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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☆

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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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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