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NEAR SOURCE DEPOSITION OF DIOXINS DURING A SNOWSTORM

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Abstract: A field observation is reported of scavenging by snow of dioxins containing particles released by a single point source.
In the Flemish region of Belgium, guideline values for monthly depositionof dioxins range between 6 to26 pg TEQ/m².day. Three deposition gauges are located near a sintering plant. In autumn 2008, dioxin deposition wasmeasured as 19 and 29 pg TEQ/m².day in two of the gauges and 485 pg/m².day in the third gauge. As the congeners profile of the high deposition value matched the congeners profile of the sinteringplant plume, the hypothesis of any other contributing dioxin source in the vicinity of the third gauge could be excluded.
The hypothesis of a very high incidental dioxin emission, when the wind blew straight from the sintering plant to the third gauge, was also rejected after thorough investigation of the real-time monitored working conditions of the sintering plantand because hypothetical worst emission case modelling with meteorological data could not explain the measured high deposition value. The focus then shifted to the meteorological conditions during the deposition measurement. An hour by hour analysis revealed that during a 3 hour long snow storm, the plume of the sintering plant was blown straight towards the third gauge. Next, two mechanisms were formulated by which snow could lead to high deposition. 1) The air, enclosed during the formation of snowflakes, carries high concentrations of dioxins from the plume to the ground. 2) During the fall from cloud basis to the ground, 'dry' deposition on the fractal surface of the snowflakes took place. The mathematical model for both mechanisms is an integration of the bi-gaussian transport and diffusion equation along the trajectory of a snowflake ending in the deposition gauge. This model showed that the first mechanism cannot explain the increased deposition observed.The second snow hypothesis can explain the observed increase. For this, a snowflake of 2 x 2 x 2 cmshould have a fractal area for deposition 25 times larger than the area of that cube. By the same parameterisation, it follows that all dioxins emitted by the sintering plume during the snow storm were brought to the ground within 5 to 8 km from the source.

Key words: *dioxin deposition, snowflakes, near source scavenging*

INTRODUCTION

In late autumn 2008, an extremely high monthly dioxin deposition was measured by the Flemish Environmental Agency (VMM)in the neighbourhood of a sintering plant. This high value (485 pg TEQ/m².day) was found in one the three deposition gauges located near the sintering plant, while the two other gauges had 19 and 29 pg TEQ/m².day, which are 'normal' values in the time-series of measurements since 1990. The Environmental Inspectorate Division (EID) of the Flemish Government was alerted to find quickly the source and the cause of the extremely high deposition. An initial investigation of stack emission concentrations data of the sintering plant, meteorological data and congener profiles of dioxins in emission and deposition, led to more questions than answers. EID asked VITO whether they could give a plausible science based explanation for this high deposition value. In this paper, we give an account of the investigations done to explain this high deposition.

LEGAL CONTEXT

As an aside, within the current environmental legislation in Flanders, this high deposition measured could have important consequences for the sintering plant. Relevant details of this legislation are:
Legislation: in the Flemish region, the general and sector-related environmental conditions for industrial activities are integrated in Vlarem II (1995), which is an implementing order of the 1985 Environmental Licence Decree. The Flemish environmental legislation is based upon the principle of prevention of pollution, nuisance and damage. Vlarem II contains a legally binding PCDD/F emission limit value for (biomass)waste incinerators inclusive biomass waste, brickworks, oil refineries, crematories, ferrous and non-ferrous metals plants and iron sintering plants. The emission limit value for sintering plants is 2,5 ng TEQ/Nm3 calculated for an oxygen volume in the flue gases of 16%. Besides that, Vlarem also contains a guideline emission value of 0,4 ng TEQ/Nm3 for sintering plants.
Inspection and law enforcement: the Environmental Inspectorate Division (EID) of the Flemish Government is responsible for the enforcement of the environmental health legislation. For air pollution control, the findings of the inspectors are generally based on the results of emission measurements, that have to be performed by officially recognised labs. If necessary, the inspectors of the EID can decide to take measures in the field of criminal and/or administrative law. They always make an official report of the legal infringements to the Public Prosecutor and they can give exhortations. If needed, they can take coercive measures, even leading to closing-down of the plant.
Monitoring: the Flemish Environmental Agency (VMM) is responsible for monitoring the environmental levels of PCDD/F. It has a deposition measurement programme at some 70 locations throughout the region. Guideline values for monthly deposition of dioxins of 6 pg TEQ/m².day (moderately high) and 26 pg TEQ/m².day (high) are commonly used, although not legally binding.

DATA AND FACTS

Figure 1 shows the location of the sintering plant and the three deposition gauges around it. The 60 m factory stack releases 444.4 Nm³/s process gas at a temperature of 130 °C. A local meteorological tower, 30 m high, provides local wind data. According to the Briggs plume rise formulae, this plume reaches an effective height of 185 m when wind speed measured at 30 m above the ground is 9 m/s. The deposition gauges are situated at 2.5 km, 3.5 km and 4.6 km north-east of the factory so that they monitor the plume during the dominant south-western winds. Distance between the gauges is 1.5 km to 2 km. This is slightly more than the width of a bi-Gaussian plume that originates at the factory. The ground level concentration profile due to such a plume (centre line plus/minus three times the horizontal dispersion parameter $\sigma_y(x)$) is shown in Figure 1.

QUESTIONS AND MORE QUESTIONS

Just natural variability?

Dioxins deposition around the factory has been monitored since 1990. The depositions found are: Site 1:9.5±3.9 pg TEQ/m².day, Site 2: 13.2±9.0 pg TEQ/m².day and Site 3: 6.9±2.4 pg TEQ/m².day. Given this long record of observations, the probability that a deposition of 485 pg TEQ/m².day in Site 1 could occur, due to normal variability of factory and meteorological conditions during the spring and autumn measuring campaigns, is, assuming a log-normal distribution, 1 upon $2x10^{17}$.

Not continuous over space

Figure 19 shows the highest monthly dioxins deposition pattern one could expect to happen if the sintering plant had a constant emission. The maximum deposition is 106 pg TEQ/m².day. It was calculated with the emissions that would occur if there were two sintering facilities working all month long without any gas cleaning. The deposition field is calculated using the IFDM transport and dispersion model. The wind data used were the most unfavourable wind conditions observed within a (moving) 30-days period during 11 years; thus all other periods would have given a lower deposition. But there are important differences between de deposition patterns in Figures 1 and 2. Assuming very high emissions all month long (Figure 2) would result in high deposition in all three gauges, and not only in one gauge.

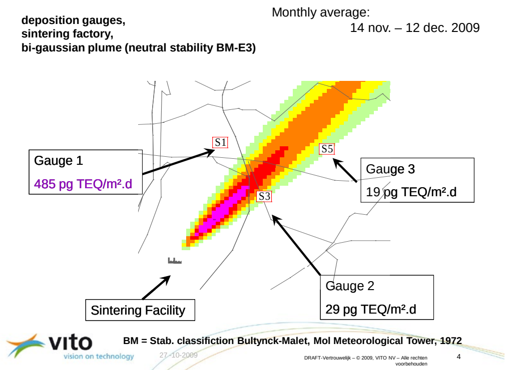

Figure 18: Sintering plant, measured dioxins deposition in gauges S1, S2 and S3 and ground-level concentration profile under the plume axis ± 3 horizontal standard deviation $\sigma_y(x)$ during the 23 November snow storm conditions.

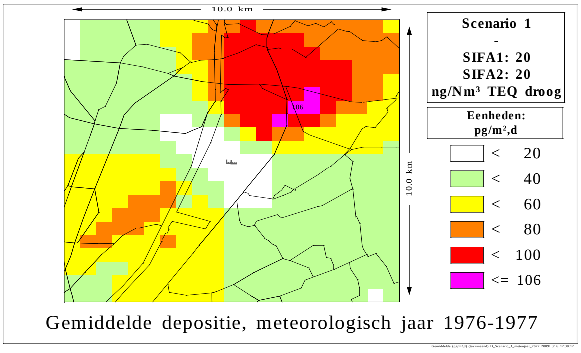

Figure 19: Monthly deposition if two sintering facilities worked all month long without flue gas cleaning.

The congener mystery

Investigation of the congener profile of the dioxins found in the gauges produced another mystery. The congener profile of the high deposition value is shown on the top-left graph in Figure 20. The indices on the x-axes on Figure 20 refer to the following congeners:

1	2,3,7,8-TCDD	**7**	OCDD	**13**	2,3,4,6,7,8-HxCDF
2	1,2,3,7,8-PeCDD	**8**	2,3,7,8-TCDF	**14**	1,2,3,7,8,9-HxCDF
3	1,2,3,4,7,8-HxCDD	**9**	1,2,3,7,8-PeCDF	**15**	1,2,3,4,6,7,8-HpCDF
4	1,2,3,6,7,8-HxCDD	**10**	2,3,4,7,8-PeCDF	**16**	1,2,3,4,7,8,9-HpCDF
5	1,2,3,7,8,9-HxCDD	**11**	1,2,3,4,7,8-HxCDF	**17**	OCDF
6	1,2,3,4,6,7,8-HpCDD	**12**	1,2,3,6,7,8-HxCDF		

This congener profile is almost identical to the congener profiles found in the sintering stack (all figures on the right side of Figure 20) in December 2008. Furthermore all of these profiles show a peak for congener 15.

The congener profile in the two gauges with a low (normal) deposition (Left middle and Left bottom graph in Figure 20) show a different pattern, with a peak at congener 7. (This shows that the sintering factory is not the sole contributor to the deposition in these gauges. In fact, house heating and open fires are other potential sources of dioxins.)

Paradox

From the congener profiles, it is clear that the high deposition found has something to do with the sintering factory plume. But all other circumstantial evidence, such as the low deposition in the two other gauges, the long time series of deposition measurements and also the real-time recordings of the particulate matter emitted by the sintering plant stack do not reveal an extreme high emission by the plant.

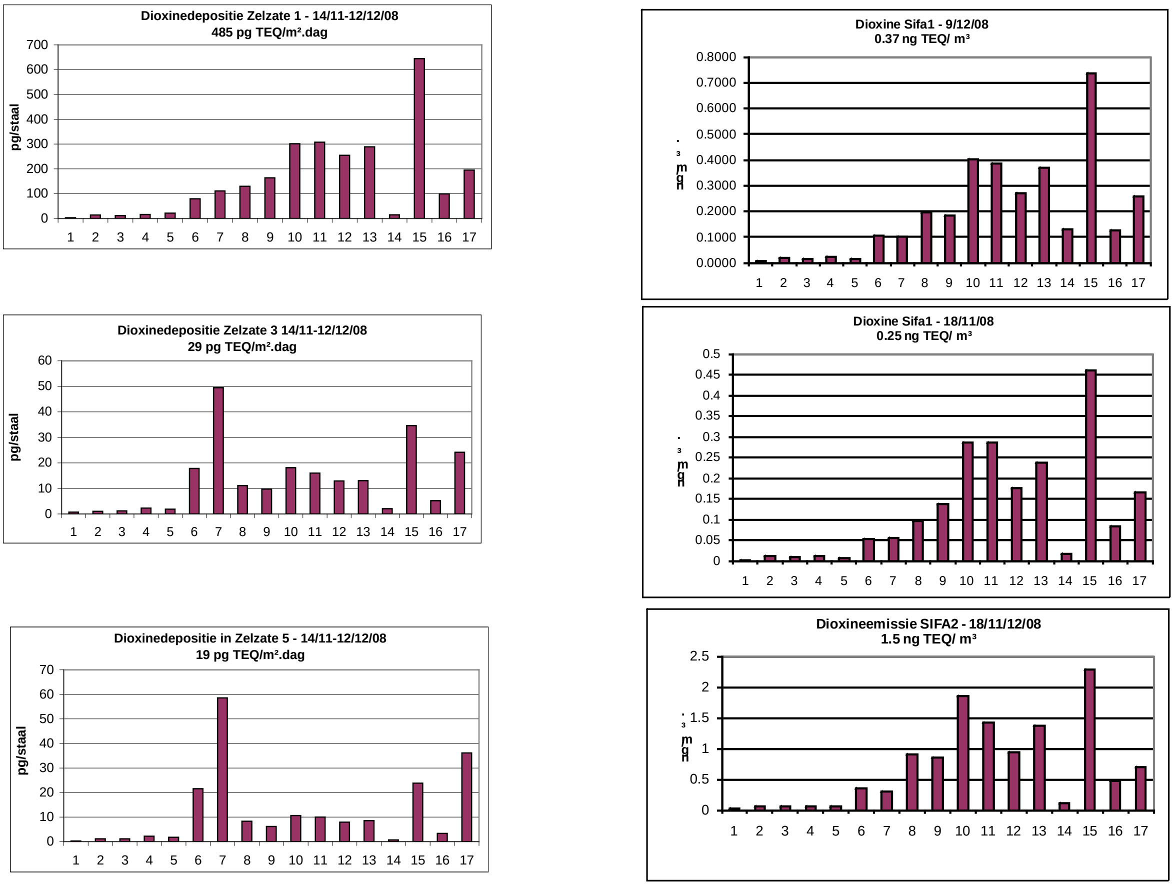

Figure 20: Dioxins congener profiles in the depositions gauges (left) and in the stacks of the sintering facility (right)

Figure 21: Left: first 4 iterations of the Koch snowflake curve. The length of this curve is (4/3)N, where N is the number of iterations.. Right: Diffusion limited aggregation snow/fern like structure. (http://classes.yale.edu/fractals/panorama/Physics/DLA/DLA.html)

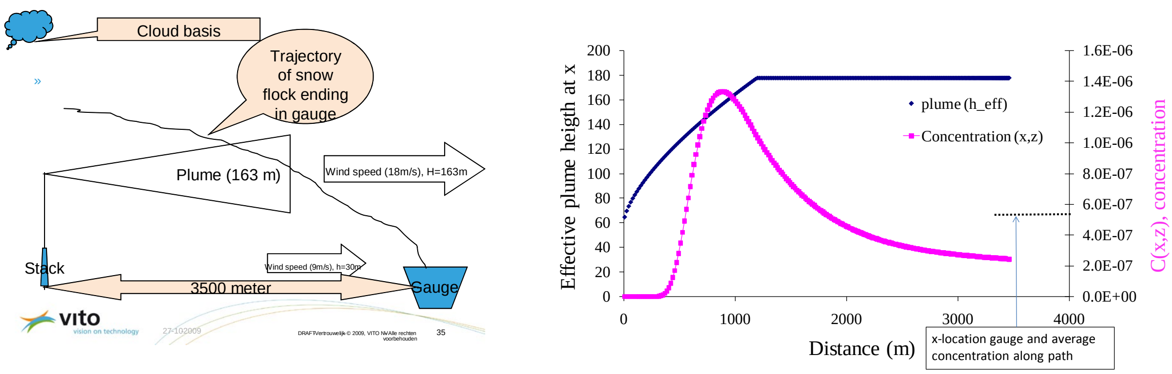

Figure 22: Left: schematic representation snowflakes falling through the plume into the deposition gauge.
Right: Effective height of plume axis and concentration C(x(t),z(t)) along the path of a falling snowflake from cloud till the deposition gauge through the plume of an unit emission ($1\ s^{-1}$).

The only way out is to assume that something very anomalous and of short duration, either in the sintering process or in the meteorological conditions, caused the very high and very localized deposition.

The answer
Concerning the sintering process, continuous measurements of PM10 emission and two-weekly determination of PCDD/F concentration in the flue gas did not reveal any anomaly.

The only abnormal meteorological event during the monitoring period was a snow storm. Heavy snowfall has been exceptional in Northern Belgium over the last 40 years, so the time series of monthly deposition values measured at the beginning and the end of the vegetation growing season might not have reflected the influence of snow yet. Furthermore, it is uncommon to have southwesterly winds in Belgium during a snow storm.

During this 3 hours lasting snow storm, the wind blew all the time straight from the sinter plant to the gauge where the high deposition value was found. Ambient temperature was 3 to 5 °C above zero, windspeed (at 30 m) was 10 m/s, snow cover thickness was 15 cm equal to 12.3 liter per square meter of melt water or 4100 g H_2O/m².hour. Cloud basis height was 224 m. The meteorological data is provided by the VMM except for the cloud basis height for which the data originates from the Antwerp-Deurne airport.

SNOW
Snow is known to be an efficient scavenger for many substances, especially hydrophobic ones (*Kyrö et.al*., 2009, *Lei and Wania*, 2004, Wania et.al., 1998). The most beautiful star-like snowflakes start as ice-crystals in clouds of -12 °C to -16°C. Below the cloud basis, these large snow crystals collide and stick together into snowflakes. The largest snowflakes are formed when ambient temperature is 3-5°C above freezing point (*Libbrecht K.G.* ,1999, 2005). The following properties of snow, taken from (*Rasmussen et.al.,* 1988)are used in the computations that follow:

- the density of falling snow is one tenth of that of fallen snow;
- the terminal fall speed of large snowflakes is 1 m/s;
- the density of large falling snowflakes is between 0.01 g/cm³ and 0.005 g/cm³;
- large snowflakes have a diameter of up to 2 cm (although individual flakes can be much larger).

As many natural shapes, snowflakes have a fractal structure, as do fern leaves and coastal lines. The best known mathematical model for a snowflake-like fractal is the Koch-curve (Fig. 4, left). It is constructed iteratively by replacing the inner third of each side by a triangle, (which creates more sides), and repeating this substitution on the sides of the resulting curve. The length (circumference) of this curve grows exponentially with the number of iterations. The Koch curve has a relatively round form. The growth of a snow crystal is better reproduced by diffusion limited aggregation (Fig. 4, right). As snowflakes are three-dimensional shapes, their outside area can be approximated roughly as the product of a circumference and a thickness. As the circumference is a fractal, this area can grow very large for even small snowflakes.

NUMERICAL ASSESSMENTS
Required deposition: A monthly deposition value of 485 pg TEQ/m².day means a deposition of 14 550 pg TEQ/m² over that month. If this mass was realized by deposition during the snow storm, then deposition during the snow storm must have been 4850 TEQ pg/m².hour.

Source term: Emission take place through a 60 m high stack. The plume has an heat content 72 MW. The volumetric flow is 1.6 x 10^6 Nm³/h with 1.95 ng TEQ/Nm³. Dispersion calculations are done with the formulas of *IFDM* (2006).

Concentration along snowflake path: Fig. 5 (left) shows the path of a snowflake through the plume. Fig.5 (right) shows the plume axis height (left vertical axis) and the changing dioxin concentration around the falling snowflake. The independent variable is the time, which is zero when the plume leaves the cloud basis, and 224 seconds (see later) when it falls in the gauge. The left drawing in Fig. 5 shows that the position of the falling snowflake, which we denote by x(t) and h(t), changes during the fall. x(t) is changed by the (height dependent) wind speed, h(t) by the (constant) falling speed. The concentration around the snowflake is zero when the plume is still in the cloud (and upwind of the source). Between cloud basis and plume axis, the concentration increases. Between plume axis and the ground, the concentration decreases again. At x(t) equal to 3500 m, the snowflake falls in the gauge, the concentration at ground-level being 2.0E-07/m³. For the following concentrations, we only need the average dioxin concentration$C_{average}$along the path of a snow flake that falls in the gauge. This concentration is 357 fg TEQ/m³.

Hypotheses: If the high deposition value is caused by the three hour heavy snow storm, one of the two following mechanisms should formally allow to compute the measured deposition value:

1. during coagulation, material in the plume is enclosed in the snowflakes. The pollutant mass in this enclosed air caused the high deposition;
2. deposition in the gauge is the result of dry deposition of dioxins on the fractal area of the snowflakes during their fall.

For the first hypothesis, the snow cover after the storm was 15 cm. This is 5 cm per hour, and corresponds to 0.05 m^3 fallen snow per square meter.The density of falling snow is one tenth of that of fallen snow. Consequently, snowflakes have carried down 0.5 m^3 of air, most of it is enclosed during the coagulation process while falling from cloud basis to the ground.
The amount of dioxins included in this volume is 178.5 fg TEQ (One halve m^3 contains 50 % of what is in one m^3.). This contribution is negligible, as 4850 pg TEQ/m^2h is required.

For the second hypothesis, we use the results of *Vanderborght e.a*., (1983) for the deposition of condensation aerosol near heavy metal industries: up to several kilometres from the source, the (dioxin-carrying) condensation aerosol is hydrophobic and has a dry deposition speed v_d = 0.01 m/s for deposition in an gauge. Deposition (mass) on a single snowflake that ends in the gauge is given by in integration of Area* v_d*C(x(t),0,z(t)) over the trajectory of the snowflake. With a terminal fall speed of large snowflakes of 1 m/s and with the cloud basis at 224 m, it takes 224 seconds for a snowflake to travel the distance from the cloud basis to the ground. We first neglect the fractal nature of snowflakes and simplify them to be cubes with edges of 2 cm, their outer surface being 24 cm^2 or 0.0024 m^2. Deposition on one such snowflake that falls in the gauge is:

Time_of_fall * area_of_snowflake * dry_deposition_speed * average concentration –or-
224 [s] * 0.0024 [m^2/flake] * 0.01 [m/s] * 357 [fg TEQ/m^3] = 1.92 fg TEQ

The number of snowflakes per m^2 and per hour falling in the gauge is:

1. using a density of 0.005 g/cm^3, the weight of a single cubic snowflake with edges of 2 cm is 0.04 g;
2. in order to have an hourly precipitation of 4100 g/m^2, it takes 102 500 snowflakes of 0.04 g each to fall;
3. the total area of these 102 500 snowflakes is 246 m^2.

So, in one hour, with 102 500 snowflakes falling per square meter, this gives 196.7 pg TEQ/m^2.hour

This deposition was assumed to take place on the sides of a falling 2x2x2cm^3 cubic snowflake. However, snowflakes have a fractal surface. In order to obtain the required hourly deposition of 4850 pg TEQ/m^2.hour, a fractal surface (suitable for dry deposition) 25 times larger than the smooth surface of a mathematical cube is required. This required factor of 25 seems to be no problem, given the complex shape of large snowflakes.

Scavenging of material in the plume: Snowflakes that hit the ground at distances shorter than the deposition gauge will have removed some material from the plume, which is then no longer available for deposition by snowflakes that fall into the gauge. Taking this plume depletion into account will alter the above computed fractal area, without invalidating hypothesis 2. Performing further quantification of the scavenging of dioxins during the snow storm shows that most of the dioxins are removed from the plume within 5 to 8 km from the source.

CONCLUSIONS

An extremely high dioxin deposition value, measured in the neighbourhood of a sintering plant, puzzled the Environmental Inspectorate Division of the Flemish government: while congener profiles clearly indicated that the cause of the high deposition was to be found in the sintering process, no evidence was found for something anomalous in the sintering process and measured PCDD/F emission concentrations were below the emission limit value. VITO was requested to investigate the possible causes. It was revealed and proved that a brief, heavy snowstorm, with wind directed straight from the sintering factory to the deposition gauge, scavenged the dioxins from the plume of the sintering plant to such an extent as to cause the measured high deposition value. Convinced by this snowstorm explanation and finding no infringement of emission limit values nor other license conditions by the sintering plant, the Environmental Inspectorate Division was able to close this case. Additional measurements by the Belgian Federal Agency for the Safety of the Food Chain (FAVV) showed no contamination of the food chain.

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