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Contamination levels and congener distribution of PCDDs, PCDFs and dioxin-like PCBs in buffalo's milk from Caserta province (Italy)

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ABSTRACT

An extraordinary plan of official control was carried out in 2008 in Campania (Italy) with the aim to monitor polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) levels in buffalo milk and to detect the contaminated farms, most of which are located in Caserta province.

For these companies has been ordered seizure and execution of additional analyses has been requested in farms falling in the nearness, within a distance of 3 km, for a total of 304 farms examined. Moreover, all non-compliant farms were subjected to a periodic sampling in order to monitor trends in the levels of contamination.

In this paper the distribution and the concentrations of 17 PCDD/Fs and 12 dioxin-like PCBs in 460 samples of buffalo milk collected in the province of Caserta (Italy) are presented.

The range of WHO-TEQ values for the PCDD/Fs in milk was 0.17 pg TEQ g^{-1} fat and 87.0 pg TEQ g^{-1} fat with a mean value 3.63 pg TEQ g^{-1} fat and medium value 2.25 pg TEQ g^{-1} fat.

The concentrations of dioxin-like PCBs in the analysed samples ranged from 0.21 pg TEQ g^{-1} fat to 15.9 pg TEQ g^{-1} fat and the WHO-TEQ values of sum of PCDDs, PCDFs and dl-PCBs ranged from 0.45 pg TEQ g^{-1} fat to 103.0 pg TEQ g^{-1} fat.

The geo-referencing analysis allowed to individuate a restricted area of the region object of the present study where is located the majority of the non-compliant farms.

The study of the congeners distribution has finally suggested that the likely cause of contamination is to be attributed to the illegal burning of waste.

1. Introduction

The PCDD/Fs are a class of polychlorinated tricyclic compounds highly stable and extremely persistent; due to these properties they are ubiquitous environmental contaminants. Even though they can form through natural processes such as bush fires or volcanic processes, the main sources are anthropogenic processes as incineration of chlorine-containing wastes, industrial plants, cement factories and paper production, use and production of PVC and use and manufacturing of chlorinated aromatic chemicals, in which these compounds are formed as unwanted by-products.

These persistent organic pollutants are lipophilic and accumulate in fat tissues, then they enter the food chain and consequently can be found in humans in considerable concentrations. They are potent toxicant with a potential to produce a broad spectrum of adverse effects (Fry, 1995; Kerkvliet et al., 1996; Dienhart et al., 2000; Hassoun et al., 2000). Among all PCDD/Fs, the most toxic is the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) which was included in the list of the human carcinogens from IARC (McGregor et al., 1998; Steenland et al., 2004) even if others congeners show similar features of toxicity, particularly those having chlorine atoms in all of the 2, 3, 7 and 8 positions.

The dioxin-like PCBs (dl-PCBs) are a group of 12 polychlorinated biphenyls, showing chemical and toxicological properties similar to those of PCDD/Fs.

Various cases of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and/or dioxin-like polychlorobiphenyls (dl-PCBs) contamination have been reported in Europe since 1997.

Recently in Italy, at the beginning of 2008, during the monitoring plans implementation (Residues National Plan, Regional Law 3/

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2005, Surveillance Plan) for the presence of PCDD/Fs in animals and food of animal origin made in Campania region, levels above the permitted maximum limit were detected in some samples of buffalo milk and *mozzarella* cheese.

In order to protect human health, the Italian Ministry of Health, in collaboration with Campania Region and in accordance with the provisions of the European Union, has developed an extraordinary monitoring plan (so-called EU plan) for a detailed analysis of the buffalo milk produced in the Campania region.

Applying this EU plan, through the analysis of buffalo milk samples, all the cheese factories for the production of *mozzarella* cheese have been reviewed in a few days.

The results of this monitoring plan in the Campania region have revealed a global situation of low contamination, very close to background levels, whereas contaminated milk samples were from a restricted area of the Caserta province. Therefore, samples from the majority of farms, where buffaloes are reared for milk production, were collected in this area.

In this paper we report the results of analysis of buffalo milk samples taken from farms located in the Caserta province between April 2008 and December 2008. The levels and the profile of PCDD/F and dl-PCB congeners are reported below to provide information about their distribution in this area and to hypothesize the sources of contamination.

The aim of this survey is also to fill the gap of data about the presence of PCDD/Fs and dl-PCBs in milk of buffaloes, an animal specie that is reared in this region of southern Italy.

2. Materials and methods

2.1. EU monitoring plan design

In the first two phases of the EU plan, during April 2008, 387 buffalo milk samples were collected in 239 cheese factories producing buffalo mozzarella, located in the five Campania provinces: Avellino, Caserta, Benevento, Salerno and Napoli.

Each sample of milk taken from the dairies was made of different milk samples constituting a pool ranging from one to a maximum of four samples.

The results of this first survey show that most of the contaminated buffalo milk came from the province of Caserta.

During the third phase, in case of non-compliant pool, samples were collected and analysed in all farms contributing milk to that specific pool sample. Once a non-compliant (positive) sample was identified, a buffer of 3 km around each contaminated farm was created and then milk samples were collected in all farms included in the area (Fig. 1).

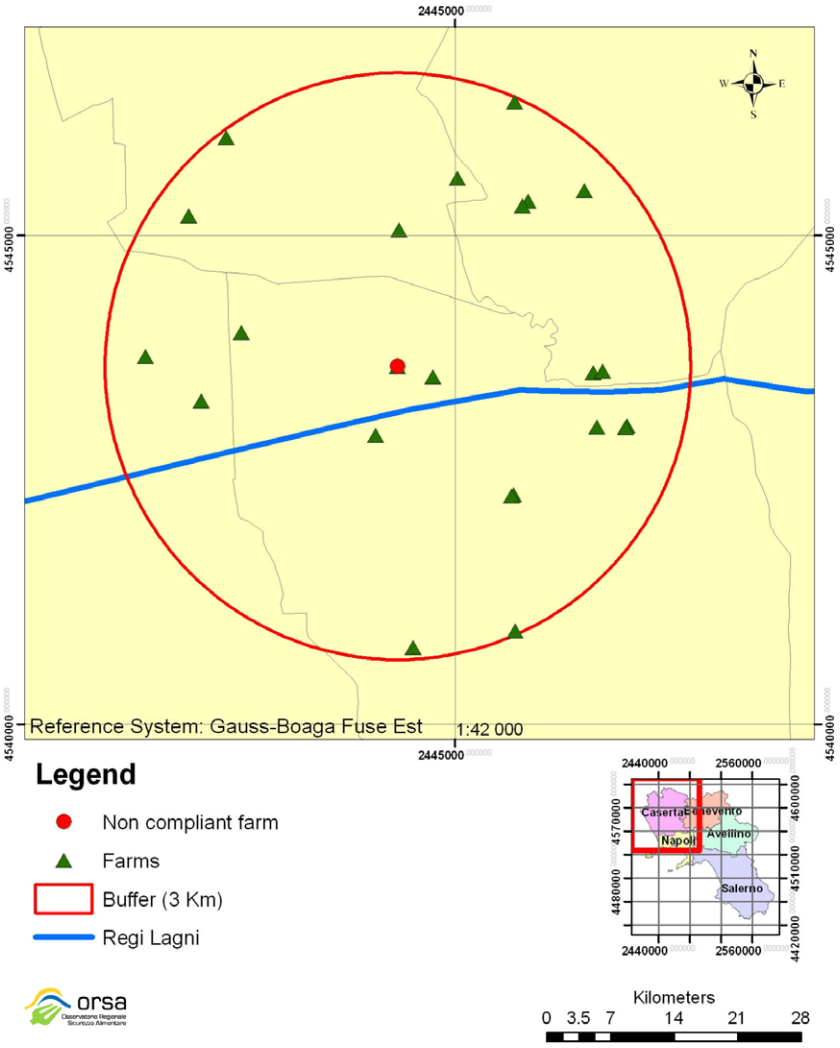

Fig. 1. Typical example of a buffer around a farm does not comply.