



Four Decades of Progress in Monitoring and Modeling of Processes in the Soil-Plant-
Atmosphere System: Applications and Challenges

Contamination of the environmental matrices in agricultural
areas produced by industrial discharges: the case study of the
land of the city of Statte (Taranto, Southern Italy)

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Abstract

The diffusion of pollutants in the atmosphere, agricultural soil, irrigation water, crops and food chain can produce potential environmental health risk. The aims of this study are the environmental risk assessment for the aquifers and the estimation of pollutants concentration in the forage for evaluating the risk for human health. The risk analysis was applied in the rural territory of Statte (Taranto, Italy) using an innovative methodology based on the integration of models for estimation of pollutant leaching in the groundwater and for the evaluation of bio-transfer of pollutant in the plant. The model results are in accordance with the experimental values and therefore the proposed methodology allows the evaluation and management of environmental health risks in agricultural areas interested by pollution phenomena generated by industrial plants.

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1. Introduction

The contamination of the agricultural soil is mainly caused by entrainment and deposition of the atmospheric pollutants released by industrial plant [1]. In reality, the industrial combustion processes can

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produce emissions with organic micro pollutant such as dioxins (polychlorinated dibenzo-p-dioxins PCDDs), polychlorinated biphenyls (PCB), furans and polycyclic aromatic hydrocarbons (PAH) [2].

Owing to the atmospheric streams, the PCDDs and PCB, owing to their chemical-physical properties, can be easily conveyed by the emitting sources. For this reasons the aforementioned pollutants often involve the rural territory where the agricultural and/or animal production may be taken place.

The PCDDs are undesired by-products of chemical, thermal, photochemical and enzymatic reactions [3] and the PCB are approved synthesis products for the industrial use (dielectric fluids, lubricants, flame retardants).

PCDDs and PCB are both halogenated persistent organic pollutants, highly lipophile and characterized by a high organic carbon-water partitioning coefficient (K_{oc}) [3-4]. These chemical-physical characteristics facilitate the close connection of PCDDs and PCB with the agricultural soil organic matter, the diffusion in the aquatic environment and the bioaccumulation in the food chain [5-6].

PCDDs and PCB are poorly water-soluble but can spread in rivers and lakes owing to the water erosion of contaminated soils [6] with production of sediments in suspension carried out by streams. On the other hand the displacement of PCDDs and PCB in the groundwater is due to the leaching processes produced by infiltration of meteoric waters in the contaminated unsaturated soils [6]. The leaching of the pollutants present in the surface soil is the main pollution reason of the aquifer and has a meaningful impact on the qualitative state of the groundwater [7]. In this way the pollutants present in the surface soil can reach and contaminate the aquifer, but during migration their concentration decreases. The leaching factor [8] enables to evaluate this attenuation by considering the chemical-physical processes that occur in the path between the surface soil and the aquifer, the pollutant biodegradation phenomena, the dilution and leakage in the aquifer. These aspects are assessed according to the chemical-physical properties of the pollutant (Henry's constant, soil-water partitioning coefficient) and to the hydrogeological characteristics of the unsaturated soil (soil density, air and moisture content, effective infiltration) and the aquifer (Darcy velocity, mixing zone depth in aquifer).

In the soils having a high content of organic matter, PCDDs and PCB are often adsorbed by the soil particles without migrating toward the aquifer [1-3]. Soil pollution and simultaneous infiltration in the groundwater occur in the territory of Statte (Puglia, Italy) and of Valley of Susa (Piemonte, Italy) [2-9]. Therefore the evaluation of PCDDs and PCB concentrations in the agricultural soil and the calculation of the leaching factor enable to assess their concentration in the aquifer and to estimate the environmental risk for the groundwater resources. This hazard is admissible if the ratio between the concentration of pollutants in the aquifer and the legal limit concentration [10] is less or equal than unit [11].

Furthermore the simultaneous presence of PCDDs and PCB in the agricultural soil and waters may produce sanitary risks for humans. Recent studies highlight that approximately the 90% of the exposures to PCDDs and PCB take place through consumption of contaminated foods [3-12]. Basically PCDDs and PCB go into the chain food through the animals to grazing that eat contaminated forages and soil flakes [13]. The forage contamination can take place through atmospheric deposition of PCDDs and PCB and their absorption from vapor phase, agricultural soil and irrigation waters [6-14].

These contaminants concentrate in the fatty tissue of the animals and turn into the human consumption through products such as milk and meats [15-16-17]. The harmful effects on the human health caused by the ingestion of PCDDs and PCB contaminated foods are: modifications of the chemical and the hormonal blood parameters [2]; endocrine-metabolic diseases; generative pathologies and immune-complex diseases. In reality the prolonged assumption of milk and meats produced by animals fed with contaminated forage can cause blood levels of PCDDs and PCB to eight times higher than the mean values [12]. In regard to this, European Regulations [18] established the threshold concentrations for the animal foods in order to safeguard the quality of the animal productions and the human health.

The aim of this paper is the characterization and the analysis of the relationships among the pollution caused by PCDDs and PCB of the surface soil, of the groundwater and of the forage in a sample area with remarkable agricultural and animal productions such as the rural territory of the city of Statte (Taranto, Italy). With this object, the PCDDs and PCB leaching from the surface soil to the aquifer, the environmental risk for groundwater and the forage root absorption of the PCDDs and PCB were assessed by means of stationary modeling tools. These evaluations can support the authorities to characterize and to reduce the sanitary-environmental risks due to contamination of the surface soil in areas employed for agricultural and animal productions [19]. Furthermore such evaluations may be useful for the farms in order to estimate the possible concentrations of PCDDs and PCB in the food productions and to carry out soils and aquifers safekeeping or decontamination operations.

2. Materials and Methods

2.1. Study area

The sample area of the present study is the rural territory of the city of Statte (Puglia, Italy), characterized by the presence of breeding farms and large grazing lands. Therefore the presence of pollutants inside the environment can contaminate both the agricultural and animal productions. This territory has a high environmental risk factor and is included among the 14 national interest sites to decontaminate [20~21] since it has a particularly compromised sanitary-environmental land [21] due to the presence of various industrial plants producing injurious emissions, placed in the neighborhood of the city of Taranto [22~23].

Actually, in the territory of Statte, the presence of PCDDs and PCB was found in the environmental matrices (soil and groundwater), in the forage and in the food of animal origin [24~25]. Hence in 2008 the Local Health Authority established the no grazing area and the extermination of two thousands head of livestock [26]. Furthermore the Regional Agency for Environmental Protection of the Puglia Region carried out in the rural territory of Statte the analyses concerning: the air quality, the atmospheric deposition, the concentration of PCDDs and PCB in the surface soil and groundwater [27].

In the air of Statte, the mean concentration of PCDDs was 40 fg WHO-TEQ/m³air and the deposition on the soil was in the range 4.5÷12.2 pg WHO-TEQ/m²day [26,28]. The concentration of PCDDs in the surface soil samples was in the range 0.84÷10.3 ng WHO-TEQ/Kg_{soil} [9] with a mean value of 2.5 ng WHO-TEQ/Kg_{soil}, lower than the threshold contamination value of 10 ng WHO-TEQ/Kg_{soil} established by the Italian Regulation [10].

On the other hand the concentration of PCB in the surface soil was in the range of 0.04÷26 ng WHO-TEQ/Kg_{soil} with an average value of 1.6 WHO-TEQ/Kg_{soil} [26]; however the Italian Regulation does not set any limit for PCB in the surface soil.

The concentration of PCDDs in groundwater of the hydrogeological basin of Statte was 0.46÷5.71 pg WHO-TEQ/l with an average value of 2.55 pg WHO-TEQ/l [9]. The PCDDs registered value of 5.71 pg WHO-TEQ/l, higher than the legal limit, was caused by the heavy rain occurred in the preceding the extraction (Esposito et al., 2010). Therefore it needs to analyze the effects in the groundwater produced by the leaching of PCDDs from the surface soil to the aquifer.

The concentration of PCB in groundwater was 0.67÷1.53 pg WHO-TEQ/l with an average value of pg WHO-TEQ/l.

The effects on the human health caused by the environmental exposure to dioxins and PCB in the area of Statte were analyzed within the project "Sentieri". Even if the average concentrations of PCDDs and PCB in the environmental matrices were lower than the legal limits, the results showed that the residential

population is exposed to high death rate for lung or pleura cancer, respiratory, digestive apparatus diseases [29].

2.2. PCDDs e PCB soil – aquifer leaching

The concentration of pollutants in groundwater (C_{poe}) is evaluated according to their average concentration in the surface soil (C_{soil}) by fate and displacement models [11]. The most used analytical model of the displacement is founded on the leaching factor (LF) formulated by ASTM (American Society for Testing and Materials) [31] and recently updated [8~32]:

$$C_{poe} = C_{soil} \cdot LF \quad (1)$$

The leaching factor LF , dimensionless, can be evaluated by the following equations [8]:

$$LF = \frac{\alpha_{leach} \cdot \alpha_{dep}(t)}{K_{sw} \cdot LFD} \quad (2)$$

where: α_{leach} , dimensionless, is the attenuation factor of the pollutant concentration during the surface soil-aquifer path; α_{dep} , dimensionless, is the depletion factor of the pollutant concentration in the soil; K_{sw} , dimensionless, is the soil-water partitioning coefficient of the pollutant; LFD , dimensionless, is the dilution factor in the aquifer.

In this paper the attenuation and depletion factors are neglected as the pollutants PCDDs and PCB present in the study area are characterised by low rates of biodegradation, low solubility and high elimination half-life [2]. Therefore the leaching factor is estimated according to the ASTM-RBCA (American Society for Testing and Materials – Risk based corrective action) [31] approach, founded on the hypothesis of the invariable chemical concentration of pollutants in the soil. This hypothesis expects a steady redeposition on the soil of pollutants as these leach in groundwater and is admissible till containment systems of pollutants emissions are applied. In this paper then the leaching factor is evaluated by the following equation [11]:

$$LF = \frac{K_{ws} \cdot SAM}{LFD} \quad (3)$$

with:

$$K_{ws} = \frac{\rho_s}{\theta_w + H \cdot \theta_a + \rho_s \cdot K_{oc} \cdot f_{oc}} \quad (4)$$

$$SAM = \frac{d}{L_F} \quad (5)$$

$$LFD = 1 + \frac{v_{gw} \times \delta_{gw}}{I_{ef} \cdot W} \quad (6)$$

where: K_{ws} , dimensionless, is the water - soil partitioning coefficient of the pollutant, which regards the distribution of the pollutant among water, air and soil; SAM , dimensionless, is the attenuation factor of soil, which considers the path of the pollutant for reaching the aquifer; LFD , dimensionless, is the dilution factor in the aquifer which contemplates the thinning undergone by the pollutant during the transition from unsaturated soil to saturated soil. The parameters in the equations are related to the chemical-physical properties of pollutant and hydrogeological properties of soil and aquifer. Specifically, these parameters are: θ_a , dimensionless, air volume content in the soil; θ_w , dimensionless, water volume content in the soil; ρ_s , g/cm^3 , bulk soil density; d , cm, thickness of the contaminated soil; L_F , cm, distance between the groundwater and the contaminated surface soil; v_{gw} , cm/year , Darcy velocity; δ_{gw} , cm, thickness of the mixing zone; W , cm, extension of the contaminated area in the way of aquifer flow; I_{ef} , cm/year , effective infiltration; H , dimensionless, Henry constant of the pollutant; K_{oc} , $1/\text{Kg}_{\text{soil}}$, organic carbon-water partitioning coefficient; f_{oc} , percentage, fraction of organic carbon in soil. The geological and hydrogeological properties of saturated and unsaturated soil, which affect the leaching in the aquifer, were deduced from the geological map of Italy (Table 1). The chemical-physical properties of PCDDs and PCB are reported in the ISS/ISPESL data base [30].

Table 1. Geological and hydrogeological properties [11]

Properties	Value	Units of measurement
θ_a	9.50×10^{-2}	dimensionless
θ_w	2.46×10^{-1}	dimensionless
ρ_s	2.32	g/cm^3
L_F	6.0×10^2	cm
v_{gw}	6.5×10^{-4}	cm/year
δ_{gw}	20.0	cm
W	2.0×10^3	cm
I_{ef}	20.0	cm/year
f_{oc}	1.0×10^{-3}	$\text{g}_{\text{carbon}}/\text{g}_{\text{soil}}$

2.3. Risk analysis for groundwater

The risk analysis for groundwater is carried out according to the expected concentrations of PCDDs and PCB in the aquifer (C_{poe}), caused by the leaching from the surface soil. This environmental risk is evaluated according to the “Methodological criteria for the application of the absolute risk analysis at contaminated sites” established by ISPRA (Institute for Environmental Protection and Research) founded on the ASTM-RBCA approach [11~31].

This methodology allows to calculate the risk for groundwater (R_{GW}) by the ratio between the expected concentration of pollutants in groundwater (C_{poe}) and the concerning threshold concentration (CSC_{GW}) established by the Italian Regulation [10]. Such risk is admissible if the aforementioned ratio is less or equal to unit:

$$R_{GW} = \frac{C_{POE}}{CSC_{GW}} \leq 1 \quad (7)$$

The threshold concentration value is 4 pg WHO-TEQ/l, taking into account of the contribution of both PCDDs PCB in groundwater [10].

2.4. PCDDs and PCB absorption by plant

The main ways for deposition of PCDDs and PCB inside plants are: root absorption from soil and irrigation water, absorption from vapor phase and atmospheric deposition [33]. Therefore in this paper the concentrations of PCDDs and PCB in the plants (C_{Plant}) are determined by the following formula [34]:

$$C_{Plant} = C_{ru} + C_{va} + C_{dp} \quad (8)$$

with:

$$C_{ru} = C_{soil} \times FT \times (1 - 0,12) \quad (9)$$

$$C_{va} = C_{air} \times B_v \quad (10)$$

$$C_{dp} = \frac{D_d \times I_j}{K_w \times Y_j} \times (1 - e^{-K_w T_p}) \quad (11)$$

where: C_{ru} , ng WHO-TEQ/Kg_{Plant}, is the concentration produced by the root absorption; C_{va} , ng WHO-TEQ/Kg_{Plant}, is the concentration due to the absorption from the vapor phase; C_{dp} , ng WHO-TEQ/Kg_{Plant}, is the concentration caused by the atmospheric deposition; FT , dimensionless, is the soil-plant bio-transfer factor; B_v , dimensionless, is the air-plant bio-transfer factor; D_d , ng/m²/year, is the atmospheric deposition; I_j , dimensionless, is the portion intercepted by the plants; K_w , year⁻¹, is the air-plant dissipation constant; Y_j , kg/m², is the dry matter contents of the plants; T_p , year, is the lifetime of the plant. These parameters are estimated in the following manner.

The values suggested by Harrad and Smith (1997) for herbaceous crops are used for I_j , K_w , Y_j and T_p [34]. The assessment of bio-transfer factors is very important for the estimation of the pollutants concentration inside crops as strictly connected to specific pollutants, to physical-chemical characteristics of soils and to specific crops carried out [35]. Soil-plant bio-transfer factors can be evaluated by empirical, semi-empirical and mechanistic models [19] or by experimental analyses carried out on crops cultivated on contaminated soil. In this paper the PCDDs and PCB soil-plant bio-transfer factors (FT), dimensionless, are calculated through the Travis and Arms (1988) empirical model [17]:

$$\log FT = 1,588 - 0,578 \log K_{ow} \quad (12)$$

where K_{ow} , dimensionless, is the octanol-water partition coefficient of the pollutants under investigation. This coefficient characterizes the propensity of pollutants to stock in the plants [36].

The air-plant bio-transfer factors can be evaluated by means of experimental equations represented in the EPA (Environmental Protection Agency) procedures [37] and adjusted by Lorber [38]. In this paper the PCDDs and PCB air-plant bio-transfer factors, calculated by Schuhmacher et al. [39] and EPA [40], are utilized.

The concentrations of PCDDs and PCB in the forage crops are estimated using the suggested equations and compared with both the measured concentrations [25] and the legal limits established for animal feeds [18].

3. Results and Discussions

3.1. Environmental risk for groundwater in the rural territory of Statte

The average concentrations respectively of PCDDs and PCB undergo a significant attenuation during the migration from the surface soil to the aquifer. This attenuation is estimated by the leaching factor (LF) in its turn founded on the water-soil partitioning coefficient (K_{ws}), on the attenuation factor of soil (SAM) and on the dilution factor inside aquifer (LFD). The values of these factors are reported in Table 2.

Table 2. Factors for evaluating the attenuation during soil–aquifer leaching process.

Factors	PCDDs [dimensionless]	PCB [dimensionless]
K_{ws}	2.84×10^{-3}	6.32×10^{-5}
SAM	3.33×10^{-2}	3.33×10^{-2}
LFD	1.00	1.00
LF	9.46×10^{-5}	2.11×10^{-4}

According to the equation 1, the mean concentrations of PCDDs and PCB in the surface soil and the concerning leaching factors allow to calculate the concentrations of PCDDs and PCB in the aquifer.

The estimated concentrations of PCDDs and PCB in groundwater of Statte are respectively 0.24 pg WHO-TEQ/l and 0.33 pg WHO-TEQ/l and the attenuations of these concentration during the migration path from the surface soil to the aquifer are respectively 99.99% for PCDDs and 99.98% for PCB. These reductions are largely due to the PCDDs and PCB absorption by the particles of the agricultural soil.

The environmental risk for groundwater (R_{GW}) is $0.14 < 1$ and therefore the presence of PCDDs and PCB in the agricultural soil of Statte does not produce environmental risks for this resource. On the other hand, environmental risk conditions for groundwater may occur just if the PCDDs and PCB concentrations in the agricultural soil are higher than 40 ng WHO-TEQ/Kg_{soil}.

3.2. PCDDs and PCB absorption inside forage crops in the territory of Statte

The PCDDs and PCB soil-plant bio-transfer factors (FT), evaluated through equation 12, are respectively 2.9×10^{-3} and 8.9×10^{-3} . The PCDDs and PCB air-plant bio-transfer factors (B_v), obtained by bibliographic sources, are respectively 5.6×10^3 e 6.3.

The concentrations of PCDD and PCB in the forage crops, caused by root absorption, atmospheric deposition and absorption from vapor phase, are reported in Table 3.

Table 3. Territory of Statte. Estimated concentrations of PCDDs and PCB in the forage crops

Absorption ways	PCDDs [ng WHO-TEQ/Kg _{plant}]	PCB [ng WHO-TEQ/Kg _{plant}]	PCDDs+PCB [ng WHO-TEQ/Kg _{plant}]
Root absorption	7.15×10^{-3}	1.26×10^{-2}	1.98×10^{-2}
Atmospheric deposition	4.91×10^{-2}	6.18×10^{-3}	5.53×10^{-2}
Absorption from vapor phase	7.11×10^{-1}	3.59×10^{-4}	7.12×10^{-1}
Total absorption	7.67×10^{-1}	1.92×10^{-2}	7.87×10^{-1}

The results highlight that the main transfer way of PCDDs and PCB into forage crops existing in the case study is the absorption from the vapor phase (90.5%), followed by the atmospheric deposition (7.0%) and the root absorption (2.5%).

The concentrations of PCDDs and PCB inside forage crops, evaluated through equation 8 and the bio-transfer factors in their turn calculated by equation 12 and/or by EPA [40] are within the range of the concentrations measured by Diletti et al. [25]. Indeed the measured PCDDs and PCB values are in the range $0.05 \div 1.11$ ng WHO-TEQ/Kg_{plant} with an average value of 0.30. However the estimated and measured concentrations values are always less than the legal limits (1.25 ng WHO-TEQ/kg) established for animal feeds [18].

4. Conclusions

The aim of this paper is the environmental fate analyses in the agricultural ecosystems of the PCDDs and PCB, produced by an industrial pole with dramatic sanitary-environmental impact. To that end the bio-transfer of PCDDs and PCB from the environmental matrices (air, soil, groundwater) to the forage crops, in an agricultural area characterized by animal farms and large grazing lands, are estimated by integration of analytical models already in use.

The obtained results show that PCDDs and PCB present in the air move to the agricultural soil and then into groundwater. Indeed, as result of rain, PCDDs and PCB contaminate the soil and undergo leaching process while percolate for the aquifer. In this migration path however the concentrations of PCDDs and PCB significantly weaken (99%) because of their low solubility and high propensity to join to organic matter of soil. Then the environmental risk of groundwater resources is poor, for slightly contaminated agricultural areas by PCDDs and PCB.

Furthermore the results highlight that the PCDDs and PCB existing in the environmental matrices (air, soil, groundwater) transfer to vegetable tissues of crops and may go into the food chain causing risks for the human health. The air-plant and soil-plant bio-transfer models of PCDDs and PCB used in this paper may allow to predict their concentrations in the plant tissues. In reality, the concentration values obtained by the bio-transfer model are in the range of the experimentally measured values.

Finally the PCDDs and PCB concentrations in the vegetable tissues can be compared with the legal limit concentrations concerning the human and/or animal foods in order to avoid the ingestion of contaminated products and the relative sanitary risks.

According to the aforementioned results, the proposed methodology can be a useful tool to evaluate and manage the sanitary and environmental risks in the rural territories involved by contamination phenomena in order to plan decontamination actions and to safeguard farmers' health.

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