

## AIR EMISSIONS AND DIOXIN IN SOIL AND VEGETATION AROUND A METAL RECLAIMING PLANT IN DENMARK

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### Introduction

In October 2000 very high air emission concentrations of dioxins, 183 ng I-TEQ/Nm<sup>3</sup>, was measured at a metal reclaiming plant in Denmark. During the next months a new emission abatement system was installed decreasing emission concentrations to below the limit value of 0.1 ng I-TEQ/Nm<sup>3</sup>. No data on the emissions of dioxin from the plant exist prior to October 2000, and in order to evaluate the total long-term dioxin load on the plant surroundings, the dioxin content in 8 soil samples and 4 vegetation samples were investigated from 7 positions around the plant. First of all the objective was to find out if the surroundings had elevated concentrations of dioxin, and if so to clarify whether that could be related to the emission from this particular plant.

### Methods and Materials

The soil samples were taken following the "satellite method" – one sample from the centre and eight satellite samples, taken from points on a circle around the centre with a radius of 10 m. A 5 cm deep soil column was sampled in each point with the help of a high-grade steel tube with a diameter of 5 cm. The samples of vegetation were a collection of leaves found at the site. Such samples are suitable to detect newly deposited dioxin, whereas soil samples reflects longer term deposition.

A composite sample was build up from the nine single soil samples of each sampling site. After homogenisation an aliquot of the sample was analysed for dioxins according to VDI 3499. Quantitative determinations of PCDD/PCDF in various samples according to the isotope dilution method were carried out by means of 2,3,7,8-PCDD/PCDF substituted <sup>13</sup>C-UL internal standards for all toxic congeners. The sample was soxhlet extracted with toluene. Cleanup was done on multicolumn systems involving various kind of treated silica gel, aluminium oxide, carbon-on-fibre or carbon-on-celite. The final extract was reduced to dryness and dissolved in syringe standard. Determination was carried out by using an HRGC/HRMS combination with HP 5890 series II / VG-AutoSpec on DB 5 and SP2331 capillary columns. For each substance, two isotope masses were measured.

### Results and Discussion

The measured air emission concentrations from the secondary metal reclaiming plant are shown in Table 1. After discovering the very high emission in October, dioxin abatement was commissioned very fast, and the next table shows the results of the efforts to make the flue gas cleaning system working properly in short time. After 2½ month, the emission concentrations came below the emissions limit value of 0,1 ng I-TEQ/m<sup>3</sup>.

Date	ng I-TEQ/Nm <sup>3</sup>	Date	ng I-TEQ/Nm <sup>3</sup>
October 4, 2000	183	November 24, 2000	0.8
November 15, 2000	113	December 19, 2000	0.15
November 20, 2000	14	December 20, 2000	0.04 – 0.05
November 23, 2000	1.8	December 19, 2001	0.009

Table 1. Measured dioxin emission from the metal reclaiming plant

The seven sampling sites around the plant are shown in Figure 1, and the dioxin concentrations measured in the samples are shown in Table 2.

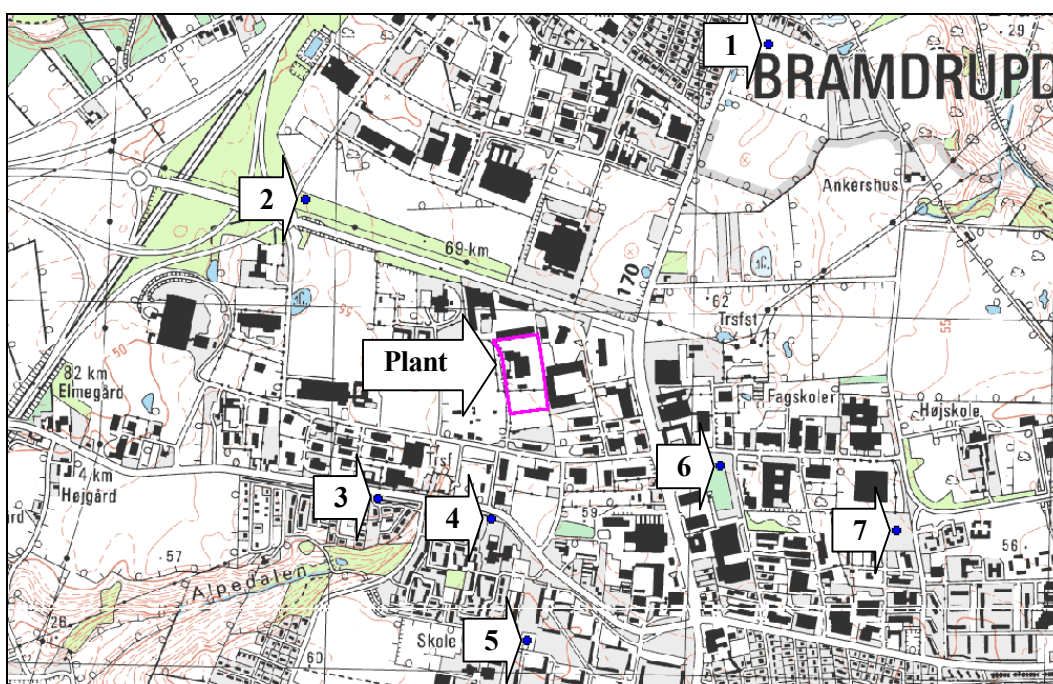


Figure 1. Sampling positions around the metal reclaiming plant.

Sampling position	Distance from the Plant	ng I-TEQ / kg dm (dry matter)	
	Meters	Samples of soil	Samples of old leaves
1	1100	1.8	No sample
2	750	3	4.2
3	550	0.95	1.1
4	400	1.4	No sample
5	750	1.7 – 3.5	2.1
6	600	5	44
7	1125	1.8	No sample

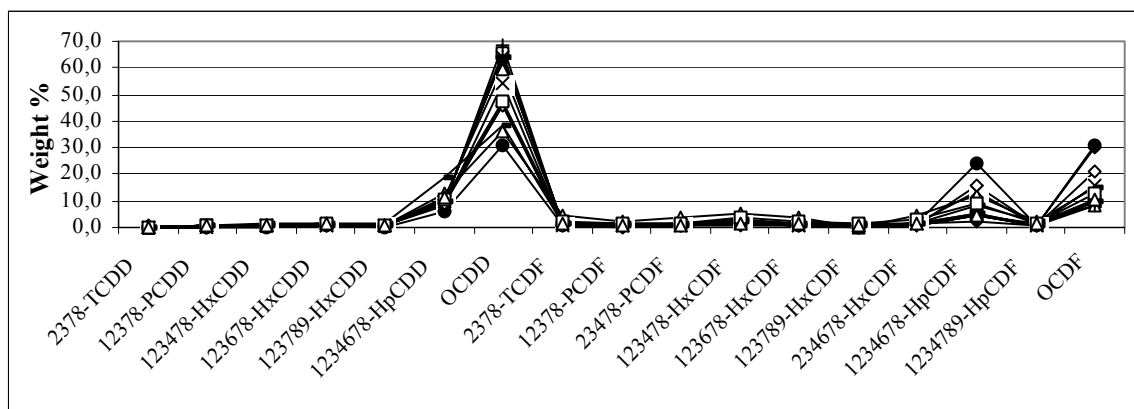
Table 2. Dioxin concentration in soil and vegetation

A new Danish investigation /3/ reports the concentration of dioxin in Danish soil to be  $0.7 \pm 0.2$  ng I-TEQ/kg dm (dry matter) for rural areas and  $6.2 \pm 5.6$  ng I-TEQ/kg dm. for urban areas. Dioxin concentration in soil from unpolluted grass areas has been reported to be in the range from 0.4 to 4.8 ng I-TEQ/kg dm /2/. According to the present German soil protection law, there is no restrictions is for concentrations of dioxin in soil below 100 ng I-TEQ/kg dm, where the limit was 5 ng I-TEQ/kg dm in the former recommendation, and concentrations between 5 and 40 ng I-TEQ/kg dm required additional monitoring /2/. All the soil samples contain dioxin within the interval for urban areas in the newest Danish investigation, and they must be regarded as normal values for Danish urban soil.

The samples from position 6, both the soil and the vegetation sample, are higher and much higher than the samples from the other sites. This position is situated in the prevailing wind direction from the plant, and the area was polluted with different types of waste, including plastic and old tyres. The elevated concentration could be influence from the plant, but it could as well be other local sources, indicated by the waste. Other investigations have shown, that vegetation samples typically have higher dioxin concentration than soil samples from the same site, which is also the situation here.

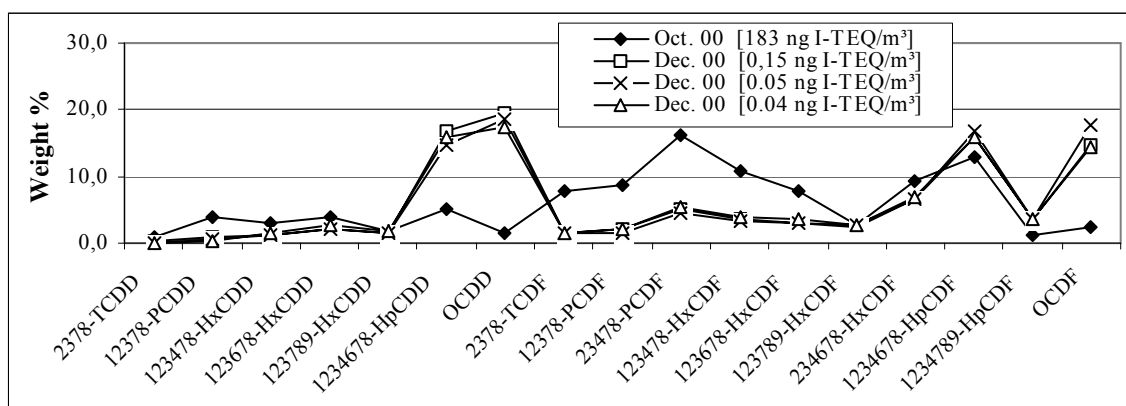
**Dioxin pattern**

Dioxin congener patterns in all the samples have been examined in order to evaluate, whether the emission from the plant could be directly related to the dioxin found in the soil or vegetation samples. The congener pattern was calculated in percent of contribution of every native congener, to make it possible to compare all the different patterns, independent of the concentrations. Previous investigations /4 / have shown the possibilities to distinguish between the contribution from different sources by using this kind of comparing the dioxin pattern. The pattern for the soil and vegetation samples is shown in figure 2, and the pattern for some of the emission samples is shown in figure 3. All profiles are very similar to each other, despite pos. 6 is 10 to 20 times higher in concentration.



Figur 2. Dioxin congener pattern for soil and vegetation samples.

Apparently, the cause of the extremely high level at 180 ng I-TEQ/Nm<sup>3</sup> was a wrongly adjusted natural gas burner. This is supported by the analysis of the dioxin pattern, which is remarkable



Figur 3. Dioxin congener pattern for emission samples.

different from the other samples. The dioxin patterns in the other samples are rather identical and look more like dioxin patterns from common MSWI plants.

A comparison between the dioxin patterns for the emission samples and the soil and vegetation samples does not show a great conformity. The pattern for the extremely high emission sample is very different from the soil and vegetation samples, and the unusual very high concentration of the low chlorinated furans, cannot be recognized in any of the soil or vegetation samples. On this basis, the measured and potential former high emission from the metal reclaiming plant cannot be identified as a major contributor to the dioxin deposition in the near surroundings. The pattern supports the assumption that the very high dioxin emission has only occurred for a shorter time. The other dioxin patterns shows more similarity with the soil and vegetation samples, but as they also look like profiles from MSWI plants, where one is situated a few hundred metres away, the potential contribution from the metal reclaiming plant cannot be distinguished from other sources.

### Conclusion

Slightly elevated dioxin concentration in both soil and vegetation was found at position 6, which is in the prevailing wind direction from the plant, but the reason could also be a local pollution indicated by the observation of littering in the area.

By comparing the dioxin patterns it is obvious that dioxin emissions from the plant have not affected the local environment significantly. The soil samples are within the range reported in a new Danish investigation, and they should consequently be seen as normal urban samples.

### References

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4. Schleicher O, Jensen AA, Blinksbjerg P. Måling af dioxinmissionen fra udvalgte sekundære kilder. Miljøprojekt nr. 649. Copenhagen: Danish EPA, 2001 (in Danish). Available from internet site: [www.mst.dk/udgiv/publikationer/2001/87-7944-868-2/pdf/87-7944-869-0.pdf](http://www.mst.dk/udgiv/publikationer/2001/87-7944-868-2/pdf/87-7944-869-0.pdf)