H13-208

MONITORING POPS IN A COMPLEX ENVIRONMENT: THE ROLE OF MODELLING

Rossella Prandi[1], Silvio Di Savino[2], Enrico Ferrero[3] and Francesco Pavone[4]

[1]Simularia Srl, via Principe Tommaso 39, Torino - Italy
[2]Fondazione per l'Ambiente "T. Fenoglio", via G. Pomba 23, Torino – Italy
[3]Università del Piemonte Orientale, Dip. di Scienze e Tecnologie Avanzate, v. le Teresa Michel 11, Alessandria - Italy
[4]Provincia di Torino, Servizio Qualità dell'Aria e Risorse Energetiche, C.so Inghilterra 7, Torino - Italy

Abstract: Pollutants released by large industries are often a cause of major concern for local communities living nearby. Traditional monitoring consists of continuous emissions controlling systems (CEMS) and regular sampling of flue gas associated with monitoring stations positioned at best for checking on air quality where people reside. Sometimes a remote monitoring station is employed to set a background pollution reference value.
In the case of Persistent Organic Pollutants (POPs) this may not be the best planning strategy for monitoring exposure. In fact, direct exposure through inhalation forms just a minor contribution to the total people exposure. A much more relevant exposure is indirect, due to the ingestion of food, either vegetable or animal, which has been contaminated. For this reason, a great care should be put in placing monitoring instruments where deposition of POPs is larger, especially when industrial and rural areas are bordering.
As an example, we present the case of a steel foundry in an alpine valley, emitting PCDD/Fs and PCBs besides traditional air pollutants.
Using all the available data registered by the CEMS installed on the main chimney, hourly concentration and deposition fields have been obtained by running a one year long simulation with the three dimensional lagrangian model SPRAY, capable of simulating both dry and wet deposition.
Due to the complexity of the local topography, a 250m horizontal spatial resolution grid has been used. Meteorological fields have been obtained at the same resolution by a downscaling procedure with a mass-consistent model (SWIFT). The statistical analysis of the results shows the relevance of secondary fallout patterns in remote areas, where vegetables could be grown for local consumption or dairy cattle could frequently pasture, thus suggesting the need of specific monitoring for remote areas in order to attain a wider assessment of human exposure.

Key words: *Impact assessment, PCDD/Fs, PCBs.*

INTRODUCTION

In recent years, with a better knowledge of Persistent Organic Pollutants health effects, an increasingly greater effort has been devoted to the environmental impact assessment of sources emitting POPs.
POPs are highly toxic and persistent species which are ubiquitous in the environment. They are normally present at extremely low concentrations, since the atmosphere redistributes them in the environment. Being liposoluble, they tend to accumulate in fat. The principal route to human exposure is thus the ingestion of meat and dietary products, while through inhalation human exposure is almost negligible.
Great care should then be posed in the monitoring of areas where livestock are raised and graze. Wet and dry deposition on the ground is a key mechanism for POPs to enter in the food chain. In the case of toxic micropollutants, modelling of atmospheric dispersion should be coupled with a reliable modelling of the deposition fluxes in order to gain information on the amount of deposited substance and the extent of areas possibly contaminated.
In the following, we present the case of a steel foundry located in an alpine valley, which provides a good test case for assessing the capabilities of the three-dimensional lagrangian model SPRAY to correctly describe fall-out patterns of organic micropollutants both in terms of concentrations in the air and depositions on the ground. Numerical results, referred to 2005 meteorology and 2008 emissions, will be compared with values measured in 2008 by the monitoring network run by the local environmental agency (ARPA Piemonte).

DOMAIN AND EMISSION SOURCE DESCRIPTION

The industrial source under investigation is located in an alpine valley with a main east-west orientation following the hydrographic basin of a river of medium size.
Eastward, the valley opens up in a plain region, while the alpine mountain chain develops in the northern and western direction. The numerical simulation was conducted in a domain of size 23x12 km^2, on a grid with horizontal step size of 250 m.

The topography, shown in Figure 1, depicts the complexity of the domain, in which peaks as high as 2500 m are present. The vertical grid is formed by 25 levels up to 10800 m above ground.

Due to channelling, winds tend to follow the orientation of the valley with a clear diurnal/nocturnal cycle. During the night, cold breezes blow from all the western directions, while during the day warmer air blows from ESE, since, where the plant is situated, the valley is slightly curving in that direction.

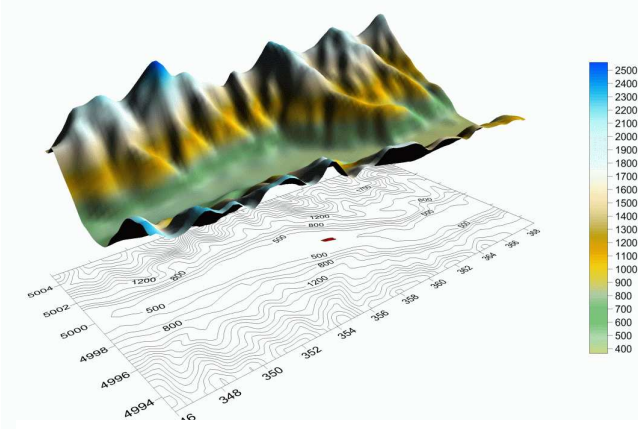

Figure 1: Topography of the area of interest. The red spot indicates the position of the industrial area.

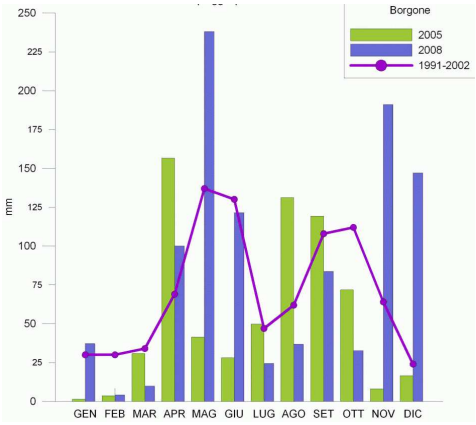

Figure 2: Monthly precipitation (mm) in the years 2005 and 2008 compared with the climatological mean 1991-2002.

For a realistic description of wet deposition, the code SPRAY needs to be fed with a two-dimensional precipitation field. In this case, we have used hourly precipitation measured in 2005 in a monitoring site less than 5 km away from the industrial area and we have assumed a homogeneous distribution of rain in the whole domain.
The comparison with the precipitation climatological mean (1991-2002), in Figure 2, shows that year 2005 was much drier than usual, especially during the winter months. On the contrary, year 2008, during which deposition measures were taken, was wetter than usual, especially in May, November and December.

For what concerns emissions, pollutants mass emission rates were defined after analyzing data registered by the CEM installed on the main stack (45 m tall with a 6.6 m diameter), that is hourly values for flue gas temperature and volumetric flow rate. Lacking a continuous sampling of PCDD/Fs and PCBs, six 2008 samples were considered in order to define an average scenario, in which mass emission rates are calculated using the mean concentration value of chimney flue gas samples, and a "worst case" scenario, in which mass emission rates are calculated using the maximum concentration value.
The foundry is working 7 days a week, 24 hours a day, except for 8 hours on Thursdays for maintenance, with a reduced activity. Finally, the industry stops for a three weeks summer break and a two weeks winter break, which were simulated with no emissions.

MODELLING AND RESULTS

In order to run the dispersion simulation, three dimensional meteorological fields have been derived with a 250 m horizontal resolution, through a downscaling procedure, from an original dataset at 1 km resolution. This dataset has been obtained by Arpa Piemonte with the same mass-consistent model Swift/Minerve (Aria Technologies, 2001) used in this study and it is based on local wind and temperature measures (ground and profiles) and ECMWF analysis.
The high resolution 8761 hourly meteorological fields (from 00 01/01/2005 to 00 01/01/2006) have then been processed by the code SurfPro (Silibello, 2006) in order to obtain two-dimensional turbulence scale parameters, employing topographic and land use data at the same spatial resolution. Hourly size-dependent deposition velocities were calculated following Seinfield and Pandis (1998). Geographic radiation was corrected using data from a local radiometer.
The three-dimensional lagrangian model SPRAY (Tinarelli, 2007) was employed to simulate the dispersion of pollutants coming from the foundry stack. The model describes the motion of pseudo-particles, each of them representing a certain amount of pollutant. Particles are transported by mean wind (read from an external file) and turbulence, whose effect result in a stochastic component in particle velocities. The stochastic term is calculated according to Thomson (1987) with third-order Gram-Charlier (Ferrero and Anfossi, 1998). A plume rise algorithm was activated in order to take into account buoyancy (Anfossi *et al.*, 1996). Ground level concentrations were calculated as hourly averages in 250x250x20 m^3 cells.
Dry deposition module is based on a removal mechanism derived from a solution of the Fokker-Planck equation (Boughton *et al.*, 1987), in which the probability of mass removal depends on the deposition velocity.
Wet deposition is modelled as a time-dependent exponential decay, with a decaying coefficient proportional to the precipitation rate through a species-dependent washout coefficient. No cloud height is taken into account.
When deposition modules are activated, masses removed from particles are cumulated into 250x250 m^2 cells below particle positions and hourly averages are calculated for dry and wet deposition fluxes.
Since precise measurements on granulometry and gaseous/vapour ratio of PCDD/Fs and PCBs emissions were missing, we have assumed that micropollutants are emitted in solid phase (Knight Merz, 2004), adsorbed on particles. We tested two particle sizes, fine (1 μm) and coarse (4 μm), while larger sizes are likely to be blocked by the baghouse filter.
Correspondent washout coefficients have been derived by the EMEP model (Simpson D. *et al.*, 2003).

In Figure 3 a comparison between fallout patterns of PCDD/Fs emitted from the main stack is reported for the average scenario: on the left, results refer to the assumption that dioxins are adsorbed on fine particles (1 μm), while coarser particles (4 μm) results are on the right. The yearly mean ground level concentration maps show a very similar outcome. Due to wind channelling, close to the emitting source there are two main spots, in the NW and SE directions, but the maximum value (14.8 fg m^{-3} for 1 μm size and 13.7 fg m^{-3} for 4 μm size) occurs on the mountain side 4 km eastward from the plant, because of nocturnal collisions of the plume on the sloping relief, an effect possibly emphasized by the model. On average, since coarser particulate tends to deposit more effectively, ground level concentrations of PCDD/Fs are higher for fine particles.
Dry deposition flux is always positive in the presence of pollutants: for this reason the shape of the yearly mean of dry deposition flux (expressed per unit surface and per day) mimics the shape of the yearly mean ground level concentration. The amount of deposited dioxins on a square meter per day is almost negligible in the case of fine particles, being at most 0.27 pg m^{-2} d^{-1} as yearly mean. Higher values take place for coarser particles reaching 3.15 pg m^{-2} d^{-1} on the mountain side, where the highest concentrations also occur.
In terms of absolute values, wet deposition fluxes are much more relevant, even if they are centered on the industrial area and have limited spatial extension. In the case of fine particles, the maximum value is 14.1 pg m^{-2} d^{-1} and values greater than 2 pg m^{-2} d^{-1} have only been obtained on a small region elongated 1 km westward from the plant.
The phenomenon is amplified in the case of coarse particulate, with a maximum value of 52.5 pg m^{-2} d^{-1} and values greater than 2 pg m^{-2} d^{-1} occurring on a region elongated 4 km westwards.

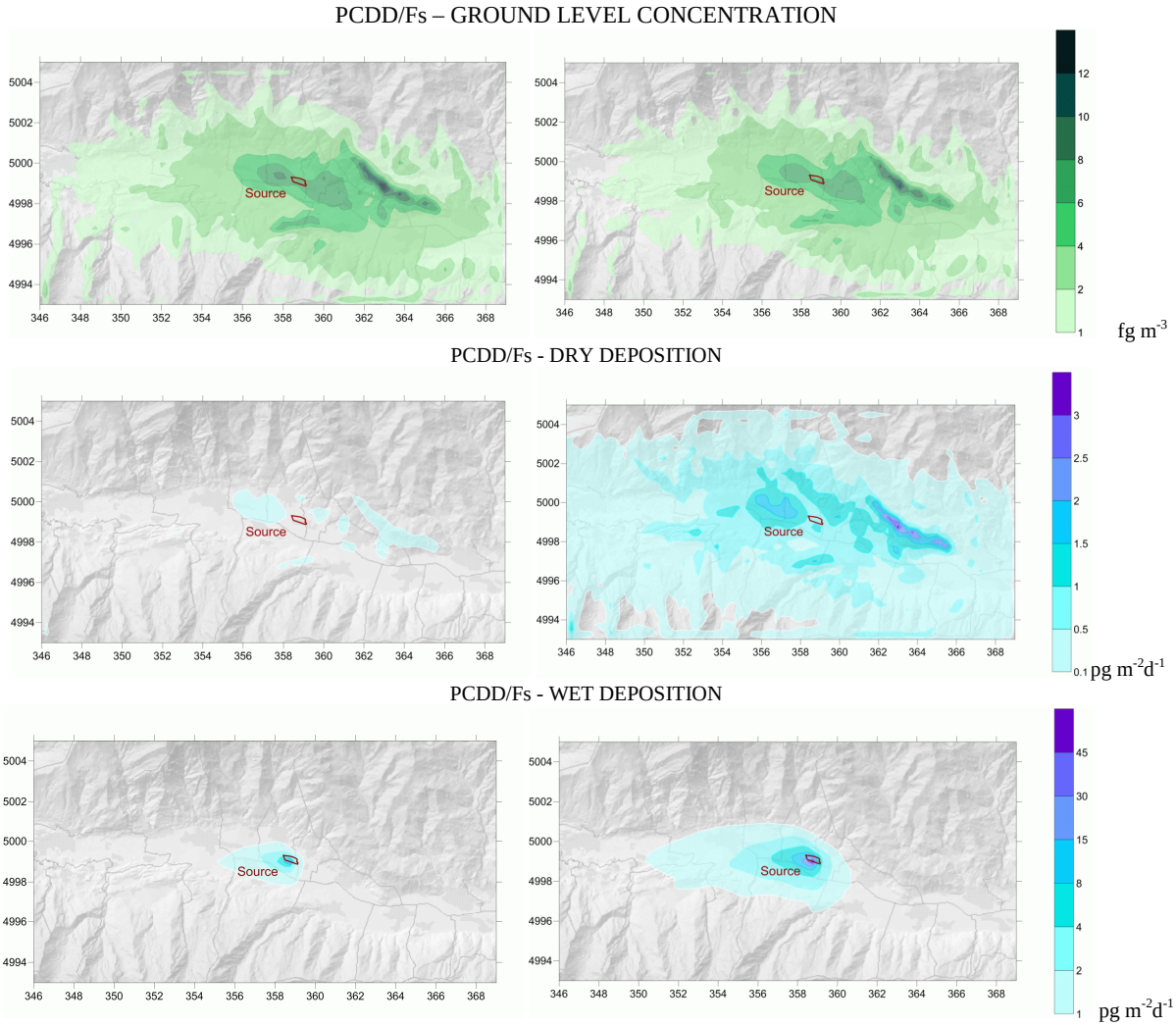

Figure 3: From top to bottom, yearly means for PCDD/Fs ground level concentrations, dry and wet depositions for the average scenario. On the left, results are obtained under the assumption that PCDD/Fs are adsorbed on particles of size 1 μm; on the right, the correspondent results for size 4 μm.

COMPARISON WITH EXPERIMENTAL DATA

When the industry was granted with the IPPC permit, the regional environment protection agency (ARPA Piemonte) began a monitoring campaign in order to assess the levels of toxic compounds in the surroundings. Both total depositions and air concentrations of PCDD/Fs and PCBs were measured in four sites near to the plant.

The siting choice favoured residential and industrial areas. In each site, a bulk collector was placed in order to obtain three monthly samples of total depositions during spring (March/April), summer (June/July) and fall (October/November) season. In the mean time, six fortnightly samples of air were collected by means of a high volume sampler (ECHO PUF). The mean of these measures will be considered as the average value in 2008 and will be compared with the results of the numerical simulation.

A word of caution before comparing experimental and numerical data can be helpful in reading the results.

First of all, the numerical simulation was driven by the 2005 meteorological fields, while measures refer to 2008. Even if some long period indicators like yearly means of concentration fields are just partially affected by this choice, we can expect some effects on wet deposition fields which depend on precipitation rate and amount. As already noticed, both in 2005 and 2008 precipitation monthly distribution showed marked differences with the climatological behaviour (see Figure 2). These differences may be amplified by the relatively short period of monitoring, on average covering 90 days for each site.

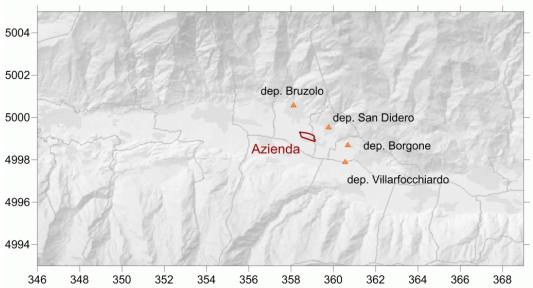

Figure 4: ARPA Piemonte monitoring sites in 2008.

Besides, the simulation takes into account just PCDD/Fs and PCBs emitted by the industrial chimney, while other minor sources could be present in the domain and outside the domain, contributing to an unknown background level. For example, in August, when the plant is stopped for the summer break, simulated fields are put to zero, while measures indicate values far from zero.

PCDD/Fs and PCBs concentrations

In Table the yearly mean concentration values for PCDD/Fs and PCBs calculated in the four monitoring sites, under the assumption of coarse and fine granulometry and average and worst scenario are compared with the experimental value in the correspondent site.

As already stated, the lagrangian model SPRAY computes *net* concentrations when wet and dry deposition modules are activated. Being coarse particles scavenged more effectively, concentrations values for 1 micron particle size are always larger than those for 4 micron particle size (while the opposite is true for the deposition values shown in the next paragraph).

Table 1: Comparison between the numerical results and measures of concentrations of PCDD/Fs and PCBs in the air in four monitoring sites. Numerical concentrations are calculated as yearly means, while experimental data refer to six fortnightly samples.

SITE	POLLUTANT	SIZE	AVERAGE SCENARIO	WORST CASE SCENARIO	MONITORING 2008
BORGONE	**PCDD/F** (fg-TEQ m^{-3})	1 μm	7.2	16.9	8.2
		4 μm	6.9	16.2	
	PCB (pg m^{-3})	1 μm	26.4	113.4	156.3
		4 μm	25.1	107.8	
BRUZOLO	**PCDD/F** (fg-TEQ m^{-3})	1 μm	3.7	8.7	8.5
		4 μm	3.4	8	
	PCB (pg m^{-3})	1 μm	13.6	58.4	110.6
		4 μm	12.5	53.7	
SAN DIDERO	**PCDD/F** (fg-TEQ m^{-3})	1 μm	5.4	12.7	10.4
		4 μm	5	11.7	
	PCB (pg m^{-3})	1 μm	19.9	85.5	97.4
		4 μm	18.5	79.4	
VILLAR FOCCHIARDO	**PCDD/F** (fg-TEQ m^{-3})	1 μm	5.9	13.8	5.6
		4 μm	5.6	13.1	
	PCB (pg m^{-3})	1 μm	21.7	93.2	89.7
		4 μm	20.6	88.5	

As for PCDD/F concentrations, in the average scenario values calculated both in Borgone and Villarfocchiardo are in very close agreement with measurements. Bruzolo and San Didero values are underestimated in the average scenario, but there is a good agreement with experimental data in the worst case scenario.

On the contrary, PCBs concentration values are considerably underestimated for all sites. In two cases, Borgone and Bruzolo, the underestimation persists even considering the worst case scenario. A reason for this poor agreement could be found in the high variability in the PCBs emissions, which depend on the type of ferrous waste sent to the furnace, or in the presence of a background, not taken into account in this study.

PCDD/Fs and PCBs bulk depositions

In Table the yearly mean deposition values (wet plus dry) for PCDD/Fs and PCBs calculated in the four monitoring sites, under the assumption of coarse and fine granulometry and average and worst scenario, are compared with the experimental value in the correspondent site.

Table 2: Comparison between the numerical results and measures of total (wet and dry) depositions of PCDD/Fs and PCBs in four monitoring sites. Numerical depositions are calculated as yearly means, while experimental data refer to three monthly samples.

SITE	POLLUTANT	SIZE	AVERAGE SCENARIO	WORST CASE SCENARIO	MONITORING 2008
BORGONE	**PCDD/F** (pg-TEQ $m^{-2}d^{-1}$)	1 μm	0.5	1.2	1.1
		4 μm	2	4.7	
	PCB (ng $m^{-2}d^{-1}$)	1 μm	1.9	8.2	11.4
		4 μm	7.4	32	
BRUZOLO	**PCDD/F** (pg-TEQ $m^{-2}d^{-1}$)	1 μm	0.6	1.5	1.3
		4 μm	2.4	5.6	
	PCB (ng $m^{-2}d^{-1}$)	1 μm	2.3	9.9	6.8
		4 μm	8.9	38	
SAN DIDERO	**PCDD/F** (pg-TEQ $m^{-2}d^{-1}$)	1 μm	0.7	1.7	2.3
		4 μm	2.9	6.8	
	PCB (ng $m^{-2}d^{-1}$)	1 μm	2.6	11	14
		4 μm	11	47	
VILLAR FOCCHIARDO	**PCDD/F** (pg-TEQ $m^{-2}d^{-1}$)	1 μm	0.5	1.1	2.5
		4 μm	1.7	4	
	PCB (ng $m^{-2}d^{-1}$)	1 μm	1.8	7.7	10.2
		4 μm	6.3	27	

As for PCDD/F depositions, the experimental value is intermediate between the fine and coarse values in the average scenario. This result seems to support the hypothesis that micropollutants are adsorbed on particles of different sizes.
In the case of Villarfocchiardo, numerically estimated PCDD/F bulk deposition is much lower than the observed one, even considering the coarse fraction. It's worth noticing, though, that this may be due to the relatively short monitoring period, since in Villarfocchiardo site both the highest deposition value and the lowest concentration value for dioxins and furans are measured.
Finally, an overall underestimation affects the PCB deposition values when compared with the experimental values, a result which strengthens what has already been commented for PCB concentrations.

CONCLUSIONS

In this paper we have described the results of a one year long numerical simulation aimed at defining fallout patterns of toxic organic micropollutants (PCDD/Fs, PCBs) emitted by a steel foundry in an alpine valley.
The topographic complexity of the area and the frequency of breezes make unavoidable the use of a three-dimensional non stationary model to correctly simulate the pollutants dispersion in the atmosphere. The relevant features of the fallout patterns suggest the need of additional monitoring far from urbanized areas, possibly in pasture land where deposition is high.
The comparison with experimental data shows an overall good agreement both for PCDD/Fs concentrations and depositions, even if a supplementary numerical simulation driven by 2008 meteorology would allow a more precise comparison on correspondent time periods.
As for PCBs, further investigation is needed to understand the causes for the underestimation found both in concentrations and depositions, by checking on local activities, by sampling more frequently the industry flue gas and by defining a background level of PCBs concentrations in the area.
Some conclusions can be drawn regarding SPRAY model improvements as well. To fully capture the variety of substances involved, the SPRAY deposition module should be enriched with a more detailed description of wet deposition, capable of taking into account a mixture of particle sizes with different scavenging coefficients, up to ultrafine particles.
Being PCDD/Fs and PCBs mainly adsorbed on particulate matter, a realistic estimate of their concentration in the air requires a better modelling of the resuspension of particles, a physical mechanism of relevance also in the evaluation of PM_{10} and $PM_{2.5}$ concentrations.
Eventually, another aspect, which may be relevant for a better estimate of the environmental impact of industries emitting dioxins, furans and PCBs, is the description of the transition between vapour and solid phase, since dioxins emitted in vapour phase are thought to condense in solid phase depending on ambient temperature, a phenomenon with a marked seasonal variability.

ACKNOWLEDGMENTS

The authors would like to thank ARPA Piemonte (Area Previsione e Monitoraggio Ambientale and Polo Microinquinanti) for the original dataset of meteorological fields and for the set of experimental data collected in 2008.
Useful comments and essential suggestions were provided by G. Tinarelli (Arianet Srl), E. Bertolo (Provincia di Torino) and Prof. G. Genon (Politecnico di Torino and Fondazione per l'Ambiente "T. Fenoglio").

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