0.3	0.3	1.6	1.2	15	12	33	28
Max	35	32	77	84	1000	1300	50	54	1500	1600	90	75	3	4.7	28	13	140	140	140	150
	Periurban																			
Mean	7.1	6.4	23	24	368	284	67	58	188	197	41	37	1.2	1.2	8.1	7.6	83	87	99	90
Median	6.9	6.4	22	22	230	180	51	50	130	170	39	36	1.2	1.1	8.1	7.6	75	84	90	81
St Dev	2.4	3	7	7	432	253	40	28	99	93	18	18	0.3	0.4	2.8	2.7	25	24	23	20
Min	1.0	1.1	15	12	110	91	33	25	90	90	4	11	0.8	0.6	4.1	3.6	60	50	76	60
Max	12	13	38	36	1900	1100	170	130	370	370	81	81	2.1	2.1	15	13	140	140	150	130
	Italian Limits																			
	20		20		150		120		120		100		10		1		90		150	

Table 3: Descriptive statistics of REEs contents in the investigated soils. Results (mg/kg) are presented divided by land use, depth (topsoil-A, subsoil-B) and as individual REE, sum, sum of heavy, and sum of light REEs

	Y		Gd		Dy		Ho		Er		Tm		Yb		La		Ce		Pr		Nd		Sm		Eu		ΣREE		HREE		LREE		L/H	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
	Agricultural																																	
Mean	19.9	19.6	5.4	5.1	4.1	4.0	0.7	0.7	2.2	2.1	0.1	0.1	1.8	1.8	27.7	26.9	56.1	54.9	7.0	6.8	26.9	26.6	5.6	5.3	1.1	1.0	159	155	34	33	124	121	3.8	3.7
Median	22.0	21.0	5.5	4.9	4.5	4.4	0.8	0.8	2.5	2.2	0.1	0.1	2.0	2.0	29.5	27.0	56.5	54.5	7.2	6.9	28.0	27.0	5.7	5.4	1.2	1.0	164	148	37	36	128	121	3.8	3.7
St Dev.	3.9	3.5	0.7	0.8	0.6	0.7	0.2	0.2	0.5	0.4	0.0	0.0	0.4	0.4	6.6	6.6	11.5	12.6	1.5	1.5	4.9	5.5	0.9	1.0	0.2	0.2	26	29	6	6	25	27	1.0	0.9
Min	13.0	13.0	4.2	4.0	2.9	2.8	0.3	0.3	1.3	1.4	0.1	0.1	1.1	1.1	16.0	15.0	37.0	35.0	4.7	4.1	19.0	17.0	4.4	4.1	0.7	0.6	122	112	23	23	83	76	2.1	2.1
Max	24.0	24.0	6.5	6.9	4.6	5.0	0.9	0.9	2.7	2.5	0.2	0.2	2.2	2.2	38.0	39.0	75.0	84.0	9.5	9.8	36.0	38.0	7.5	7.9	1.4	1.4	202	219	40	41	167	180	5.5	5.3
	Natural																																	
Mean	16.2	16.6	4.4	4.6	3.4	3.5	0.5	0.6	1.8	1.8	0.1	0.1	1.4	1.5	23.4	23.8	48.1	49.4	5.9	5.9	22.9	23.1	4.6	4.6	0.9	0.9	134	137	28	29	106	108	3.9	3.8
Median	16.0	17.0	4.3	4.7	3.4	3.5	0.6	0.6	1.7	1.9	0.1	0.1	1.4	1.5	24.0	24.0	49.0	50.0	6.0	6.0	22.0	23.0	4.4	4.7	0.9	0.9	132	137	27	30	107	109	4.0	3.9
St Dev.	5.2	5.4	1.3	1.3	1.0	1.1	0.3	0.2	0.6	0.6	0.0	0.0	0.5	0.5	7.9	9.0	14.5	17.3	1.9	2.1	6.8	7.6	1.3	1.4	0.3	0.3	37	43	9	9	32	37	1.0	1.0
Min	6.0	5.9	1.2	1.2	1.2	1.2	0.3	0.3	0.6	0.7	0.1	0.1	0.7	0.6	4.8	4.5	13.0	12.0	1.6	1.5	6.5	5.9	1.3	1.1	0.3	0.3	45	43	10	10	30	27	0.9	0.8
Max	26.0	26.0	6.5	6.8	5.0	5.5	1.0	1.0	3.0	2.9	0.2	0.2	2.5	2.6	38.0	41.0	75.0	80.0	8.9	9.5	35.0	37.0	7.0	6.9	1.3	1.4	200	209	42	45	165	174	5.7	5.8
	Periurban																																	
Mean	20.0	20.4	5.1	5.2	4.0	4.1	0.7	0.8	2.1	2.2	0.3	0.3	1.7	1.7	29.6	28.9	58.8	57.6	7.2	7.1	28.4	27.8	5.8	5.9	2.1	1.7	166	164	34	35	132	129	4.0	3.8
Median	19.0	20.0	5.1	5.0	4.0	4.2	0.7	0.8	2.0	2.3	0.3	0.3	1.6	1.7	29.0	29.0	60.0	56.0	7.2	7.4	29.0	29.0	6.1	5.9	1.2	1.2	167	162	33	35	134	130	4.4	4.2
St Dev.	2.9	3.2	0.7	0.9	0.4	0.5	0.1	0.1	0.2	0.3	0.0	0.1	0.3	0.4	9.0	9.6	15.8	18.1	1.9	2.2	7.2	7.5	1.2	1.3	2.7	2.0	33	39	4	4	34	39	1.1	1.1
Min	17.0	14.0	4.1	4.0	3.2	3.1	0.6	0.6	1.8	1.5	0.2	0.2	1.4	1.0	13.0	14.0	30.0	31.0	3.7	3.8	15.0	16.0	3.7	4.0	0.9	0.9	105	109	29	24	67	70	1.7	1.8
Max	26.0	26.0	6.0	7.1	4.6	4.8	1.0	0.9	2.7	2.8	0.4	0.4	2.6	2.6	43.0	45.0	86.0	91.0	10.0	11.0	40.0	41.0	8.0	8.6	9.7	9.6	224	238	42	41	187	198	5.5	5.2

Table 4: Descriptive statistics of organic contaminants content in the topsoils (A). Results are presented divided by land use (agricultural, natural and periurban).

	B[a]p	Σ PCB	Σ PCDD/DF
	ng/g	ng/g	ng/kg I-TE
Agricultural			
Mean	9.6	3.8	1.3
Median	5.0	2.9	1.1
St Dev	7.5	2.5	1.3
Min	5.0	1.0	0.5
Max	32.0	10.0	6.4
Natural			
Mean	13.6	5.8	1.9
Median	12	4.4	1.5
St Dev	8.4	4.8	1.4
Min	5.0	1.4	0.5
Max	32.0	23.0	5.6
Periurban			
Mean	26.8	12.8	3.0
Median	27.4	6.9	2.5
St Dev	10.2	14.7	2.0
Min	11.0	0.9	0.7
Max	47.5	50	8.2
Italian Limits	100	60	10

Table 5: Pearson correlation matrix among inorganic and organic contaminants in topsoils. Cells show Pearson correlation coefficients and the correspondent *P-value*. In bold are reported significant correlations ($r > 0.5$).

	As	Co	Cr	Cu	Ni	Pb	Sb	Sn	Zn	B[a]p	PCB
Co	-0.203										
	<i>0.119</i>										
Cr	-0.282	0.732									
	<i>0.029</i>	<i>0.000</i>									
Cu	0.126	0.085	-0.026								
	<i>0.336</i>	<i>0.516</i>	<i>0.843</i>								
Ni	-0.170	0.868	0.705	0.011							
	<i>0.195</i>	<i>0.000</i>	<i>0.000</i>	<i>0.935</i>							
Pb	0.331	-0.008	0.038	0.192	-0.080						
	<i>0.010</i>	<i>0.950</i>	<i>0.771</i>	<i>0.142</i>	<i>0.542</i>						
Sb	0.577	-0.066	-0.057	0.471	-0.100	0.608					
	<i>0.000</i>	<i>0.615</i>	<i>0.665</i>	<i>0.000</i>	<i>0.449</i>	<i>0.000</i>					
Sn	0.170	-0.068	0.034	0.324	-0.055	0.373	0.654				
	<i>0.194</i>	<i>0.607</i>	<i>0.797</i>	<i>0.012</i>	<i>0.679</i>	<i>0.003</i>	<i>0.000</i>				
Zn	0.267	0.166	0.236	0.376	0.069	0.539	0.686	0.375			
	<i>0.039</i>	<i>0.204</i>	<i>0.070</i>	<i>0.003</i>	<i>0.601</i>	<i>0.000</i>	<i>0.000</i>	<i>0.003</i>			
B[a]p	-0.070	0.144	0.141	0.143	0.102	0.571	0.172	0.116	0.168		
	<i>0.595</i>	<i>0.272</i>	<i>0.282</i>	<i>0.275</i>	<i>0.440</i>	<i>0.000</i>	<i>0.190</i>	<i>0.376</i>	<i>0.199</i>		
PCB	-0.068	0.021	0.009	0.054	-0.008	0.526	0.030	-0.019	0.042	0.553	
	<i>0.605</i>	<i>0.871</i>	<i>0.946</i>	<i>0.682</i>	<i>0.953</i>	<i>0.000</i>	<i>0.818</i>	<i>0.885</i>	<i>0.750</i>	<i>0.000</i>	
PCDD/DF	-0.162	0.068	0.082	-0.023	-0.042	0.545	-0.072	-0.073	0.064	0.424	0.668
	<i>0.217</i>	<i>0.607</i>	<i>0.534</i>	<i>0.862</i>	<i>0.751</i>	<i>0.000</i>	<i>0.585</i>	<i>0.579</i>	<i>0.628</i>	<i>0.001</i>	<i>0.000</i>

Table 6: Descriptive statistics of reference elements (mg/kg) and background values determined for B horizons.

	Al		Fe		Mn		Sr	
	A	B	A	B	A	B	A	B
Mean	29117	30283	34033	33523	790	797	84.1	87.0
Median	29000	29000	34000	33000	755	750	73.5	75.0
St Dev	9944	9755	8897	9425	278	294	44.0	47.8
Min	13000	13000	10000	8400	330	260	14.0	11.0
Max	59000	61000	63000	65000	1500	1700	260.0	270.0
CV (%)	34	32	26	26	35	37	52	55
AD normality test	0.9	0.5	0.8	0.5	0.7	0.5	1.8	1.8
P-value	0.023	0.215	0.028	0.183	0.065	0.155	<0.005	<0.005
Background values		33900		35000		1030		130