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Data on milk dioxin contamination linked with the location of fodder croplands allow to hypothesize the origin of the pollution source in an Italian valley ☆

Rosanna Desiato [a,*], Silvia Bertolini [a], Elisa Baioni [a], Maria Ines Crescio [a], Giampiero Scortichini [b], Alessandro Ubaldi [c], Bruno Sparagna [d], Giancarlo Cuttica [e], Giuseppe Ru [a]

[a] Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, Italy
[b] Istituto Zooprofilattico Sperimentale dell'Abruzzo e del Molise, Italy
[c] Istituto Zooprofilattico Sperimentale delle Regioni Lazio e Toscana, Italy
[d] ASL TO 3, Azienda Sanitaria Locale di Collegno e Pinerolo, Italy
[e] Dipartimento Provinciale di Vercelli Arpa Piemonte, Vercelli, Italy

HIGHLIGHTS

- We investigated the geographical distribution of dioxins in an Italian alpine valley.
- Data on dioxin in milk were combined to distribution of fodder cropland parcels.
- Concentration isopleth maps were obtained through the kriging technique.
- Results support a steel plant as a common point source of contamination.
- The paper presents a novel approach to investigate dioxin local contamination.

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ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) have similar toxic, endocrine-disrupting, and carcinogenic activity. They are classified as persistent organic pollutants accumulating in the environment and the tissues of living organisms. High concentrations of PCDD/F and dl-PCB have been detected in bovine milk collected in a Piedmont valley (Northwestern Italy) since 2004.

This geographic study describes the local distribution of pollution from PCDD/Fs and dl-PCBs. Since their presence in animal products could be traced back to the ingestion of contaminated fodder, dioxin levels in cow milk were related to the distribution of fodder cropland parcels. Specifically, the aim of the study was to determine, through an exploratory approach, whether the contamination was consistent with one common point source of contamination or different scattered sources.

Data for PCDD/F and dl-PCB concentrations in the bulk milk from 27 herds, sampled over a 4-year period (2004–2007), were matched to the georeferenced land parcels the dairy farmers used for growing fodder. Isopleth maps of dioxin concentrations were estimated with ordinary kriging. The highest level of pollution for both PCDD/Fs and dl-PCBs was geographically juxtaposed: in both instances, the location of the local steel plant was within this extremely highly polluted area.

The study results support the hypothesis for one common point source of contamination in the valley. The exploratory spatial analysis applied in this research may provide a valuable, novel approach to straightforward identification of a highly likely source of dioxin contamination of dairy products (even in the absence of top soil contamination data).

1. Introduction

Persistent organochlorine compounds such as dioxins and polychlorinated biphenyls (PCBs) are a family of chemicals with demonstrated endocrine-disrupting properties, neurotoxicity and carcinogenic

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* Corresponding author at: Biostatistica, Epidemiologia ed Analisi del Rischio, Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta, via Bologna 148, 10154, Torino Italy. Tel.: +39 0112686372; fax: +39 0112686371.
E-mail address: rosanna.desiato@izsto.it (R. Desiato).

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activity. The term dioxins refers to a group of 210 polychlorinated aromatic chemical compounds divided into polychlorinated dibenzo-para-dioxins (PCDDs or dioxins) and polychlorinated dibenzo-para-furans (PCDFs or furans). The majority of the 210 dioxin congeners are not thought to pose a risk to human health, and only 17 congeners are reported to have potential harmful effects on health.

Particularly stable, persistent in the environment, and toxic to humans and animals, these compounds are readily formed as unintentional by-products of many chemical, industrial and combustion processes involving chlorine-containing materials. Specifically, PCDDs are formed as inadvertent by-products, sometimes in combination with PCDFs, during the production of chlorophenols and chlorophenoxy herbicides, and they have been detected as contaminants in these products. PCDDs and PCDFs may also be produced in thermal processes such as incineration and metal-processing, as well as in the bleaching of paper pulp with free chlorine. They are also formed as a consequence of such natural phenomena as fires and volcano eruptions (U.S. EPA, United States Environmental Protection Agency, 2006).

PCBs are a series of 209 bicyclic aromatic compounds. Some of them, the 12 coplanar congeners, because of their chemical structure and biological activity, have toxic properties similar to dioxins and furans and are considered to be "dioxin-like" (dl-PCBs; WHO, 2010). These molecules were synthesized at the beginning of the last century and have been produced commercially since 1930 as plasticizers, fire retardants, and components in electrical wiring and hydraulic fluids. They are now largely banned because of their toxicity and their tendency to bioaccumulation. Although no longer produced in many countries, large quantities of these substances are present in electrical equipment and plastics (U.S. EPA, United States Environmental Protection Agency, 2006).

In the last century, PCDDs, PCDFs and dl-PCBs were extensively released into the environment, with widespread airborne diffusion over pasturelands, or entered the biosphere as by-products of herbicides in weed control. Metallurgical processes such as high-temperature steel production, smelting operations, and scrap metal recovery furnaces are typical sources of dioxin pollution of the surrounding environment (Anderson and Fisher, 2002).

Dioxin and dioxin-like compounds may enter the animal feed to human food chain though both direct and indirect pathways (National Academy of Sciences/National Research Council, NAS/NRC, 2003). The direct environmental pathways include air-to plant/soil, air-to plant/soil-to animal, and water /sediment to fish.

Atmospheric deposition produced by human activities as steelworks, cementworks, waste incinerators or motorways is usually the primary way of enter of lipophilic contaminants into plants (Welsch-Pausch and MCLachlan, 1998).

After release (mostly airborne emission) the compounds deposit on vegetation, soils, and in water and are retained on plant surface and in the surrounding soil and sediment in waterways (U.S. EPA, United States Environmental Protection Agency, 2004). The soil-borne contaminants then become a reservoir source that could reach plants used for animal feeds by volatilization and redeposition or as dust, as contamination by root absorption is considered by many authors as negligible (Wild and Jones, 1992; Welsch-Pausch and MCLachlan, 1998; Kipopoulou et al., 1999).

Moreover they can enter aquatic systems via direct discharge in water, by deposition onto soil, and by runoff from water sheds and cumulate as suspended particles and in bottom sediments. Indirect pathways are linked to agricultural practices leading to contamination of plant and animal-by-products use to formulate animal diets and manufacture animals feeds.

In the lactating cows the exposure by inhalation is considered as negligible, whereas they may ingest daily from 1% to 10% of soil when grazing or through the soil contamination of the fodder at harvesting. After ingestion of contaminated fodder or top soil by grazing cattle, these highly lipophilic compounds can accumulate in the animal's fatty tissues (Fries and Paustenbauch, 1990; Schulz et al., 2005; Rychen et al., 2008) and excreted via milk. A good correlation has been observed between PCB levels in autumn milk and in soil (Mamontova et al., 2007). The contamination of milk by POPs depends on environmental factors, rearing system and of the characteristics of the contaminants. Transfer rates to milk vary for PCBs from 5% to 90%, whereas for PCDD/Fs from 1% to 40%. The transfer of the compounds towards milk is related to the hydrophobicity of the pollutants as well as to the metabolic susceptibility of the compounds (Thomas et al., 1999; Rychen et al., 2008).

Because of their tendency to accumulate in the fatty tissues of livestock and in their food products, the risk of their transfer through the human food chain has raised cause for concern. Besides occupational and accidental exposure, the major source for humans is food of animal origin. While exposure via other routes normally accounts for less than 10% of total daily dioxin intake (inhalation, dermal absorption and ingestion of airborne particles), more than 90% of human exposure occurs through the consumption of animal food products such as meat, milk, dairy products and fish (Fürst et al., 1992).

The International Agency for Research on Cancer has classified the dl-PCBs in Group 2A (probably carcinogenic to humans), based on the limited evidence in humans and sufficient evidence in animals. The 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF and PCB 126 congeners have been classified as a Group 1 carcinogen, indicating that they are carcinogenic to humans (IARC International Agency for Research on Cancer, 2012). Other PCDD/Fs are classified in Group 3 (not classifiable as to their carcinogenicity in humans) because of the absence of convincing data from experimental animals (IARC International Agency for Research on Cancer, 1997).

When high concentrations of micropollutants in feed and in food of animal origin have been ascertained, European legislation requires back tracing to the pollution source (Commission Recommendation 2013/711/EU of 3 December 2013 on the reduction of the presence of dioxins, furans and PCBs in feed and food)

In this study, we refer to concentrations of PCDD/Fs and dl-PCBs exceeding the European Union limits detected in milk and meat samples collected in the Susa valley, a mountainous area of Piedmont, where environmental contamination by these micropollutants was first detected in late 2004 (Desiato et al., 2012). At the time of that first detection the maximum exceeding levels in force was for both bovine milk and meat 3 pg WHO-PCDD/F-TEQ/g fat (Council Regulation (EC) No 2375/2001). While there was no clear evidence of the sources of the pollution in the valley, a large steel mill has been operated there since the 1960s: it is a smelter of scrap materials using recycled materials from steel production or other iron-containing waste materials.

Following the detection of unacceptable dioxin levels in animal food products in 2005, restrictive measures (milk withdrawal and disposal and ban on sale of animals) were applied in several local farms in the area for varying periods.

At that time, a sufficient number of environmental samples (soil, vegetables and atmospheric emissions) to provide a geographic distribution of the contamination was unavailable (Cappa et al., 2010). This prompted the idea to carry out exploratory study building on the available data from the numerous dairy samples collected from the farms in the valley.

Starting from the geographic data, the aim of this study was to determine whether the dioxin contamination in the milk samples was consistent with one common point source or with different sites. Since the presence of these substances in animal products is linked mainly to the ingestion of contaminated feed, and this is particularly true for cattle during grazing, we back-traced the location of the croplands where the fodder was grown for feeding the dairy cows to identify and characterize the source of such contamination.

2. Materials and methods

2.1. Setting and datasets

The study builds on the data from a risk-based surveillance of dairy products carried out in the Susa valley which is in the Northwestern

Italy, bordering France. The valley stretches east-west in a long, narrow path through the Alps; westerly winds predominate (although with a daily rotation); farmlands and small and medium livestock holdings are predominant throughout the area.

Three datasets were available and used. The first dataset included the values of PCDD/F and dl-PCB concentrations detected in the bulk milk from 27 bovine farms in the study area (Table 1); a subgroup of 6 farmers (whose farms had shown unacceptable levels of PCDD/Fs in milk and meat) was interviewed about the origin of feed and fodder, the feeding patterns of the animals, and the use of croplands to establish whether the contamination of animal food products might have been related to general environmental contamination rather than local and hazardous practices on the individual farms. Based on our preliminary survey, the remaining farms were visited and investigated by the colleagues of the local veterinary unit to identify any particular difference with regard to additional pollutant sources. The sampling campaign on dairy products was carried out during a 4-year period (2004–2007). When more than one value of PCDD/F and dl-PCB concentrations per herd was available (this was the case in particular for the farms showing initial unacceptable values and that therefore were followed up over the years), the highest one was used for the statistical analysis: the rationale for using that value was to better reflect the impact of any potential source involved, without any confounding effect of within herd time trends that may reduce the differences between farms. However, as a cross-check, the statistical analysis was also carried out based on the median and mean values per herd.

All data were expressed as toxic equivalents (TEQs), since PCDD/Fs and dl-PCBs are usually present as complex mixtures containing several kinds of congeners.

TEQ values are calculated by using weighting factors expressing the toxicity of each individual PCDD/Fs and dl-PCBs congener compared to 2,3,7,8-TCDD, the most toxic congener, which is assigned the arbitrary factor of 1. The weighting factor, termed toxic equivalent factor (TEF), is multiplied by the concentration of the individual compounds to give a 2,3,7,8-TCDD toxic equivalent. TEF values established by the World Health Organisation in 1998 were used (Van den Berg et al., 1998). All analytes were identified, confirmed and quantified by gas chromatography with high-resolution mass spectrometry (GC–HRMS), as defined for confirmatory analysis by EC Regulation No. 1883/2006 according to the EPA method 1613 (U.S. EPA, United States Environmental Protection Agency, 1994a) and the EPA method 1668 (U.S. EPA, United States Environmental Protection Agency, 1994b), respectively. To assess if the application of the weighting factors might affect the results of the statistical analyses, a new series of values per herd was obtained based on the mass concentrations normalized on lipid base, summing up the individual absolute contribution of each congener: through this alternative calculation we were able to take into account also congeners with a low toxicity equivalent ratio but potentially relevant for the emission source identification. To allow comparison, also in this case when more than one value of PCDD/F and dl-PCB concentrations per herd was available the highest one was used for the statistical analysis.

Table 1
List of concentration values of PCDD/Fs and dl-PCBs in bulk milk from the 27 herds recruited to the study. Maximum concentration values are expressed as toxic equivalent (TEQs), i.e., pg-TE/g fat of PCDD/Fs and dl-PCB detected in milk samples collected on the 27 tested farms over the testing period 2004–2007. In the table the IDs are sorted on the base of decreasing dl-PCB values.

FARM	PCDD/Fs (pg-TE/g fat)	DL-PCBs (pg-TE/g fat)
27	5.18	26.46
10	4.74	11.69
7	3.26	11.53
11	2.02	6.19
19	0.64	6.00
17	1.39	5.87
15	0.44	5.33
6	0.73	4.89
14	2.05	4.45
4	2.09	4.43
13	0.45	4.40
22	1.53	4.29
12	0.70	4.18
16	0.18	4.05
8	0.96	3.80
23	0.26	3.22
9	3.61	3.10
26	0.22	2.56
21	1.95	2.28
1	2.08	2.16
2	3.03	2.10
25	3.11	2.04
3	1.23	1.67
24	0.87	1.49
18	1.65	1.45
5	1.80	1.26
20	1.70	0.77

The second dataset was based on the complete georeferenced data of all land parcels of the area of interest, as identified by the regional rural register. The third dataset (obtained from the Regional agricultural information system) comprised the list of individual land parcels that each of the 27 farmers uses for fodder production or for animal grazing. These two datasets were then merged by using as primary key the following four variables: municipality code; cadastral number section; cadastral sheet number; and parcel number.

The resulting dataset contained 2915 records, representing the georeferenced land parcels used by the 27 farmers whose bulk milk was sampled. The values for PCDD/F and dl-PCB concentrations detected in the bulk milk were matched as an attribute to the spatial centroid point of each georeferenced land parcel used for fodder production. Land parcels related to high-mountain pastures were excluded because of their temporary utilization.

Stata statistical software, release 10.0 (Stata Corp., College Station, TX, USA) was used for data manipulation; the Spatial Analyst extension of ArcGis 9.2 (ESRI, Redlands, CA, USA) was used to generate preliminary thematic maps to describe the distribution of the 2915 land parcels.

2.2. Data interpolation and mapping

Since the land parcels were identified as small, scattered fields (Fig. 1), it was not possible to use a common spatial explorative technique of area data. So, a specific spatial interpolation technique (kriging) was used to visualize and characterize the area of contamination and to smooth the pollutant concentration data over the entire study area. All interpolation techniques performed data as point pattern analysis. Kriging allows the estimation of an unknown value at a given point on a surface, taking a weighted average of nearby points to generate a continuous surface by a given attribute. This is carried out considering the spatial structure of the data, by studying a specific mathematical function and producing a prediction (Waller and Gotway, 2004).

Many environmental exposure variables, even if measured at point locations, can be taken to represent a spatially continuous phenomenon. The specific characteristic of these data is that their locations are not randomly distributed but are fixed and known. Kriging is based on statistical models that include relationships among measured points, taking into account the autocorrelation among them. Autocorrelation is a fundamental geographic principle: generally speaking, autocorrelation means that things closer together tend to be more alike than things that are farther apart.

Kriging takes into account not only sample measurement values and their distance to a location to be predicted, it also enters a mathematical model of the spatial dependence among sample measurements. This function, termed semivariogram, quantifies the local spatial variability as a function of distance, given a measure of dissimilarity (semivariance): pairs that are close in distance should have a smaller difference than those farther away from one another. The extent to which this

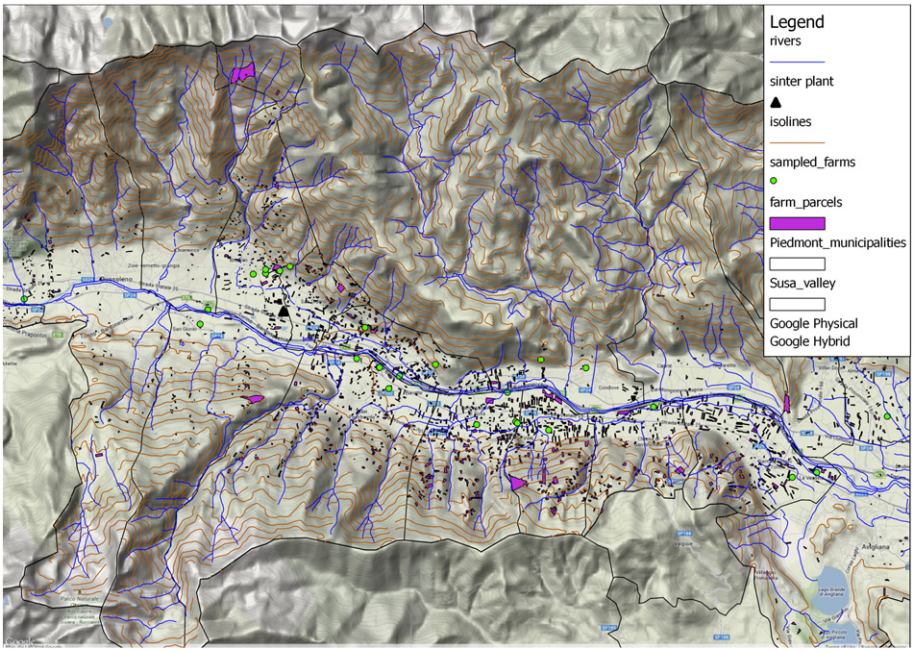

Fig. 1. Susa Valley (Piedmont, Italy). Location of the 27 sampled farms and their 2915 land parcels. The black triangle is the local steel plant; the green points represent the sites of the 27 sampled farms and the dark green polygons are the scattered land parcels (including pastures) used by farmers to produce fodder for animals (the largest polygons at the map boundaries refer to high-mountain pastures). Altitude isolines show elevation in meters.

assumption is true can be examined in the empirical semivariogram. The empirical semivariogram shows the spatial dependence as a scatter plot where distance is represented on the x-axis and semivariance on the y-axis: plotting the semivariance produces a curve that cannot be used directly for kriging, but needs a mathematical function to fit the curve. Finally, the potential for anisotropy (directional influence) must be checked: anisotropy means that autocorrelation may change in a specific direction.

All concentration values for PCDD/F and dl-PCB were log-transformed to correct the strong positively skewed sample histogram and to achieve better agreement with a normal distribution. The functional model was selected by calculating the empirical semivariogram for both the original and the log-transformed data using the gstat Geostatistical package of software R (R: A Language and Environment for Statistical Computing [http://www.R-project.org]); directional semivariograms were estimated from the sample data to check for anisotropy.

Using R, an empirical semivariogram was then fitted for either dioxins or dl-PCBs. The spatial distribution of PCDD/F and dl-PCB concentrations was modeled using ordinary kriging and plotted on isopleth maps created by the Spatial Analyst of ArcGis 9.2.

One of the advantages of kriging is that it allows the errors of the imputed values to be estimated (Pfeiffer et al., 2008), thus providing a measure of the uncertainty of the prediction; therefore, estimation error variance maps were created in order to spatially visualize the relative precision of the technique's predicted errors: the fewer are the local points available for the interpolation the larger is the uncertainty of the estimates obtained.

To assess goodness of fit, prediction performances were investigated using cross validation. In cross validation, each point in a spatial domain is individually removed from the domain; its value is estimated by kriging and compared to the actual value as if it were never there. The following parameters were evaluated: residual mean error; residual mean square error; residual mean square normalized error; correlation between observed and predicted values; and correlation between predicted values and residuals.

For an acceptable cross validation, the residual mean error should ideally be 0, the mean square prediction error should be small, the mean square normalized error should be close to 1, and the regression coefficient describing the linear regression equation needs to be as close to 1 as possible.

3. Results

The distributions of the values for PCDD/F and dl-PCB concentrations in the bulk milk of the 27 dairy farms involved in the 2004–2007 sampling campaign (Table 1) are shown in Fig. 2: the PCDD/F concentration in milk fat ranged from 0.18 to 5.18 pg-TE/g fat, with a highly positive skewed distribution; the distribution of the dl-PCB values was also extremely skewed, ranging between 0.77 and 26.46 pg-TE/g fat.

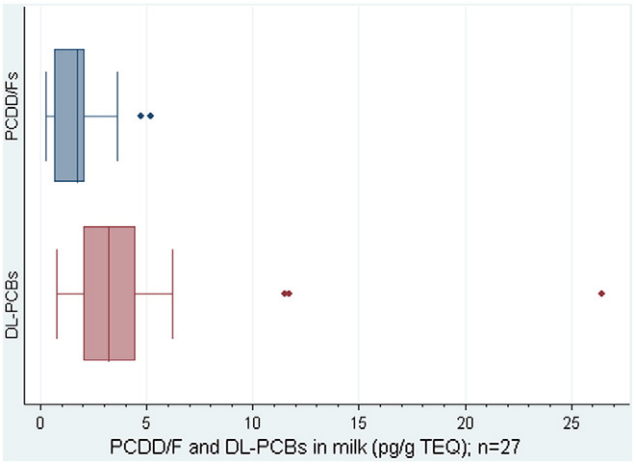

Fig. 2. Distribution of PCDD/Fs and dl-PCBs concentration in milk. The box plot shows a highly positive skewed distribution for both the chemical groups (PCDD/F mean = 1.77; median = 1.65; lower and upper quartiles, 0.7 and 2.09, dl-PCB mean = 4.88; median = 4.05; lower and upper quartiles, 2.1 and 5.33).

These concentration values resulted from environmental contamination, with subsequent effects on the animal food products. The interviews conducted on the farms where initially unacceptable values had been detected confirmed that all six farmers feed cattle with locally grown fodder, corn, silage and grass.

After matching the values for PCDD/F and dl-PCB concentrations detected in the bulk milk to the centroid of each georeferenced land parcel used for fodder production, the spatial dependence structure of the values of the parcels was modeled by an isotropic semivariogram for both PCDD/Fs and dl-PCBs: in both the cases, the shape of the function was consistent with the presence of spatial dependence, which was stronger for dl-PCBs than for PCDD/Fs. The omnidirectional semivariograms based on the original and the log-transformed concentration data for PCDD/Fs and dl-PCBs, respectively, were compared. In both cases, the best fit was obtained when the log-transformed data were used (Figs. 3 and 4, respectively).

No directional effects (anisotropy, i.e., a higher autocorrelation in one direction than another) were detected when directional semivariogram analysis was performed (data not shown).

Isopleth thematic maps were created to display the results (Figs. 5 and 6). The highest level of pollution for both PCDD/Fs and dl-PCBs was geographically juxtaposed without showing an overall directional trend. However in both instances, the location of the local steel plant was within this extremely highly polluted area. A second, less polluted area in the eastern part of the valley was also evident for PCDD/Fs. Differences in the geographical distribution of the two compounds are also suggested by the different degree of contamination by compound in the bulk milk of different herds as evident after sorting the concentrations by one of them (see Table 1). Finally a generally progressive decrease in contamination by both micropollutants was seen at increasing distance from the most polluted area. As expected, maps based on mean or median values (not shown) although resembling those obtained with the highest TEQ values made the peak contamination surrounding the steel plant less evident. Conversely, when the maps (not shown) were produced on the basis of mass concentrations rather than TEQ values, a similar distribution of the contamination was visualized. The two variance maps, with small differences between the two compounds (Figs. 7 and 8 with regard to PCDD/Fs and dl-PCBs respectively), show some extent of uncertainty only at the map boundaries, where there were fewer known land parcels available for the statistical analysis.

The predictive performance of the kriging model was very good: the cross-validation residuals (weighted with respect to the spatial dependence structure given by the semivariogram) were approximately Gaussian distributed. Moreover, for both the PCDD/F and the dl-PCB concentration values, the mean residuals errors were close to zero, the mean square prediction errors were small, whereas both the mean square normalized errors and the regression coefficients were close to 1 (Table 2).

4. Discussion

Based on the location of land parcels used for fodder production and the results of a 4-year sampling campaign on local dairy products, we were able to describe the geographic distribution of environmental contamination from PCDD/Fs and PCBs in the Susa valley. Our findings are consistent with one common point source for the PCDD/F and dl-PCB pollution. Isopleth maps of micropollutant concentrations were estimated with ordinary kriging. They show that the distribution of the most contaminated land parcels for pasturing and grass production is likely to be related to the installation of a local steel plant. We found that relating the dioxin levels in cow milk to the distribution of fodder cropland parcels, in combination with the use of kriging, to be a novel and helpful approach to singling out the location of the most probable contamination source. Outside the area where both the compounds show the highest concentration, some discrepancies in concentrations of dioxin and PCBs may be explainable with other minor sources of pollution or local mechanisms of volatilization and resuspension (EC, European Commission DG Environment, 1999).

However the absence of any evident anisotropy suggests a minimal effect of factors such as the air flow: this may be explained by the daily rotation of the direction of winds and by the extreme proximity of the farmers parcels to the steel plant. Moreover, it is unlikely that those discrepancies may be accounted for by flooding (Lake et al., 2005): the bed of the local river is very large and when, seasonally, the river is in flood it is able to collect the extra water preventing the flooding of the nearby cropland or pastureland.

In particular in the case of dioxin whose distribution in the valley in part seems to differ from that of dl-PCBs, other sources might have been concurrently active. Within this Alps valley there were no industrial plants involving combustion processes (e.g. waste incineration plants or cement kilns) or chemical productions (e.g. paper mills), whereas the residential heating in the area is commonly based on wood stoves

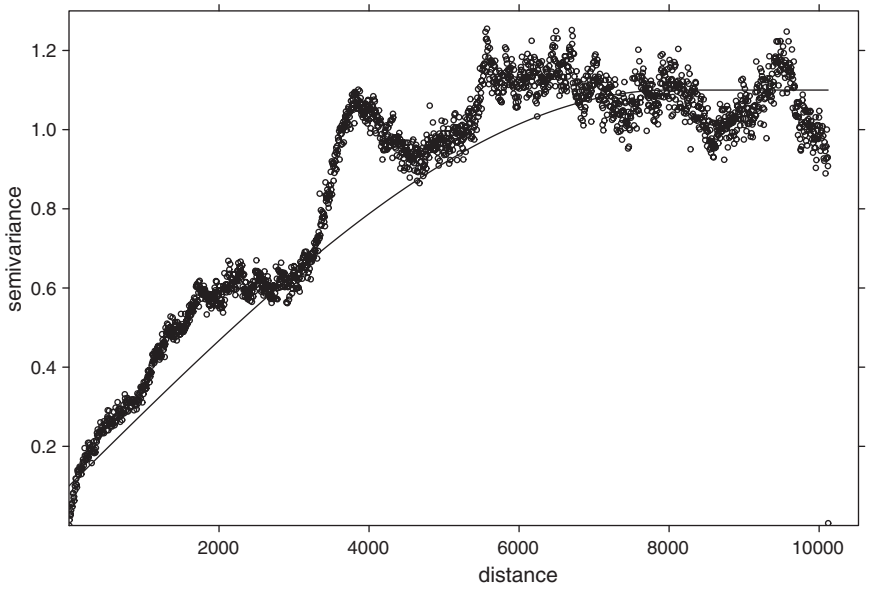

Fig. 3. Fit of semivariogram. Estimated semivariogram of log-transformed data from PCDD/F concentrations in milk (N = 2915 land parcels), and the fitted mathematical (spherical) model (line). Distance in meters.

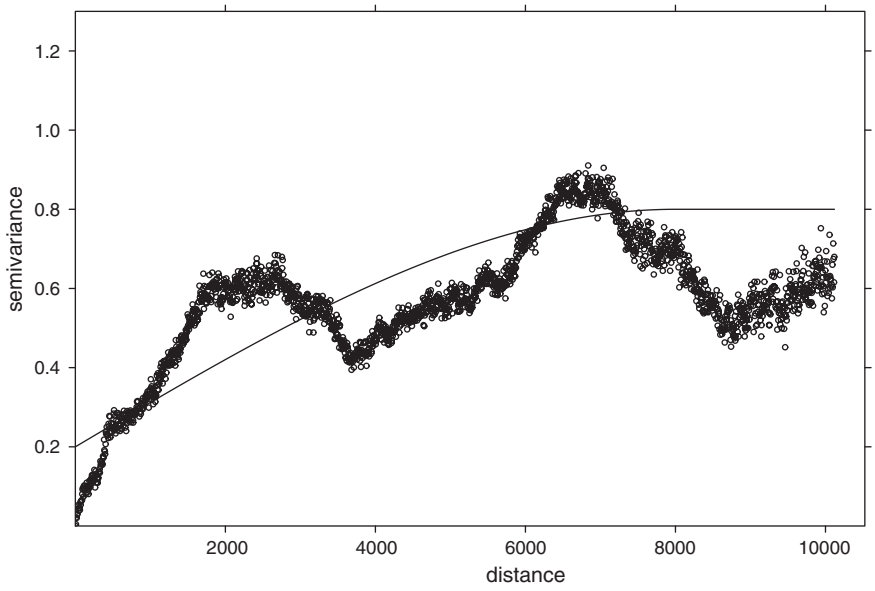

Fig. 4. Fit of semivariogram. Estimated semivariogram of log-transformed data from dl-PCB concentrations in milk (N = 2915 land parcels), and the fitted mathematical (spherical) model (line). Distance in meters.

and fireplaces and the local motorway to France might have contributed with emissions from fuel combustions.

In our study, the matching process may have led to a certain misclassification of the real degree of contamination of each land parcel, as the same value was assigned to all the land parcels of any individual farmer; however, it is unlikely that it will have created a substantial bias, as each farm usually relies on geographically clustered land parcels close to each other for fodder production. With regard to the small differences in the error maps of the two compounds, as they are based on the same number of observations they are likely explainable by the different distribution of the two contaminants in the bulk milk of different farmers: as a consequence the patterns of autocorrelation by contaminant and the two semivariograms were different as the error maps make apparent.

This study was an explorative spatial investigation with which we aimed to describe the spread of contamination over the study area.

A complementary approach to identify the pollutant source could have been used to study the phenomenon more deeply by taking into account a characterization of the micropollutants: in particular the

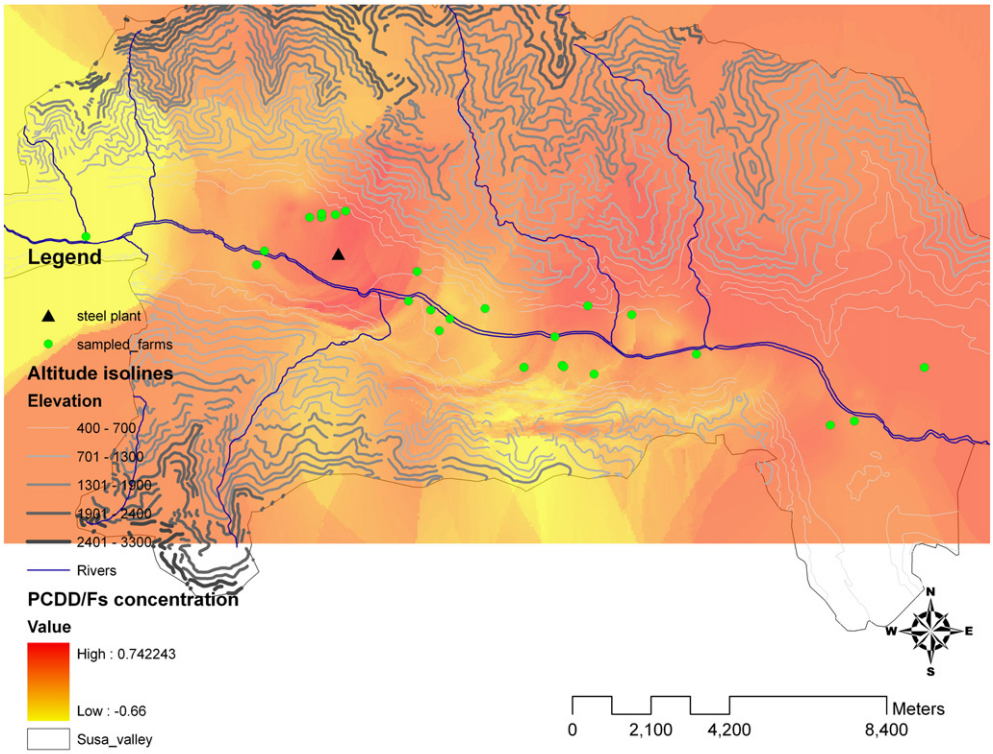

Fig. 5. Isopleth map of PCDD/Fs concentration. The map shows on a log scale the spatial distribution of PCDD/F contamination in the Susa valley, Piedmont, Italy. Ordinary kriging was applied to log-transformed dioxin concentrations in milk to generate a continuous surface showing the estimated contamination. The black triangle is the local steel plant; the green points represent the sites of the 27 sampled farms exposed to PCDD/F and dl-PCB environmental contamination. Altitude isolines show elevation in meters.

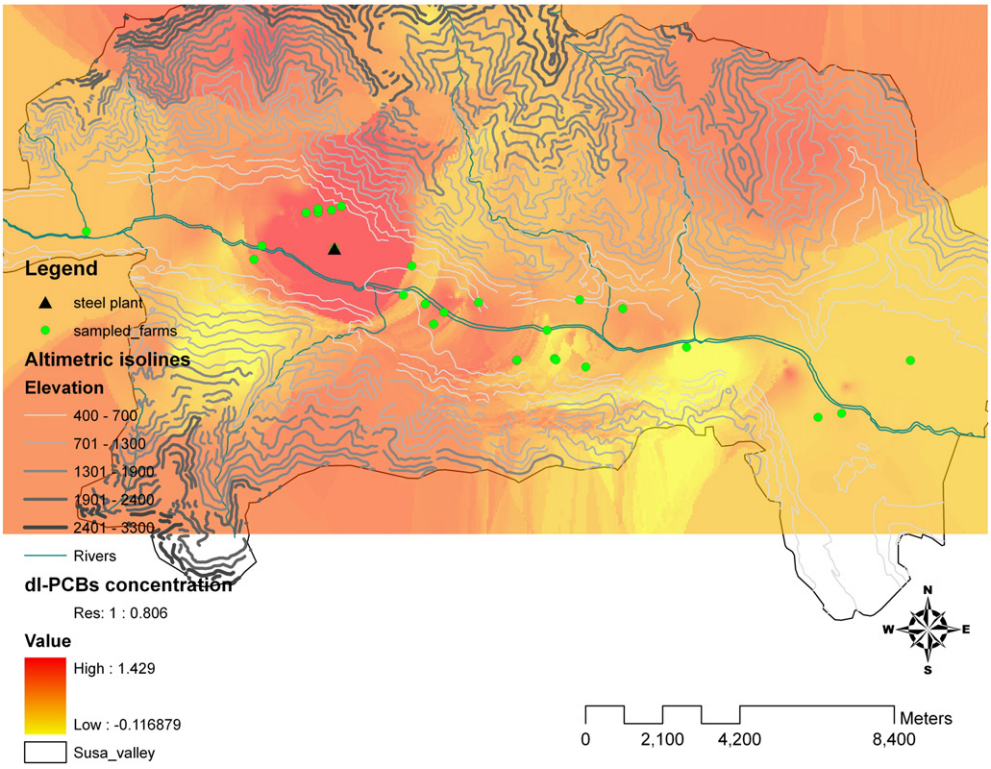

Fig. 6. Isopleth map of dl-PCBs concentration. The map shows on a log scale the spatial distribution of dl-PCB contamination in the Susa valley, Piedmont, Italy. Ordinary kriging was applied to log-transformed dl-PCB concentrations in milk to generate a continuous surface showing the estimated contamination. The black triangle is the local steel plant; the green points represent the sites of the 27 sampled farms exposed to PCDD/F and dl-PCB contamination. Altitude isolines show elevation in meters.

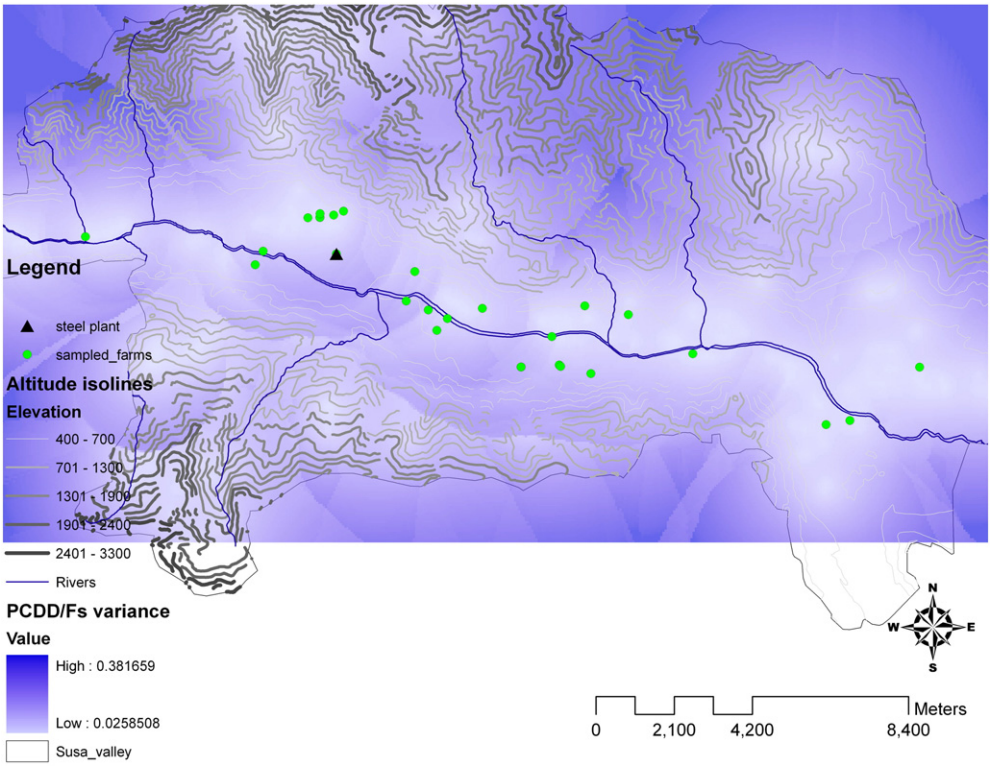

Fig. 7. PCDD/Fs variance map. Estimation error variance map for the estimated geographical contamination by PCDD/Fs: the darker the area, the larger the kriging variance values. Altitude isolines show elevation in meters.

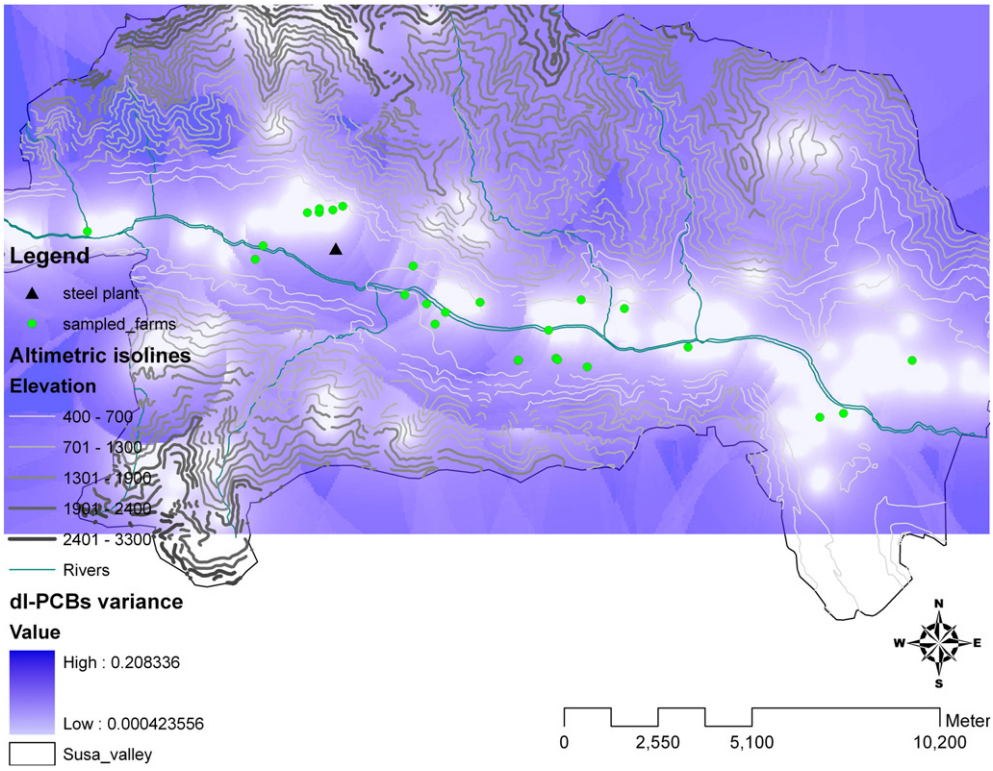

Fig. 8. Dl-PCBs variance map. Estimation error variance map for the estimated geographical contamination by dl-PCBs: the darker the area, and the larger the kriging variance values. Altitude isolines show elevation in meters.

application of a multivariate modeling technique such as Principal Components Analysis was frequently used to identify sources where a substantial amount of measured concentration data exist (Jimenez et al., 1998; Masunaga et al., 2003; Sundqvist et al., 2009). Such a study is currently in progress and, through the identification and quantification of the most common congeners involved in the environmental contamination of the Susa valley, it may concur in supporting the common point source hypothesis. However in a previous study (Desiato et al., 2012) it has been highlighted that the predominance of furans observed in the milk samples obtained from the Susa valley (with a particular abundance of 2,3,4,7,8-PeCDF congener) is consistent with a contamination from combustions industrial origin.

The correlation between a source and its effects on human populations (Nhu, 2009; Biggeri et al., 1996) has been variously studied. For example, to investigate the relationship between four sources of environmental pollution and lung cancer risk, Biggeri et al. (1996) conducted a case–control study in Trieste using a model based on the distance from the sources to the estimate the risk gradient and directional effects.

5. Conclusions

Food product contamination due to widespread pollution from one common source of contamination has been variously described (Esposito et al., 2010; Esposito et al., 2009; Turrio-Baldassarri et al., 2009; O'Donovan et al., 2011). Our findings are consistent with previous observations and confirm the relevance of steel plants as a hazard for the environmental safety of adjacent crops and the food products derived from animals raised in their vicinity.

Combining the data for pollutant concentrations in milk samples with the location of the cropland parcels instead of the farms was a novel approach that permitted straightforward identification of the most likely pollution source, irrespectively of its location. Moreover, the validity of the study strategy is supported by the converging results obtained independently for the two different pollutants (PCDD/Fs and dl-PCBs) involved.

Our approach may provide an effective tool to investigate the origin of a contamination source when micropollutants are detected in the chain food. Furthermore, we suggest that such explorative investigations be carried out in situations of suspected widespread environmental contamination. Finally, our results on the one hand were provided to each farmer involved in the monitoring campaign to manage the potential risk for public and animal health and on the other hand were used by health authorities to inform priorities for the implementation of pollution mitigation measures (modernization of the steel plant) and to improve the targeting of official monitoring activities on the local dairy products.

Table 2
Outputs of the validation of the Kriging model for either PCDD/Fs or dl-PCBs.

	PCDD/F concentration values	Dl-PCB concentration values
Mean residuals error	0.00037	0.00028
Mean square prediction error	0.09	0.06
Mean square normalized error	0.77	0.81
Regression coefficient	0.95	0.94

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