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MODELLING WET AND DRY DEPOSITIONS OF PCDD/F RELEASES FROM DIFFERENT INDUSTRIAL PLANTS IN APULIA, SOUTHERN ITALY

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Abstract: An air quality modelling system has been used to simulate the atmospheric dispersion and deposition of dioxins and furanes (PCDD/F) emitted from different industrial sources over the Province of Lecce (South-East Italy). The system couples the prognostic meteorological model RAMS, the micrometeorological model CALMET and a dispersion model CALPUFF. Comparison between deposition measurements and predictions shows that the model reproduces realistically the deposition patterns. Dry deposition of particle-associated PCDD/F extends mainly in the southern directions downwind of the sources following the prevailing wind directions of the area. Wet deposition of particles-associated PCDD/F is confined to the immediate vicinity of emission sources and it is associated with the highest PCDD/F deposition values. Sensitivity analysis suggests that model simulations are very sensitive to the particle size distributions which highly influence the dry and wet deposition velocities. Measurements of the size distribution of particulate PCDD/F are thus recommended.

Key words: *Dioxins, Deposition, Calpuff, Apulia*

INTRODUCTION

Adverse health effects of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) are well known. The knowledge of their presence in the environment is linked to many factors, being emissions in the atmosphere from localised sources one of great concern to evaluate population exposure. A major issue is the area of impact of major emission sources, that is where epidemiological studies should be conducted. Furthermore, it is important to know whether PCDD/F deposition at a given location is due primarily to local sources or distant regional/global sources, to support local authorities in their air quality management. In this study, an air quality modelling system is used to simulate the atmospheric dispersion and deposition of toxics emitted from industrial sources during a field campaign in order to estimate the contribution of single emission source to the measured deposition data.

THE STUDY AREA

The Province of Lecce is located in the south-eastern part of Italy, and is surrounded by two different seas, the southern Adriatic and the northern Ionian Sea, connected by the Otranto Strait (Figure 1). The peninsula is quite narrow, since its longitudinal axis is about 100 km long in the NW-SE direction and the transversal axis is 30-40 km wide on average. The topography is quite flat with small hills: the maximum altitude (less than 200 m) is along the central axis of the southern part. Two prevailing wind regimes characterise the area: the most frequent one is associated to wind direction from NW-N, the second one is associated to wind from the southern quadrant.

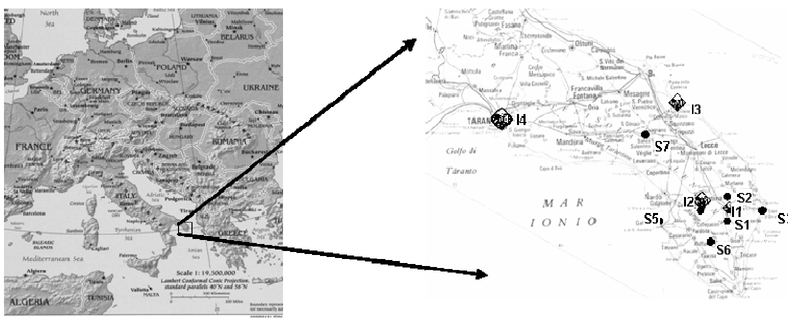

Figure 1. The area of study with the sampling locations S1-S7 and industrial emissions I1-I4

Four PCDD/F emissions have been individuated which may invest the area: an incinerator and a cement kiln located in the centre of the domain, a coal power plant located about 30 km from the northern provincial boundary of Lecce to the north, a sinter plant located in the municipalities of the city of Taranto, about 40 km from the north-western boundary of Lecce province. Table 1 summarizes the main characteristics of the four industrial emissions

Table 1. Source characteristics.

		Stack height (m)	Stack diameter (m)	Exit temperature (K)	Exit velocity (m/s)	PCDD/F Emission (I-TEQ ng/s)
I1	Incinerator	40	2.5	425	10	1400-3.3
I2	Cement kiln	87	5	408	10	1.72
I3	Coal power plant	200	6.7	358	20	0.5
I4	Sinter plant	210	8.9	409	16.6	102.5

From June 2008 to July 2009 bulk deposition samples were collected every month and simultaneously, at 7 sites distributed along the area (Figure 1). S1, S2, S3 are placed around I1 and I2 industrial sites. S4- and S5 close to the most important harbours of the area, S6 is downwind I4 and I3 emissions considering the prevailing wind direction of the area.
PCDD/F emission rates for I1, I2 and I4 were measured by ARPA-PUGLIA, while for I3 was derived from literature. Regarding emission I1, it is necessary to underline that after the first PCDD/F emission rate measurements (42ng-TEQ NM^{-3}), the incinerator was immediately shutdown and then it started up again after some days. During the field campaign, there were many start-up and shut down periods which could have given particular risks for high dioxin emissions. (De Frè and Wevers, 1997)

THE MODELLING SYSTEM
The modelling system couples the prognostic meteorological model RAMS (Regional Atmospheric Modelling System, Pielke *et al.*, 1992), the micrometeorological model CALMET (Scire *et al.* 1992) and a dispersion model CALPUFF (Scire *et al.* 1992). RAMS wind fields are used as input for the CALMET model which provides all boundary layer inputs necessary for CALPUFF. All four different sources have been considered. Due to the high sensitivity of deposition flux to precipitation, measured precipitation data were also integrated in CALMET.

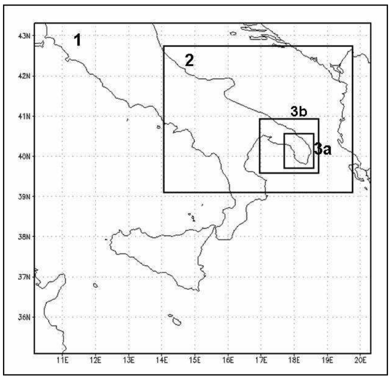

Figure 2 **.**Modelling domain and the simulation nested grids

The simulations with the RAMS model have been performed in a two-way nested grids configuration with three grids. The coarsest grid has a resolution of 40x40 horizontal grid points with a grid spacing of 24 km; the medium grid has a resolution of 82x70 horizontal grid points and a grid spacing of 6 km. Two inner grid were then considered: grid 3a, centered in the Province of Lecce with a resolution of 110x120 horizontal grid point with a mesh of 500m and grid 3b centered over a larger domain to include emissions outside of the area of study with 80x90 horizontal grid points and a mesh of 2km.
The vertical atmosphere is subdivided into 25 levels with different thicknesses, from 100 m near the surface, gradually stretching up to a maximum of 1000 m at the top. For initial and boundary conditions, the Isentropic Analysis System (ISAN) package (the module of RAMS for the generation of data analyses) is used. Initially, analyzed fields are based on the ECMWF (European Centre Medium Weather forecast) grid datasets. Every 6 hours, the lateral and the top boundary conditions are updated in the coarsest grid, by using the ECMWF grid datasets. Horizontal domains and grid sizes have been designed taking into account both computational time limitations and the capability of the model to resolve essential mesoscale features. The source categories differ in terms of source characteristics (e.g. stack height, plume buoyancy etc), PCDD/F congener profile and particle size distribution. Dioxin emissions from combustion are found both in the vapour phase and adsorbed onto the surface of particulate matter, so the characteristic atmospheric travel distance will depend on their gas/particle partitioning, the particle size distribution for particulate and deposition characteristics of the gaseous and particulate congeners. Due to the lack of data of PCDD/F specific particle size distribution for the emission sources we adopted a two-step procedure according to Basham and Whitwell, 1999, Kaupp and McLachlan 1999, Lorber *et al.* 2000, Lohman and Seigneur, 2001; Shih *et al.* 2006; Wu *et al.* 2009). Firstly, the emitted amount of each group of congeners of PCDD/F was split into vapour and particle state, at a reference temperature of 20°C (see Table 2). This step allowed for an estimation of dioxin-specific particle-bound emission rates in g s^{-1}.

Table 2. Assumed particle/vapour partition for PCDD/F congeners

TCDD	PCDD	HXCDD	HPCDD	OCDD	TCDF	PCDF	HXCDF	HPCDF	OCDF
0.49	0.87	0.97	0.99	0.998	0.53	0.80	0.945	0.985	0.998

Then, the dispersion of the contaminated particles was computed according to particle size distribution assumption from the literature for each industrial plant type. Three different classes (ranges of particle sizes) were assumed, with different reference diameter and washout coefficient. Toxic substances were partitioned over the three classes at given percentage, as shown in Table 3. The dry deposition velocity was set at 0.46 cm/sec.

Table 3. Assumed particle size classes.

Class	Fraction mass	Diameter (μm)	Washout Coeff. (1/s mm hr^{-1})
Category 1 <2μm	88 %	1	0
Category 2 2-10 μm	9 %	6.78	0.0046
Category 3 > 10 μm	3 %	20.0	0.0066

RESULTS AND DISCUSSION

As stated above, deposition amount and spatial patterns depends highly on meteorology and precipitation. Figure 3 shows the relationship between averaged deposition over the samples, for each sampling monthly period and correspondent amount of precipitation recorded at the meteorological surface station close to S1.

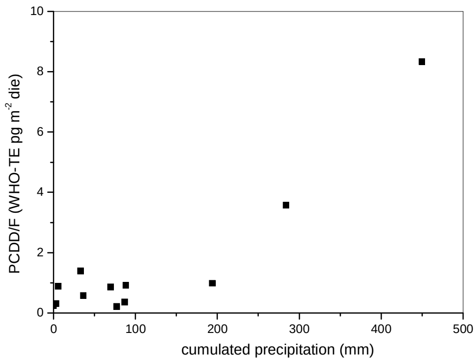

Figure 3.Average PCDD/F flux deposition over all the samples vs cumulated precipitation at site S1

Due to the sharp difference at low-no and at high precipitation amount regimes, two cases are here reported,. Case 1 (from 24 July 2008 to 22 August 2008) is characterised by absence of precipitation, and Case 2 (from 23 December 2008 to 22 January 2009), when about 450 mm of cumulated precipitation amount in one month was recorded.

Case 1. In this period, PCDD/F deposition fluxes recorded at all sample sites were lower than 0.05 WHO-TE pg/m^2 die except for the sample placed in site S1 that registered 2.73 PCDD/F WHO-TE pg/m^2 die.

Figure 4 shows the daily average deposition map for emission source I1, considering a PCDD/F emission rate of 0.1 ng-TEQ NM^{-3}. The modelling runs appear to have correctly identified the southern quadrants as being areas of highest impact. Table IV summarizes the predicted contribution from different sources for each sample. Because of the above mentioned uncertainties of emission I1 a range of values is indicated for this emission source. This accounts only for measured emission rates and not for the shut-down and startup periods. Results evidence as deposition fluxes associated to the other industrial sources are negligible.

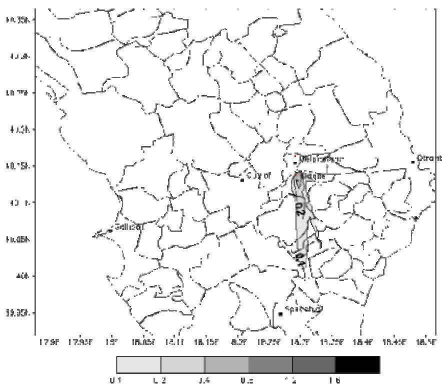

Figure 4. Simulated deposition fluxes of PCDD/F (WHO-TE pg m^{-2} die) for industrial source I1.

Table 4. Measured deposition data and predicted contribution for each emission source. Case 1

	Measured (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)
		I1	**I2**	**I3**	**I4**
S1	2.73	0.1-40	0.002	0.01	0.08
S2	0.02	0.005-2	0.002	0.01	0.08
S3	0.01	0.0001-0.04	0.002	0.00	0.07
S4	0.04	0.0001-0.04	0.01	0.01	0.08
S5	0.01	0.0001-0.04	0.0005	0.02	0.09
S6	0.00	0.0001-0.04	0.008	0.01	0.06
S7	0.01	0.0001-0.04	0.00001	0.02	0.2

Case 2. PCDD/F deposition fluxes were higher than 3 WHO-TE pg/m^2 die in most of samples, with values of 18.53 and 20.96 in S1 and S2 samples respectively. The daily average simulated deposition map for emission source I1 (Figure 5) shows how the wet deposition of particle-associated dioxins is confined to the immediate vicinity of the emission, leading to high deposition values.

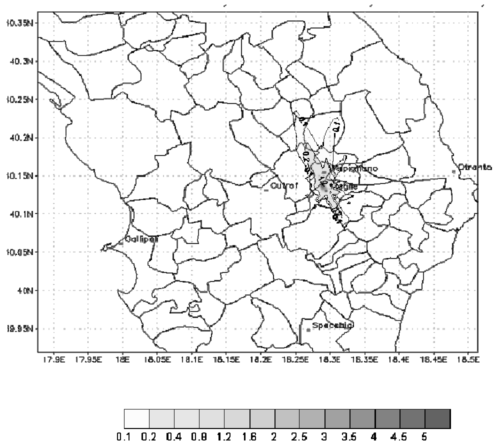

Figure 5. As in figure 4, but for case 2

Table 5 As in Table 4, but for case 2

	Measured (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)	Predicted (WHO-TE pg/m2 die)
		I1	I2	I3	I4
S1	19.13	2-16	0.004	0.02	0.08
S2	22.15	1-8	0.004	0.02	0.08
S3	5.71	0.01-0.08	0.004	0.01	0.06
S4	3.80	0.02-0.16	0.007	0.02	0.1
S5	3.52	0.01-0.08	0.005	0.002	0.3
S6	3.22	0.002 0.016	0.001	0.001	0.2
S7	2.57	0.002 0.016	0.004	0.005	0.4

Comparison between measurements and predictions indicate that in general the model is able to estimate realistically the geographical areas and to some extent the order of magnitude of the deposition of emitted toxic substances like PCDD/F (and PCB-dioxin like) from industrial stacks in different meteorological conditions. In particular, it is evident as the most relevant contribution to the measured PCDD/F deposition in S1 and S2 samples can be associated to the incinerator, as confirmed also by the congeners analysis (ARPA-Puglia, 2009). Sensitivity analysis (not shown here) was conducted to investigate the effect of various key model inputs on simulation results. Model simulations are very sensitive to the dry and wet deposition velocities highly influenced by particle size distributions. This implies that measurements of the size distribution of particulate PCDD/F are needed. Also, it would be essential to evaluate the model with experimental data. The design of a field program should include stack measurements of PCCD/F emissions including particle size distribution, ambient measurements of PCCD/F atmospheric concentrations upwind and downwind of the source with particle size distribution, deposition measurements and meteorological measurements near the ground and aloft.

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