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DRY DEPOSITION OF DIOXINS ON FALLING SNOW

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Abstract: A field observation is reported of dioxins containing particles scavenged by snowflakes.
In the Flemish region of Belgium, guideline values for monthly deposition of dioxins range between 6 pg TEQ/m² to 26 pg TEQ/m².day. Three deposition gauges are located near a sintering plant. In autumn 2008, dioxin deposition was measured 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 sintering plant plume, the hypothesis of any other 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 plant and 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 cm should 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, scavenging*

INTRODUCTION

Air quality management consists of environmental legislation, including (a) emission permit granting and air quality standards, (b) ambient air concentration and deposition monitoring and (c) prosecution of perpetrators.

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/Nm^3 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/Nm^3 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.

Co-operation and feed-back

Through mutual co-operation, there is a synergy between the authorities responsible for environmental enforcement (EID) and environmental monitoring (VMM). On the one hand, sampling locations for environmental monitoring are often chosen based on emission data, provided by the EID. On the other hand, unknown emission sources have been detected near sites of high deposition and thus subsequently are brought to the attention of the EID.

A very high dioxin deposition

In late autumn 2008, an extremely high dioxin deposition was measured in the neighbourhood of a sintering plant. Of the three deposition gauges located near the sintering plant, two of them showed 19 and 29 pg TEQ/m².day for monthly deposition of dioxins while at the third gauge 485 pg TEQ/m².day was measured. As dioxin deposition values in the vicinity of this plant were usually between 3 and 26 pg TEQ/m².day, the EID was alerted to quickly find the source and the cause of the extremely high deposition value at the third gauge. A quick initial investigation of data on stack emission concentrations of the sintering plant, meteorological data and congener profiles of dioxins in emission and deposition, led to questions more than answers. EID asked Vito whether they could give a plausible science based explanation for this high deposition value.

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 1 upon 2×10^{17}.

Not continuous over space

Figure 2 shows the highest monthly dioxin deposition pattern one could expect to happen. 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.

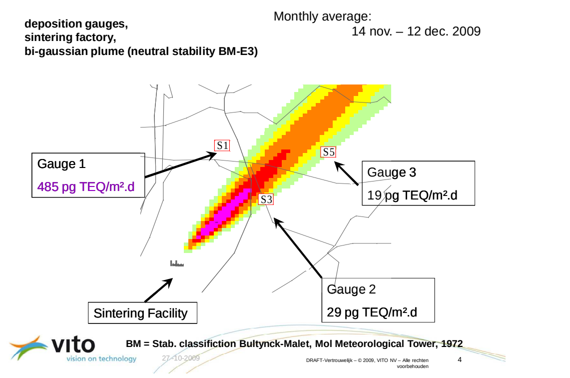

Figure 1: Sintering plant, measured dioxins deposition in gauges S1, S2 and S3 and ground-level concentration profile under the plume axis ± 3 horizontal standard deviation $\sigma_y(x)$ during the 23 November snow storm conditions.

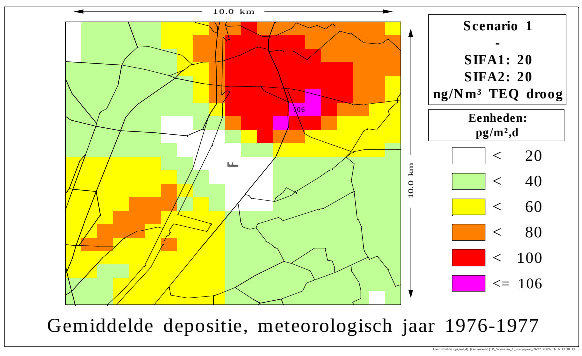

Figure 2: Monthly deposition if two sintering facilities worked all month long without flue gas cleaning.

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 3. The indices on the x-axes on Figure 3 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 3) 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 3) 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.)

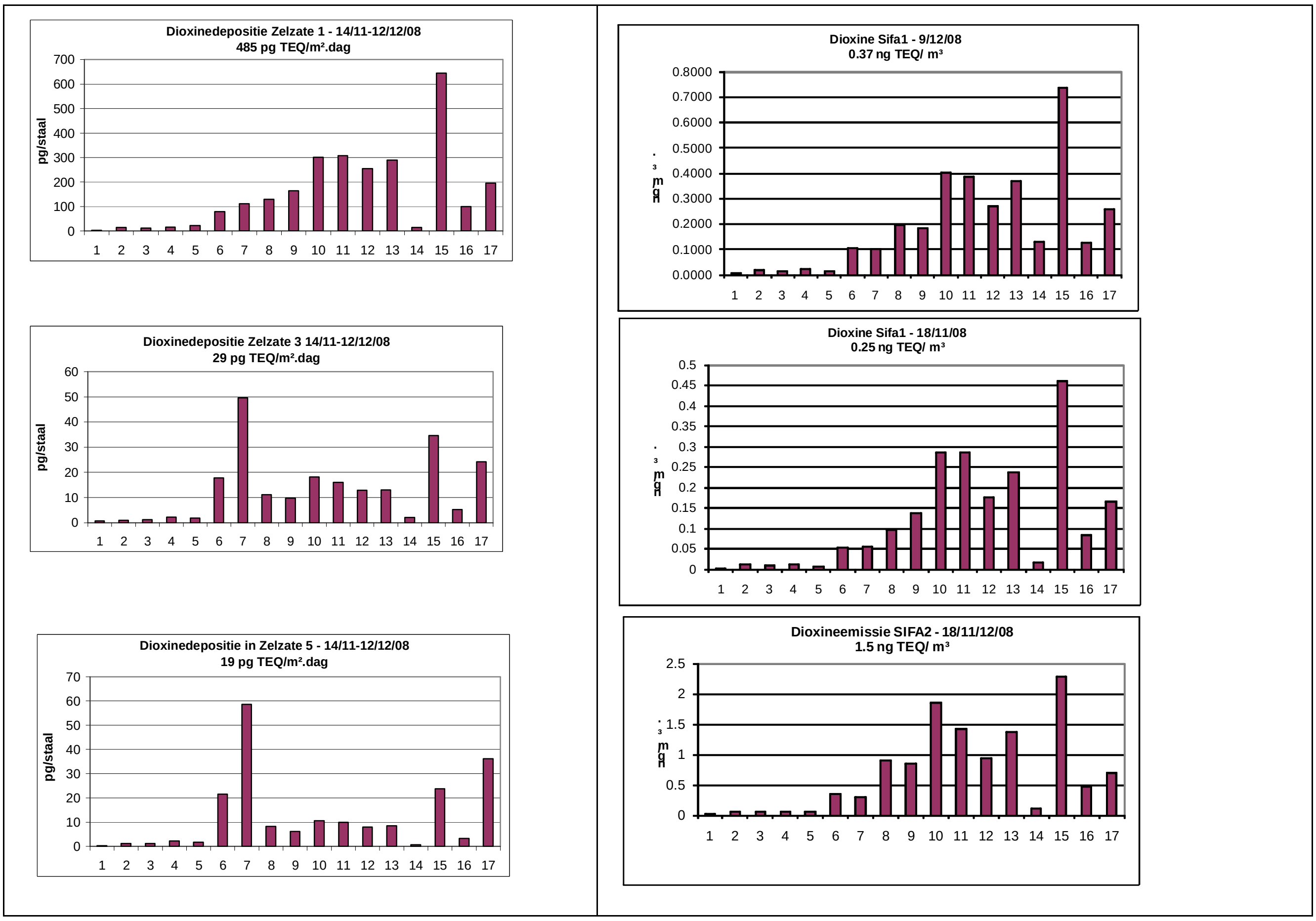

Figure 3: Dioxins congener profiles in the depositions gauges (left) and in the stacks of the sintering facility (right)

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 indicate it is not.

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

The answer

Concerning the sintering process, PCDD/F emission concentration in the flue gas of the sintering plant has been measured twice during the period of deposition measurement and did not reveal concentrations above the emission limit value.

The only abnormal meteorological event during the monitoring period was a snow storm lasting three hours, with winds (at 30 m) of 10 m/s which resulted in a blanket of snow 15 cm deep. Snowfall has become an exceptional event in Northern Belgium over the last 40 years. During the snow fall, ambient temperature was 3 to 5 °C above zero, resulting in large snowflakes.

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). Snow crystals are formed in cold clouds. Large snow crystals may collide and stick together into snowflakes. The most beautiful snowflakes start as ice-crystals in clouds of -12 °C to -16°C, and require an ambient temperature between cloud basis and the ground that is a few degrees Celsius above freezing point.

Like many natural shapes, snowflakes have a fractal structure. Some of the best known fractal shapes are fern leaves and coastal lines. The best known mathematical model for a snowflake-like fractal is the Koch-curve (Figure 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 (Figure 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.

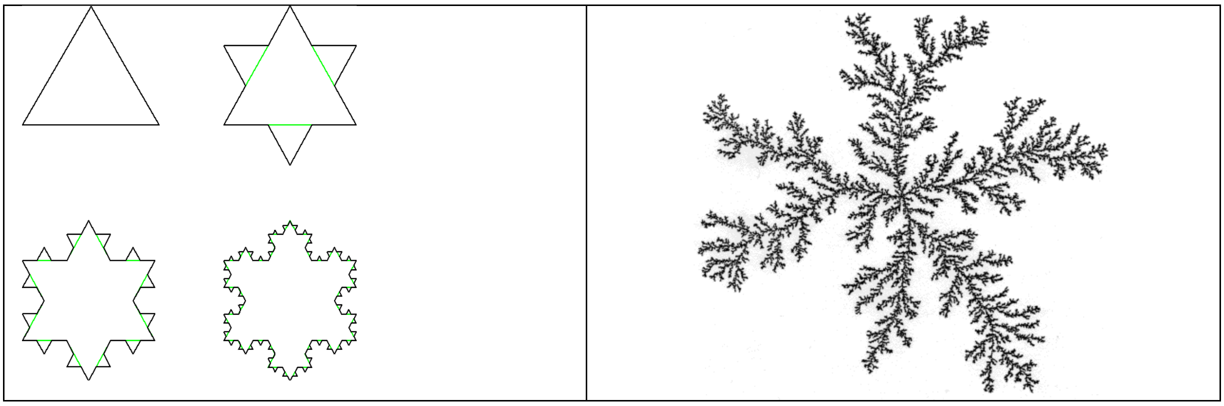

Figure 4: Left: first 4 iterations of the Koch snowflake curve. The length of this curve is $(4/3)^N$, where N is the number of iterations. Right: Diffusion limited aggregation snow/fern like structure. (http://classes.yale.edu/fractals/panorama/Physics/DLA/DLA.html)

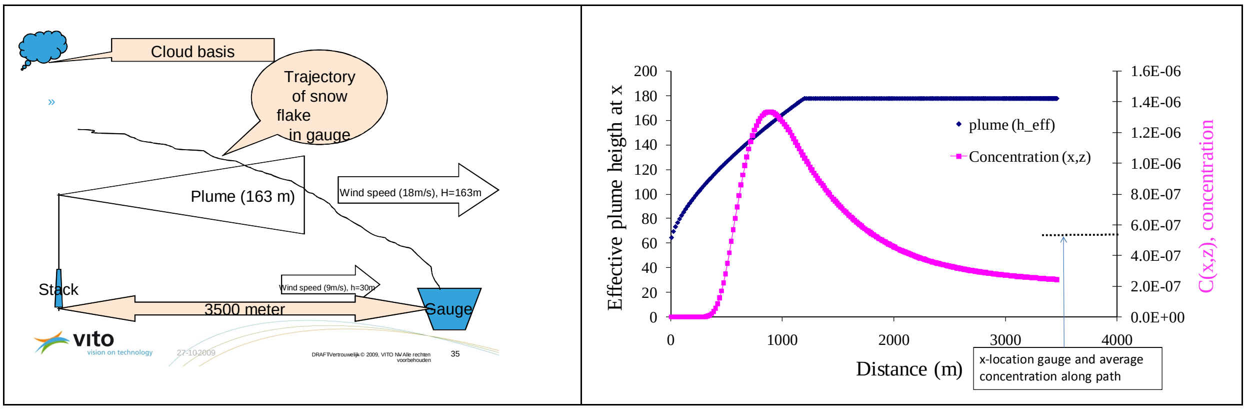

Figure 5: Left: schematic representation snowflakes falling through the plume into the deposition gauge.
Right: Effective height of plume axis and concentration C(x,z) along path of falling snowflake from cloud till deposition gauge through the plume of a unit emission (1 g/s).

NUMERICAL ASSESSMENTS

Could the three hour heavy snowstorm have been the cause of the high deposition value? This could be suspected by now or this could now be considered likely, but one may want to see some calculations that quantify the relation between emission, deposition and snow fall. Snow is a porous medium and air movements around and through fallen snow and falling snowflakes are complex.

The drawing on the left half of Figure 5 show some interesting geometric relations. Given the vertical wind speed profile, the trajectory of the snowflakes that fall into the gauge can be constructed on condition that the falling speed is known. In any case, these trajectories have to start in the cloud, high above the plume, and they have to cross that plume.

We found many interesting things about falling snowflakes and bulk properties of snow in Rasmussen *et al.* (1988). Coagulation of snowflakes takes place mainly between cloud basis and ground. The largest snowflakes are formed when the below cloud temperature is of 3 to 5°C. This was the case during the snow storm. In order to have some numerical quantification, we will investigate two hypotheses:

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

For both hypotheses, we need some estimation on the volume and number of the snowflakes.

Quantification of snow

1. The snow cover after the storm was 15 cm. This is 5 cm per hour, and corresponds to 0.05 m³ 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 m³ of air, most of it while falling from cloud basis to the ground;
2. Cloud basis for subsequent calculations is taken to be 224 m. The terminal fall speed of large snowflakes is 1 m/s. So, exposure time of a snowflake to the material in the plume between cloud basis and ground is 224 seconds;
3. Pluviometers reported a precipitation of 12.5 liter for the snow storm. Hence snow fall was equivalent to 4100 g H_20/m².h;
4. Assuming that the snowflakes were cubes with sides of 2 cm, their volume is 8 cm³;
5. The density of falling snowflakes this large is between 0.01 g/cm³ and 0.005 g/cm³;
6. Using a density of 0.005 g/cm³, the weight of a single snowflake is 0.04 g;

7. A cube has six sides, 4 cm² each. So a single snowflake has an area of 24 cm² or 0.0024 m²;
8. In order to have an hourly precipitation of 4100 g/m², it takes 102 500 snowflakes of 0.04 g each to fall;
9. The sum of the areas of these 102 500 snowflakes then is 246 m².

Concentration profile along the trajectory of the falling snowflake

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/m²h.

Concentration along snowflake path

The effective height of the plume (right half of Figure 5) is about 189 m. Using a dioxins emission halfway, the emission limit value and the guideline emission value (see legislation), the average concentration along the path of a snow flake whose trajectory ends in the gauge is 357 fg TEQ/m³.

For hypothesis 1, dioxins from half a cubic meter of air per hour is sampled from the plume towards the ground. The amount of dioxins included in this volume is 178 fg TEQ. This contribution is negligible, as 4850 pg TEQ is required.

For hypothesis 2, The amount of dioxins, collected by a single snowflake during its fall, is given by:

Time_of_fall * area_of_snowflake * dry_deposition_speed * average concentration –or-
`224 [s] * 0.0024 [m²/flake] * 0.01 [m/s] * 357 [fg TEQ/m³] = 1.92 fg TEQ`

So, in one hour, with 102 500 snowflakes falling per square meter, this gives 196.7 pg TEQ/m².hour

This deposition was assumed to take place on the sides of a 2x2x2cm cubic snowflake with a dry deposition velocity of 1 cm/s ([1]). However, snowflakes have a fractal area. In order to obtain –by hypothesis 2- the required hourly deposition of 4850 pg TEQ/m².hour, a fractal surface (suitable for dry deposition) that is 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, not any 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 investigated 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 licence 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.

REFERENCES

Kyrö, E.-M., Grönholm, T., Vuollekoski, H., Virkkula, A., Kulmala, M. & Laakso, L. 2009: Snow scavenging of ultrafine particles: field measurements and parameterization. Boreal Env. Res. **14**: 527–538.

Lei Y.D. and F. Wania , 2004: Is rain or snow a more efficient scavenger of organic chemicals? Atmospheric Environment, **38**, 3557-3571

Mitra S.K., Barth U. and H.R. Pruppacher, 1990: A laboratory study of the efficiency with which aerosol particles are scavenged by snow flakes, Atmospheric Environment. Part A. General Topics, Volume **24**, pp. 1247-1254

Rasmussen, R., J.Vivekanandan, J.Cole and E.Karplus, 1988: Theoretical Considerations in the Estimation of Snowfall Rate Using Visibility. The National Center for Atmospheric Research (Study for: Centre de développement des transports, Montreal)

B. Vanderborght, I. Mertens and J.G. Kretzschmar, 1983, Comparing the Calculated and Measured Aerosol Concentrations and Depositions around a Metallurgical Plant, Atm.Env. Vol. **17**, No. 9, 1687-1701.

Wania, F., Hoff, J.T., Jia, C.Q. and Mackay, D., 1998. The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. Environmental Pollution **102**, pp. 25–41.

[1] This value seems correct to predict the dry deposition in deposition gauges of process gasses from various industrials facilities. These value was proposed by Vanderborght *et al.*, 1983.