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# Dioxin and PCB contamination around a heavy industrial area: A case history

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**ABSTRACT:** An extended investigation carried out after the discovery of excess occurrence of dioxins and PCB in sheep and goat freely grazing around Europe's largest integrated iron and steel (I&S) factory in Taranto industrial area revealed an ubiquitous *recent* (by dioxins) and *historic* (by PCB) contamination. Experimental results, including fingerprint and PCA comparison, excluded *single-point* emission by the I&S factory as well as by other nearby industrial chimneys, pointing out to *fugitive diffuse* emission escaping from the I&S sinter plant as the contamination source. The occurrence of two routes of environment contamination and their overlapping toxicity effects through the food chain were demonstrated, due primarily to such diffuse emission and secondarily to PCB present in top soil around the industrial area.

**KEYWORDS:** dioxins, PCB, sinter plant, foodstuff, risk analysis.

## 1 INTRODUCTION

In a previous paper [1] excess gaseous and particulate emission of benzo(a)pyrene (BaP) and other polycyclic aromatic hydrocarbons (PAH) from the coke-oven batteries of ILVA, Europe's largest integrated iron and steel (I&S) factory in Taranto (South Italy) industrial area, was demonstrated, yielding to shut-down and thorough revamping of the coke-oven batteries. More recently, the occurrence of dioxins and polychlorinated byphenils (PCB) in some edible products from livestock freely grazing around the I&S factory was discovered. A 3-years long investigation on dioxins and PCB contamination of the surrounding environment, cattle and their feed products as well as on contamination source(s) apportionment was carried out as described herein.

## 2 CONTAMINATION BY DIOXINS AND $PCB_{DL}$

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) (in short *dioxins* PCDD/F) with some PCB who mimic their toxicological properties (PCB "*dioxin like*", $PCB_{DL}$) belong to the so called "*Persistent Organic Pollutants*" (POPs), toxic to humans and animals [2]. The production of POPs, characterized by strong persistency, bioaccumulation through the food chain (particularly in fatty tissue of living organisms) and long-range transport impacting the wildlife even at extreme latitudes [3], has been prohibited and their diffusion regulated after the 2001 Stockholm Convention, ratified by the European Community in 2004 [4].

Differently from PCB, used mainly as dielectric insulator and produced industrially in millions of tons until their ban in the late 1980s, PCDD/F form unintentionally as by-product of numberless combustion processes, both industrial (waste incineration and sintering plants in particular) and anthropogenic (forest fire, grass combustion, scrap tire burning, bonfires, backyard barrel burning, open burning of wood and waste, smoking, fireplaces etc.) and are massively present in pesticides and chemicals [5] [6] [7] [8]. Accordingly, the occurrence of $PCB_{DL}$ is considered today the heritage of *historic* contamination, while that of dioxins proves *recent* contamination, often in progress. As a consequence, dioxin and $PCB_{DL}$ source apportionment in the frequent cases of food-chain contamination is often questionable.

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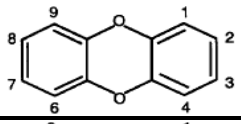
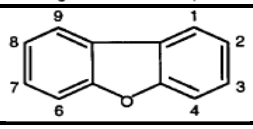
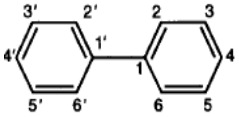
As shown in Table 1, however, only 29 out of their 419 congeners are toxic, depending on their chlorination degree and substitution pattern, with TEF (toxicity equivalent factor) ranging from 1 to 0.00001 for 2,3,7,8 TCDD and 2,3',4,4',5,5'-HxCB respectively [9] [10].

Following the enforcement of the stringent emission limit of 0.1 $ng_{TEQ}/Nm^3$ for waste incineration plants by Directive 2000/76/EC, adopted in Italy with Leg. Decree No. 133/05, approx. 90% reduction of dioxin emission to the environment has being achieved in the EU, where the sintering process of I&S industry is rated the #1 dioxin industrial emission source [11]**.** In Italy the Leg. Decree No.152/06 limits to 10,000 $ng/Nm^3$ *all* the 210 PCDD/F congeners in the I&S emission.

After the IPPC Directive 1996/61/EC, dioxin regulation among other EU member countries relies on Best Available Techniques that, due to process optimization (mainly by input control) and emission abatement by electrostatic precipitators and fabric filters, usually allow a concentration in the 0.5-5 $ng_{I\text{-}TE}/Nm^3$ range, i.e., a dioxin output of 1-10 $\mu g_{I\text{-}TE}/t_{sinter}$ based on an average production of 2,100 $Nm^3/t_{sinter}$ [12].

***Table 1. PCDD, PCDF, PCB and their congeners***

| Compound | Chemical formula | Total congeners | Toxic congeners |
|---|---|---|---|
| PCDD |  | 75 | 7 |
| PCDF |  | 135 | 10 |
| PCB |  | 209 | 12 |
| Total | | 419 | 29 |

## 3 TARANTO CASE

The 220,000 Taranto (Apulia region, South Italy) inhabitants closely neighbour their heavy industrial area which, in addition to ILVA since the 1970s, hosts several potential dioxin-emitting plants, i.e., a large oil refinery and a big cement kiln, one ongoing and two exhausted MSW sanitary landfills (where waste often used to undergo uncontrolled burning in the past), three sanitary landfills for (non) hazardous waste, the MSW and the hospital waste incinerators, one RDF modern waste-to-energy plant plus several mechanic SMEs, including in particular a plant for dismantling PCB-based appliances (MATRA), now dismissed. The city also hosts relevant infrastructures like Italy's 2nd busiest industrial harbour, NATO's largest European Navy basis, a military arsenal etc., prompting its inclusion among Italian "areas at high risk of environmental crisis" (Laws No. 349/86 and No. 305/89).

Among over one hundred chimneys in the industrial area, the E312 main stack from ILVA sinter plant, Europe's tallest (220 m) and most powerful (≈3$MNm^3/h$) of its kind, is blamed on emitting 92% of industrial dioxins to air in Italy [13], with ≈7.5 kg of dioxins emitted in its half-century life, i.e., almost the triple than escaped in the well known Seveso accident [14]. Although not formed in the I&S industrial cycle, PCBs were largely used until the last decade.

Following a Framework Agreement signed in 2006 by Apulian Regional Government and Local Authorities, in 2007 the Regional Environment Protection Agency (Arpa) started to carry out regular monitoring campaigns on the emission of the E312 stack of ILVA sinter plant AGL2.

In such scenario, uncultivated land in the industrial area was utilised for unrestricted livestock grazing by local shepherds. In 27 February 2008 the discovery of excess dioxins and $PCB_{DL}$ in cheese produced by said livestock prompted Arpa to carry on an extensive survey on the environmental matrices (dust, air, groundwater, soil etc.) and Taranto' Sanitary Surveillance Authority (Asl-Ta1) to increase the veterinary controls on cattle and food derivatives in local farms in a 20 km radius area around ILVA E312 sinter stack. In addition to prohibiting grazing activities within the industrial area, the Regional Government issued the regional law 44/08 that, first and still unique in Italy, limits to 0.4 $ng_{I\text{-}TE}/Nm^3$ the emission of *toxic* dioxin congeners from point sources of industrial plants.

The evaluation of the results of controls carried out by Arpa and Asl-Ta1 – that led to abate 2,170 contaminated sheep - and the attempts of apportioning the contamination source(s) of dioxin and $PCB_{DL}$ in Taranto area are now presented.

## 4 MATERIALS AND METHODS

### 4.1 PCDD/F AND $PCB_{DL}$ CONTROLS IN ENVIRONMENTAL MATRICES AND IN CATTLE AND THEIR EDIBLE DERIVATIVES

Within the period of this investigation Arpa carried out 3 monitoring campaigns on the emission of E312 sinter stack, in 12-16 June 2007, 26-28 February and 23-26 June 2008 (this latter occurring after ILVA had started *urea* addition test in the sinter process) [15] [16] [17]. Emission samples were collected at a suitable height (53 m) of the stack in steady operating conditions (gas temperature 150°C, flow rate 3 $MNm^3/h$, i.e., 17 m/h, 17% $O_2$ and 7% humidity, with sinter plant producing 1,158÷1,200 t/h, i.e., 2,134÷2,440 $Nm^3/t_{sinter}$) and analysed according to UNI-EN 1948 1-2-3:2006. Similar controls occurred at the main stack of other major suspected plants in the industrial area.

Following the results of the above *point source* controls, Arpa looked also for *diffuse fugitive sources* of dioxin emission inside ILVA sinter plant, wherein the suspended dust (reportedly made by ore minerals) intolerably floating in the working environment, subjected to indoor/outdoor wind transportation, and the toxic fines filtered by electrostatic precipitators (ESP) ahead of the E312 stack were analysed.

Furthermore, Arpa controlled PCDD/F and $PCB_{DL}$ in 106 representative samples of environmental matrices within/beyond the no-grazing area, upwind/downwind the E312 stack: air (36 samples), atmospheric deposition (21), industrial (26) and agricultural (17) top soils, aquifer (3 samples), marine sediments (2) and sludge from the municipal wastewater treatment plant (1) used as soil amendment.

Asl-Ta1 carried out veterinary controls in livestock breeding in 86 farms in the 20-km radius area investigated, measuring PCDD/F and $PCB_{DL}$ concentration in 276 representative samples (mainly from sheep and goats and their edible products).

All the environmental and veterinary analyses were carried out in duplicate/triplicate according to the acknowledged standard analytical methods at Arpa and Asl-Ta1 laboratories.

### 4.2 SOURCE APPORTIONMENT

Not all the 419 PCDD/F and $PCB_{DL}$ congeners occur simultaneously, nor in the same amount, in dioxin-forming processes, each usually having its own characteristic molecular emission spectrum (i.e., congeners profile or *fingerprint*). By comparing the fingerprint of the contaminated matrices and the suspected process(es) one may be able to apportion the contamination source(s) more or less affordably. To that aim, the following occurrences are usually considered in each matrix:

1) PCDD *vs.* PCDF (% on 17 congeners total concentration);
2) PCDD/F *vs.* $PCB_{DL}$ (% on 17+12 congeners total concentration);
3) single congeners (% on 17+12 congeners total concentration).

Among the various procedures for deriving congeners profile Erreur ! Source du renvoi introuvable. [18] the "Falcon" method by the U.S. EPA, relating the toxic contribution of each congener to the overall toxicity of the given matrix in order to better account for the large differences among concentration and TEF of each PCDD/F and $PCB_{DL}$ congener, was used [19].

When different sources emitting from different time overlap their spectra, like in the present situation, not even the Falcon method allows to apportion the contamination source affordably and the use of more rigorous statistical procedures like the well-known *Principal Component Analysis* (PCA) [20], becomes mandatory. The PCA submits all the analytical results achieved in a complex investigation to serial statistic evaluations ending up with clusters in a dimensionless pseudo-Cartesian diagram: less overlapping/more homogeneous are the clusters, more reliable is the contamination source apportioned.

### 4.3 HEALTH RISK ASSESSMENT

Health risk assessment for people consuming contaminated cattle and their food derivatives was carried out following the European Food Safety Agency methodology [21] accounting for local uses. To that aim, by reference to the average body weight (bw) of male and female adult consumers (60 kg), the following conservative assumptions were made [22] [23]:

- average overall consumption of animal fat: 80 g/person$_*$d (1.33 g/$kg_{bw}$xd)
- local percentage of sheep in overall meat consumption: 10% (more than triple than 3% Italian average).

Once the percentage of contaminated sheep in the area and the concentration of toxic PCDD/F and $PCB_{DL}$ in contaminated sheep (mean $v_m$, highest $v_{max}$, 95$^{th}$ percentile $v_{95}$) are known, the exposure scenarios may be calculated by reference to 3 types of consumers (% of meat eaten coming from sheep):

- ordinary (10%)
- super (50%)
- farmer (90%)

to obtain the **TWI** (*Tolerable Weekly Intake* of toxic dioxins) and the **BB** (*Body Burden* of toxic dioxins build-up in a 70 years half-life), calculated as ***BB*** = ***f**intake*half-life/ln2***, where ***f*** is the fraction of dose absorbed (assumed to be 50% for absorption from food for humans), ***intake*** is the daily consumption of contaminated animal fat ($ng_{WHO-TE}/kg_{bw}$*day) and ***half-life*** refers to the human metabolism of the most toxic dioxin 2,3,7,8-TCDD (2740 days).

The results are compared with the limits stated by WHO [24]: TWI ≤14 $pg_{WHO-TEQ}/kg_{bw}$*week and BB ≤4,000 $pg_{WHO-TE}/kg_{bw}$.

## 5 RESULTS AND DISCUSSION

As anticipated [25], Arpa controls on chimney from other investigated plants excluded appreciable emission of PCDD/F and PCB compared with E312 main stack of ILVA AGL sinter plant. Accordingly, ILVA emissions only will be discussed.

### 5.1 PCDD/F AND $PCB_{DL}$ IN THE EMISSION OF E312 STACK AT ILVA AGL SINTER PLANT

***Table 2. PCDD/F and $PCB_{DL}$ emissions from the E312 stack of ILVA AGL sinter plant***

| Monitoring campaigns | **Σ**$PCD_{DL}$ [$ng_{WHO-TE}/Nm^3$] | **Σ**PCDD/Fs [$ng/Nm^3$] | [$ng_{I-TE}/Nm^3$] | Absolute Emission Factor [$g_{I-TEQ}$/yr] | Specific Emission Factor [$\mu g_{I-TEQ}/t_{sinter}$] |
|---|---|---|---|---|---|
| I) 12-06 June 2007 | 0.13÷0.28 | 89÷188 | 2.39÷4.94 | 58÷130 | 5.5÷12.4 |
| II) 26-28 February 2008 | 0.29÷0.52 | 118÷212 | 4.44÷8.34 | 117÷219 | 11.1÷20.9 |
| III) 23-26 June 2008(*) | 0.16÷0.29 | 66÷110 | 1.94÷3.37 | 50÷89 | 4.8÷8.5 |

(*) with *urea* addition

Table 2 shows the results of controls carried out by Arpa during the period covered by the present investigation. As predicted, the occurrence of $PCB_{DL}$ was almost negligible. From these data the following considerations may be drawn:

1. *total* PCDD/F concentration was ≈3 orders of magnitude lower than the Italian limit (10,000 $ng/Nm^3$), but their *toxic* congeners exceeded the regional limit to be in force by 2011 (0.4 $ng_{ITEQ}/Nm^3$);
2. addition of *urea* decreased by ≈30% PCDD/F concentration in stack emission, but it is not sufficient to that aim;
3. due to stack huge flow rate (3 $MNm^3/h$), the Specific Emission Factor largely exceeds the 1 g/yr recommended Italian limit [13] and the performance of best-performing European sinter plants using Sector BREF/BAT [26].

### 5.2 PCDD/F AND $PCB_{DL}$ OCCURRENCE IN ENVIRONMENTAL MATRICES

Table 3 summarizes the results of the extensive survey carried out by Arpa (bold numbers for values exceeding the limit).

***Table 3. PCDD/F and $PCB_{DL}$ concentration in environmental samples in Taranto area***

| | **Σ PCDD/F** (WHO-TE) | **Σ** $PCB_{DL}$ (WHO-TE) | **PCB** |
|---|---|---|---|
| **A) Air [$fg/Nm^3$]** | | | |
| Min | 9.3 | 0.6 | $0.03*10^6$ |
| Max | 252.5 | 12.3 | $44.34*10^6$ |
| Guide Value by WHO [27]: PCDD/F = 300 $fg_{TE}/Nm^3$; PCB = 300.000.000 $fg/Nm^3$ | | | |
| **B) Atmospheric deposition [$pg/m^2$ d]** | | | |
| Min | 2.8 | 0.1 | 5 |
| Max | 42.0 | 5.8 | 210 |
| German Guide value [28]: PCDD/F = 15$pg_{TE}/m^2$d; proposed Belgian Guide value [29]: (PCDD/F+$PCB_{DL}$) = 8 $pg_{TE}/m^2$d | | | |

| | | | |
|---|---|---|---|
| Min | 0.5 | 1.2 | 2,359 |
| Max | **5.6** | 1.5 | 4,087 |

Limit value by Ital. Legs. Decree No.152/2006: PCDD/F = 4 $pg_{TE}$/L; PCB = 10.000 pg/L

**D) Soil (agricultural) [ng/kg dry matter]**

| | | | |
|---|---|---|---|
| Min | 0.8 | 0.7 | 2,8 |
| Max | **10.3** | 6.1 | **90,280** |

Limit value by Ital. Legs. Decree No.152/2006 for residential site: PCDD/F = 10 $ng_{TE}$/kg; PCB = 60.000 ng/kg

**E) Soil (industrial) [ng/kg dry matter]**

| | | | |
|---|---|---|---|
| Min | 0.78 | 0.46 | 4,669 |
| Max PCDD/F | **351,6** | 25,6 | 111,148 |
| Max $PCB_{DL}$ | 55.8 | **2.575** | 39,427,011 |

Limit value by Ital. Legs. Decree No.152/2006 for industrial site: PCDD/F = 100 $ng_{TE}$/kg; PCB = 5.000.000 ng/kg

**F) Marine sediments [ng/kg dry matter]**

| | | | |
|---|---|---|---|
| Min | 2.3 | 2.1 | 85,635 |
| Max | 8.3 | 12.9 | 476,041 |

Guide value proposed by Ital. Env. Ministry [30]: ($PCDD/F+PCB_{DL}$) = 30 $ng_{TE}$/kg;PCB = 190.000 ng/kg as Σof 24 given congeners

**G) Sludge [ng/kg dry matter]**

| | | | |
|---|---|---|---|
| Unique | 8.8 | 0.5 | 16,739 |

Guide value proposed by the EC [31]: PCDD/F 100 $ng_{TE}$/kg; PCB 800.000 ng/kg

As shown by the data in Table 3, the contamination by PCDD/F and $PCB_{DL}$ was ubiquitous. However, only 4 out of 106 samples exceeded the environmental limits in force. The occurrence of dioxins, symptomatic of *recent* contamination, seems to be reasonably blamed on ILVA sinter plant, as confirmed by a recent study [32]. The source(s) of $PCB_{DL,}$ not produced in the I&S cycle (*historic* contamination), should be looked at in mismanagement of electric insulators and other PCB-containing devices in previous years, when ILVA utilized over 1,000 electric transformers and the MATRA plant for dismantling such devices was active in the area.

Overall PCDD/F and $PCB_{DL}$ concentration in the air (36 samples), increasing when winds come from the industrial area, was below the WHO guide-value and the 100 $fg_{WHO-TE}/m^3$ typical value for urban ambient [33] [34] [35]. In spite of their low concentration and the negligible contribution to direct human exposure, however, PCDD/F and $PCB_{DL}$ in the air may contaminate the food chain through soil deposition (particularly relevant near the industrial area investigated).

Atmospheric deposition (21 samples) showed ≈30% of $PCDD/F+PCB_{DL}$ measurements beyond the German Guideline . Re-suspension of crustal soil dust (coarse particles) has much higher deposition rate than fresh emission (ultra/fine particles) and may potentially account for ≤90% of total dioxin deposition in urban/industrial areas and ≤40% in rural regions [36] [37].

Industrial top soil showed abnormal concentration of PCDD/F and $PCB_{DL}$ in 2 out of 26 samples, taken at the electrostatic filters discharge of ILVA sinter plant.

Agricultural top soil exceeded the limits for PCDD/F and PCBDL in 1 out of 17 sample, taken near *Fornaro Stazionamento,* where part of the 2,170 infected sheep had to be abated later on.

Aquifer, often used by local farmers for animal beverage and domestic uses, exceeded the limit in 1 out of 3 samples, taken near *Masseria Carmine* (where other infected sheep were found), but 2 weeks later the outcome was not confirmed.

Neither the marine sediments or the WWTP sludge samples showed appreciable contamination by PCDD/F and $PCB_{DL}$.

According to these results, the overall level of dioxins and $PCB_{DL}$ contamination of the various environmental matrices in the area investigated appears comparable with other intensively urbanized/industrial sites in the world [38]. This is not in contrast with the impressive dioxins emission from ILVA E312 stack as its fallout, thanks to the height, the high rise plume and local prevailing meteorological conditions, occurs at ≥100 km distance, as shown by fluid-dynamic models [39].

### 5.3 PCDD/F AND $PCB_{DL}$ OCCURRENCE IN LIVESTOCK AND THEIR FOOD DERIVATIVES

Table 4 reports the results of controls carried out by Asl Ta/1 on 276 animals and their edible parts (86 farms controlled), where 60 samples in 11 farms, all from sheep and goat, except 1 chicken egg, did not comply with EC Regulation no.1881/06.

***Table 4. PCDD/F + $PCB_{DL}$ concentration in non-compliant animals in Taranto area***

| No. of samples | foodstuff | Limit of EC Regulation no.1881/2006 ($pg_{WHO-TE}/g_{fat}$) | | PCDD/F + $PCB_{DL}$ ($pg_{WHO-TE}/g_{fat}$) | | $PCB_{DL}$ (%) | |
|---|---|---|---|---|---|---|---|
| | | (PCDD/F) | (PCDD/F + $PCB_{DL}$) | Range | Mean | Range | Mean |
| 24 | liver | 6.00 | 12.00 | 9.5÷279.2 | 87.6 | 31÷80 | 48 |
| 12 | muscle | 3.00 | 4.50 | 4.9÷26.5 | 14.5 | 47÷92 | 72 |
| 11 | fat | 3.00 | 4.50 | 4.5÷37.1 | 14.1 | 66÷93 | 76 |
| 11 | milk | 3.00 | 6.00 | 6.45÷31.2 | 13.7 | 21÷92 | 69 |
| 1 | cheese | 3.00 | 6.00 | 6.0 | | 58 | |
| 1 | egg | 3.00 | 6.00 | 11.3 | | 60 | |
| Σ60 | | | | | | | |

Differently from the environmental survey, sheep contamination percentage was remarkable (22%) and prevailingly due to $PCB_{DL}$ (≤76%). As already shown, $PCB_{DL}$ was largely present in pastured top soil, probably as deposition after re-suspension from the industrial area and nearby hotspots contaminated during previous improper dismantling of PCB-containing devices. It must be pointed out that farm contamination (13% in the area investigated) was not continuous, with some conforming farms very close to non-compliant ones in the so called "*leopard*" scenario. Although top soil is a typical accumulation sink of POPs, that once adsorbed tend to remain relatively immobile therein with poor transfer to plant and groundwater, direct deposition, vaporization, re-suspension and re-deposition on grass and leaves contribute to PCDD/F and $PCB_{DL}$ entry into the food-cycle as livestock pasture [40] [41]. Sheep in particular play a well-known "sentinel role" towards POP contamination, due to the large amount of soil ingested with grazing [42]. Accordingly, almost uniquely their edible organs (mainly liver) and food derivatives (milk, cheese), i.e., 59 out of the 60 samples, were found contaminated in all non-compliant animals.

As for the health risk assessment for humans consuming contaminated cattle and their food derivatives, dioxins and $PCB_{DL}$ are ranked as being of high potential concern, owing to their bioaccumulation in the food chain and their frequent occurrence particularly in sheep liver [43] From a scientific point of view, however, comprehensive studies on dioxin and $PCB_{DL}$ transfer mechanism to livestock are very difficult, depending on congener molecule, type of animal (sheep, cow, pig), pasture (leaves, grass, soil), metabolic specificity (usually reaching steady state in 100 to 200 days), organ (muscle or fat tissues) etc. so that even laboratory studies quite often yield contradictory results, not to mention the few studies on non-laboratory and farmed animals [44] [45].

As stated in Paragraph 4.3, calculation for a 60 $kg_{bw}$ consumer eating 80 $g_{fat}$/day was referred to the 3 values of toxics concentration experimentally found in sheep (mean $v_m$, 95$^{th}$ percentile $v_{95}$ and maximum $v_{max}$) and 3 consumer profiles (ordinary, super and farmer, eating 10-50-90% sheep with their meat diet respectively), considering that 13% of sheep-farms was found contaminated in the area. Table 5 shows the resulting calculation for TWI and BB.

***Table 5. Tolerable weekly (TWI) and life-long (BB) human exposure to toxic dioxins and $PCB_{DL}$ in the area investigated***

| Consumer profile | | Ordinary | | Super | | Sheep Farmer | |
|---|---|---|---|---|---|---|---|
| Toxic concentration in contaminated sheep ($pg_{WHO-TE}/g_{fat}$) | | TWI* | BB** | TWI* | BB** | TWI* | BB** |
| $v_m$ | 43,4 | 4.2 | 1,142 | 20.2 | 4,269 | 36.4 | 7,358 |
| $v_{95}$ | 162,0 | 15.1 | 5,712 | 75.6 | 21,346 | 136.1 | 36,788 |
| $v_{max}$ | 279,2 | 26.1 | 10,281 | 130.3 | 38,422 | 234.5 | 66,218 |

**Tolerable Weekly Intake*: WHO limit ≤14.0 $pg_{WHO-TE}/kg_{bw}$xweek; ***Body Burden*: WHO limit ≤4,000 $pg_{WHO-TE}/kg_{bw}$

It can be seen that for the ordinary consumer the calculated health risk of exposure is largely below the WHO limits. However, accounting for the super consumers and the sheep-farmers, the precautionary principle made the abatement of the 2,170 infected sheep mandatory.

### 5.4 SOURCE APPORTIONMENT OF THE CONTAMINATION

Fig.1 shows the % occurrence of PCDD *vs.* PCDF and PCDD/F *vs.* $PCB_{DL}$ TEQ concentration in the various samples of the different matrices examined (for sake of simplicity, results of air samples, agreeing quite well with those from atmospheric deposition, are omitted). From these data it clearly appears that dioxins occurrence in E312 stack emission (top row) is due

almost exclusively to furans (PCDF:PCDD ≈90:10%, left) with negligible $PCB_{DL}$ presence as expected (PCDF+PCDD:$PCB_{DL}$ ≈95:5%, right).

A completely different, yet reasonably homogeneous, situation is shown by the other 3 environmental matrices examined (industrial top soil, atmospheric deposition and agricultural top soil, 2nd, 3rd and 4th row), where the presence of furans and dioxin is almost comparable (PCDF:PCDD ≈50:50%, left) and the occurrence of $PCB_{DL}$ is appreciable (PCDF+PCDD:$PCB_{DL}$ ≈65:35%, right).

These results exclude ILVA E312 stack point-emission from potential source(s) contaminating the environmental matrices that closely surround it.

A still different scenario is shown by sheep and their edible part (bottom row), with a minor contribution of dioxin *vs.* furans (PCDF: PCDD ≈20:80%, left) and the contamination due prevailingly to $PCB_{DL}$ (PCDF+PCDD:$PCB_{DL}$ ≈35:65%, right).

The results of sheep seem contradictory as their contamination should originate almost exclusively from ingestion of top agricultural soil (none of the infected sheep was bred with feedstuff) wherein, on the contrary, $PCB_{DL}$ is minority and the occurrence of dioxins and furans is comparable.

This conclusion was matched with fingerprint comparison. Fig.2 shows that the fingerprints of industrial top soil, air deposition and agricultural top soil (2nd, 3rd and 4th row) are almost perfectly comparable, with OCDD and 1,2,3,4,6,7,8-HpCDD predominating among dioxins and 1,2,3,4,6,7,8-HpCDF (and, to a lower extent, OCDF) among furans and 126 and 114 among $PCB_{DL}$, thus calling for a common contaminating source. This source, however, cannot be ILVA E312 stack emission (top row in Fig.2), whose fingerprints are remarkably different.

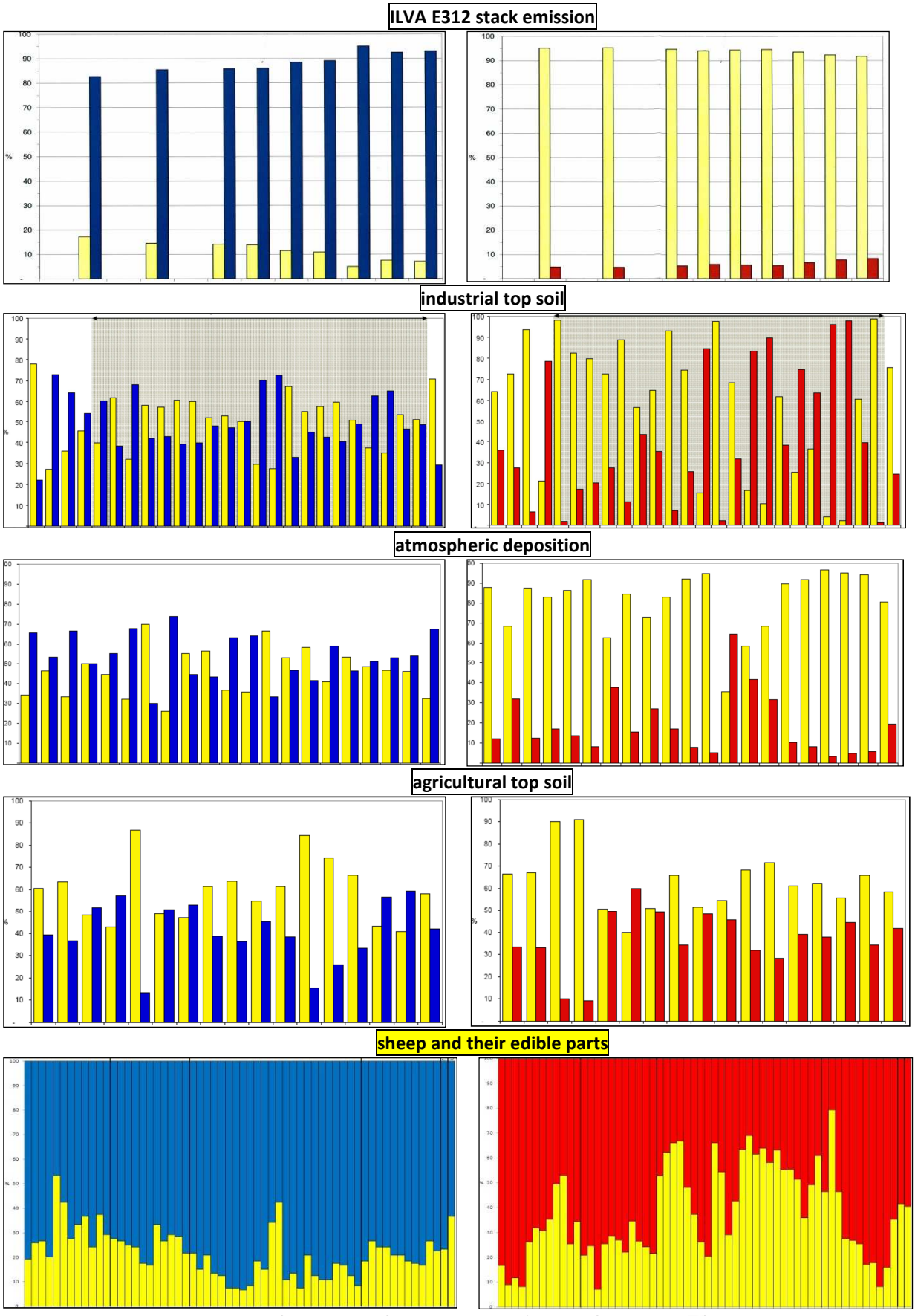



Fig.1. TEQ occurrence of PCDD (□) *vs.* PCDF (■) (left) and PCDD/PCDF (□/■) *vs.* $PCB_{DL}$ (■) (right) in various matrix samples

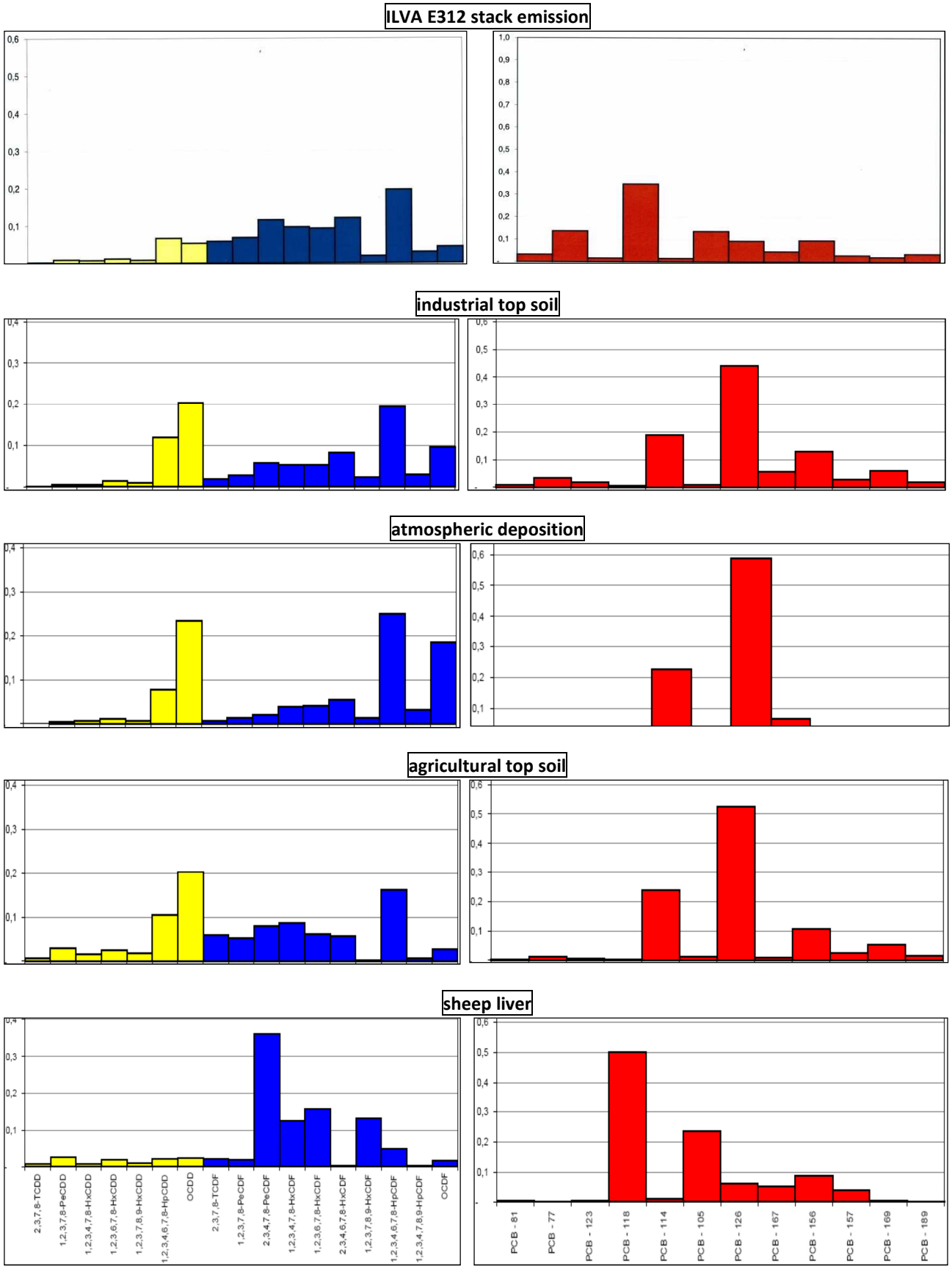



Fig.2. Comparison of toxic congeners profile (*fingerprint*) in investigated matrices (PCDD and PCDF left, $PCB_{DL}$ right)

Still different fingerprints are exhibited by sheep liver and other foodstuffs examined (bottom row in Fig.2), where not only animal contamination is due prevailingly to $PCB_{DL}$ (as already seen in Fig.1), but their $PCB_{DL}$ fingerprint is predominated by other congeners than in environmental matrices, namely by PCB 118 and 105.

Fingerprint comparison confirmed that point-emission from ILVA E312 sinter stack cannot be the source of dioxins and $PCB_{DL}$ contaminating the surrounding environment nor the sheep and their food derivatives examined.

Finally, the multivariate PCA statistical analysis of all the experimental data collected was carried out (Fig.3).

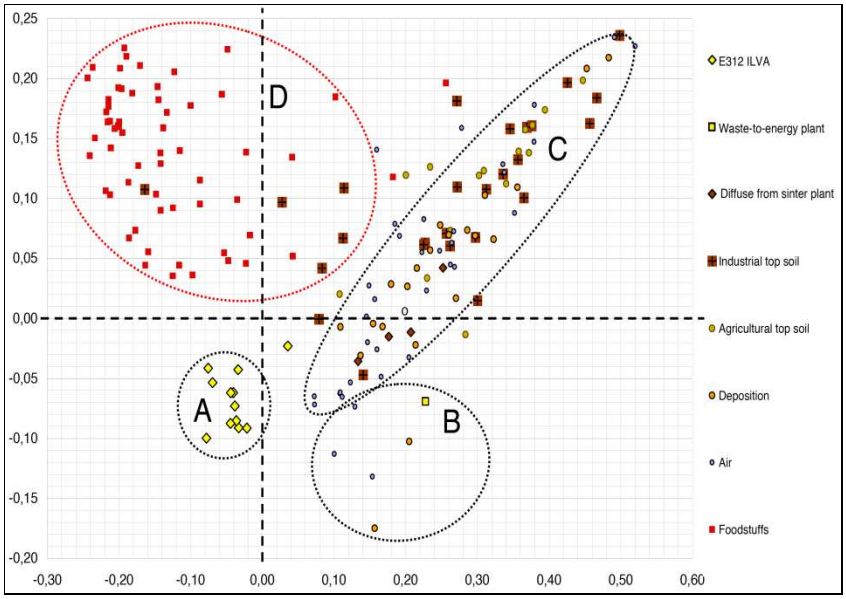



Fig.3 Results of PCA evaluation

As shown in Fig.3, PCA gave origin to 4 clusters, satisfactorily homogeneous and with poor overlapping, aggregating:

- ILVA E312 sinter stack emission only (cluster A);
- waste-to-energy plant stack emission and some samples of air and atmospheric deposition (cluster B);
- almost all the environmental matrices (cluster C);
- almost all animals and their food derivatives, including part of industrial top soil (cluster D).

From these data the following considerations may be drawn:

- PCDD/Fs emitted by ILVA E312 sinter stack lie in a definitely different cluster (A) from those contaminating the environmental (cluster C) and animal/food matrices (cluster D);
- some affinity exists among some samples of air/atmospheric deposition and the single available sample of the RDF waste-to-energy plant (cluster B);
- the vast majority of the environmental matrices examined, including agricultural top soil, lies in cluster C, well separated from cluster D that aggregates animal and food matrices, apparently indicating that these latter were contaminated by different source(s);
- animal and food matrices are closely and homogeneously clustered (D), where the appreciable occurrence of some industrial top soil samples is also registered.

The evidence achieved at this point of the investigation converged on the following conclusions:

1) point-emission from E312 main flue gas stack serving ILVA sintering plant is not the source of the *recent* (probably on-going) dioxins and *historic* $PCB_{DL}$ contamination;
2) intoxication of the 2,170 infected sheep and their food products apparently did not originate from the agricultural top soil were they grazed freely.

Although hard to believe, the latter conclusion may be easily explained. PCDD/F and PCB are a family of lipophilic hydrophobic congeners, highly recalcitrant to biodegradation by the natural micro-organisms present in environmental matrices. This is so in particular in agricultural soil, where they tend to remain at the top for ≈100 years, with poor ability to migrate to crops and groundwater, while persisting ≈10 years in humans and only ≈1 month in rat [40]. Since the pioneering studies of Bjerke [46] and Flesh-Janys [47], still little is known on PCDD/F and PCB metabolic degradation in living bodies,

wherein the fingerprints may soon be completely altered [48] [49] [50] [51] [52]. Accordingly, the remarkable difference between fingerprints soil and in sheep grazing thereupon should not be a surprise nor should PCDD/F and $PCB_{DL}$ in agricultural top soil be denied as the main vehicle of sheep contamination.

Excluding the *point-source* emissions examined (ILVA E312 stack and other chimneys), the occurrence of *diffuse fugitive* emissions close to ground level was looked at in search of the source(s) of environmental and animal contamination. To that aim, an inspection was authorized in 23rd February 2010 to ILVA sinter plant. Samples of the dust continuously deposited on the pavement and floating inside the plant, reportedly made by ore minerals, were collected and analysed, together with toxic fines filtered by the electrostatic precipitators (ESP) ahead of the E312 stack and collected in big bags for transportation to a sanitary landfill. Fig.4 shows the results of the analysis carried out.

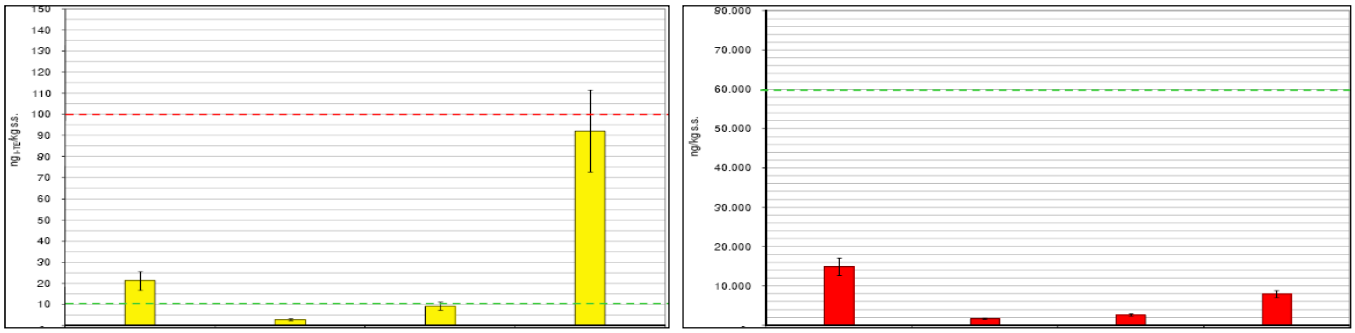



Fig.4. PCDD/F (left) and $PCB_{TOT}$ (right) in 4 dust samples collected inside ILVA AGL sinter plant
(Maximum Allowable Concentration in industrial [---] and public [---] sites ex Legs. Decree n.152/2006)

Fig.4 indicates a finite presence of dioxins (although below the limits in force) and almost negligible of PCB in the dust.

More important, Fig.5 shows a strict similarity of PCDD *vs.* PCDF and PCDD/F *vs.* $PCB_{DL}$ occurrence between that dust and the fines filtered by ESP as well as between their PCDD/F fingerprints (PCB were negligible), thus indicating a common origin.

Finally, Fig.6 confirms that both fingerprints match perfectly with those of samples taken from ILVA industrial top soil surrounding the sinter plant, already shown in Fig.1 (2nd row).

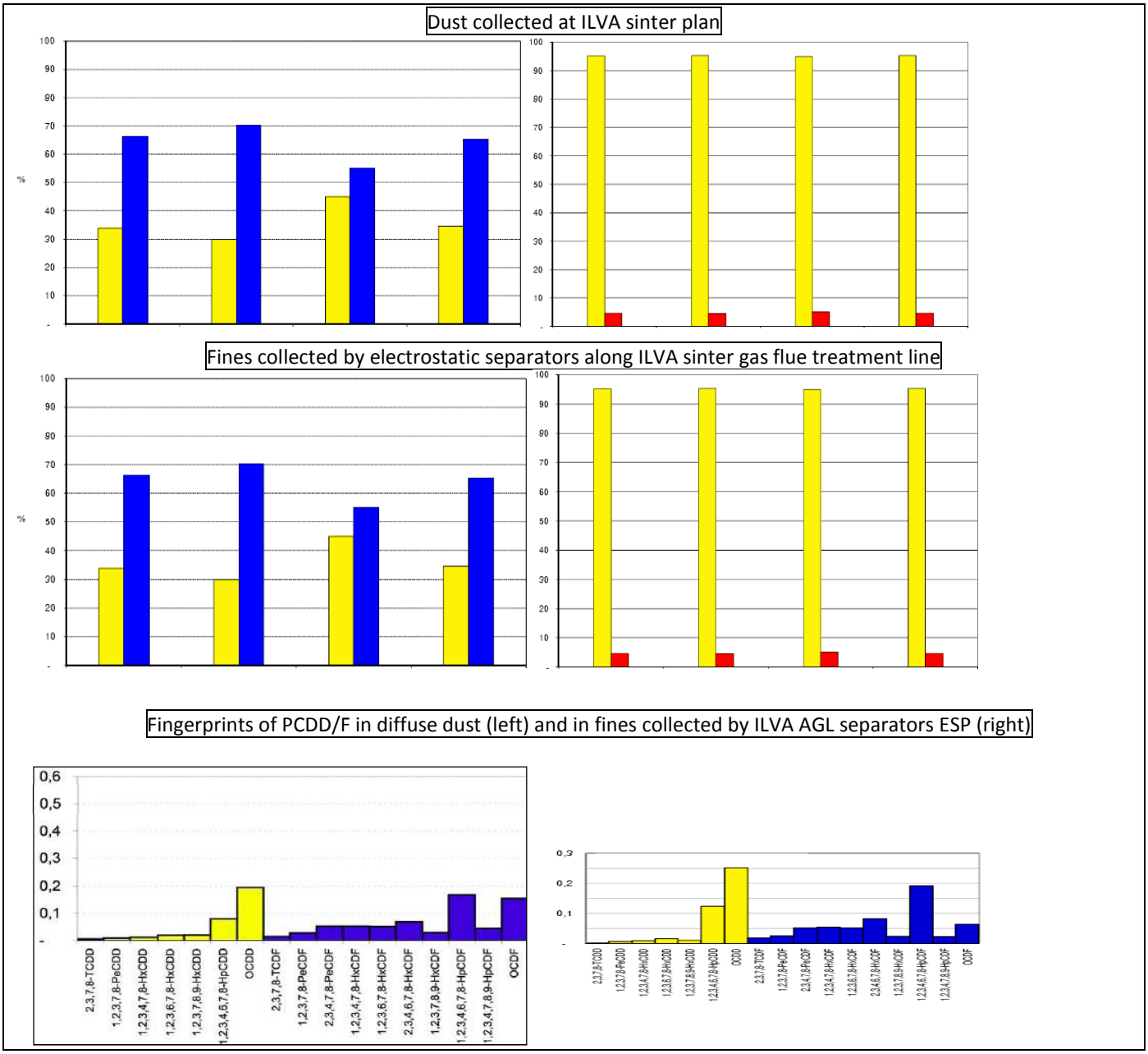



Fig.5. PCDD *vs.* PCDF (left), PCDD/PCDF *vs.* $PCB_{DL}$ (right) and fingerprints at ILVA sinter plant

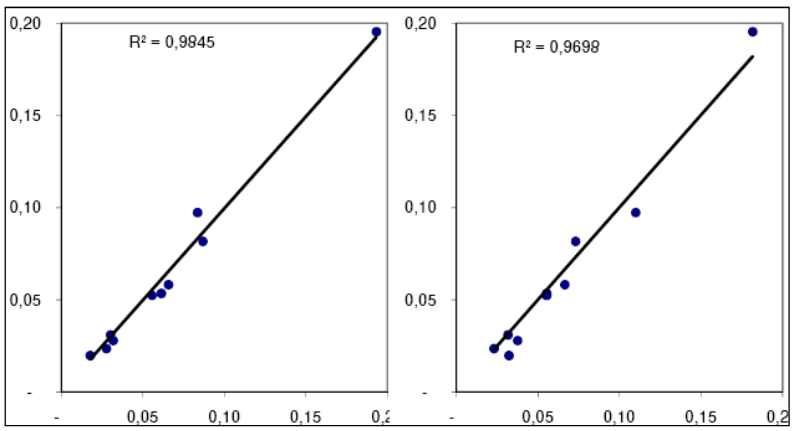



Fig.6. Fingerprint correlation of dust (left) and toxic fines (right) at ILVA sinter plant with outdoor top industrial soil

## 6 CONCLUSIONS

The results of this extensive investigation showed a remarkable ubiquitous contamination by dioxins (*recent*) and $PCB_{DL}$ (*antique*) of environmental and cattle matrices in an area with 20km radius surrounding Taranto industrial zone. On the basis of the various evidences achieved, it may be reasonably concluded that *fugitive diffuse* emissions escaping from ILVA sinter plant, not the largely suspected *point source* emission from its E312 main stack, are the main source of dioxin contamination.

On the other hand, the contaminating source of $PCB_{DL}$ (not produced during the I&S cycle) should be found in previous mismanagement of PCB-containing devices largely used in the past in the area.

As for animal contamination, the difference of dioxin and PCB fingerprints between the intoxicated sheep (2,170 were abated) and the uncultivated top soil around ILVA were they used to graze is due most probably to the relatively fast, although still largely unexplained, biodegradation rate of those contaminants in living organisms.

Following these results, a regional law reduced dramatically the threshold of *point-source* emission of toxic dioxins from industries (chimneys and stacks) in Apulia region. Major attention, however. should be dedicated to regulating and eliminating the shifty *fugitive diffuse* toxic industrial emissions in order to ensure better working conditions and safer living situation for the surrounding population.

Furthermore, given the differences in source, toxicity and diffusion route into the environment and living organisms of dioxins and PCB, it is appropriate that separate actions for their control could be considered by the responsible authorities.

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