Dioxin emissions after installation of a polishing wet scrubber in a hazardous waste incineration facility

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Abstract

Dioxin levels measured after wet scrubbing systems have been found to be higher than levels measured before the scrubber. It is believed that there is an adsorption of PCDD/Fs on plastic materials in the scrubber. The PCDD/F levels after a polishing wet scrubber were followed continuously for 18 months using long-time sampling equipment at a hazardous waste incineration facility in Sweden. Each sampling period lasted two weeks. It was found that the levels during and shortly after start-up periods were elevated. The decline was very slowly, which supports a memory effect in the scrubber. Further, a multivariate model showed that the relation between different homologues changed over time, which is in agreement with a desorption model, taking into account the vapour pressures for different congeners. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Dioxin formation from incineration is known since 1977 when dibenzo-dioxins and dibenzo-furans were found in fly ashes and flue gases (Olie et al., 1977). Their toxic effects are well known and dioxins have been in focus in the environmental discussions for almost 20 years (Van den Berg et al., 1998). Throughout these years efforts have been made to minimize the formation and emission of dioxins from incineration facilities, both by means of primary measures, i.e. combustion control and by secondary measures such as the supply of additives or catalysts to the flue gas treatment system. One of the most used methods is the injection of activated carbon into the flue gas channel just before a bag house filter, where the carbon together with the fly ash form an adsorption layer on the bag on which dioxins are adsorbed. Emissions after such an installation are known to be well below the EU emission limit of 0.1 ng/m³ (Chang and Lin, 2001).

According to the EU directive 94/67/EG and EU directive 2000/76/EC emission measurements of PCDD/Fs only have to take place once or twice yearly and such measurements are made under normal, i.e. good operation conditions. Typical CO levels are well below the stipulated 50 mg/m³ normal dry gas. The emission levels under other operating conditions have been poorly studied until recently, when Belgian MSW incinerators started continuous flue gas sampling for dioxin analyses. Blumenstock et al. (2000) found an increase in PCDD/F levels after a period with bad operating conditions in a pilot scale incinerator. This
was later confirmed by several other authors (Gullett et al., 2000; Zimmermann et al., 2001; Gass et al., 2002). Gass et al. (2002) investigated the emissions from a full scale incinerator and obtained the same results as earlier were shown in pilot scale.

Wet scrubbing, i.e. the physical or chemical absorption of gases in a liquid, has been used for a long time for the removal of acid components in flue gases from incineration facilities because of its good removal efficiency (Onnen, 1972; Korell et al., 2003). High dioxin emissions have, however, been found after wet scrubbers when they have been placed as the final step in a flue gas cleaning system. It has further been shown that this is caused by the so-called memory effect, where dioxins are adsorbed on plastic details such as scrubber fillings when the formation and emission from the incinerator is high. The adsorbed dioxins are then desorbed slowly when the plant is running under more stable conditions. A comparative study using a pilot scale scrubber made of glass showed no such increased emission levels (Hunsinger et al., 1998). This memory effect can be distinguished from high emissions caused by bad combustion through its different congener pattern (Kreisz et al., 1996; Gass and Neugebauer, 1999; Adams et al., 2001; Giugliano et al., 2002).

To comply with the hazardous waste incineration directive (EU directive 94/67/EG), which came in force on the first of July 2000 in Sweden, a hazardous waste treatment facility in Kumla, Sweden was equipped with an enhanced flue gas cleaning. A wet scrubber was installed after the existing semi-dry system, which consisted of a spray dryer and a fabric filter with activated carbon injection. Already five weeks after the new scrubber was taken into operation, elevated PCDD/F emissions were observed. In order to learn more about the dynamic behaviour of the scrubber as to dioxin emissions a continuous sampling device was installed in July 2001. The results from these measurements are presented in this article.

2. Material and methods

The hazardous waste treatment facility studied mainly consists of an incineration line with a rotary kiln, secondary combustion chamber, boiler and a flue gas cleaning system. The flue gas cleaning consists of a semi-dry absorber, a fabric filter and the new wet scrubber. In the absorber lime milk is injected to neutralize the main part of HCl and SO2 present in the flue gas. Between the absorber and the fabric filter activated carbon is injected for dioxin removal. The incineration temperature in the rotary kiln is above 1100°C. Outlet temperature from the boiler is 280°C. In the semi-dry flue gas cleaning system the temperature is lowered to 160°C and in the scrubber the temperature is 70°C.

The scrubber consists of a quench and a 28 m high scrubbing tower, 5.5 m in diameter, filled with filling material of polypropylene (Rauschert hiflow rings type 50–6). The scrubber and quench shell are made of glass fibre reinforced plastic (GRP) Derakane 470. After the scrubber the flue gas fan is situated and the gases leave the plant through a 60 m high chimney, which interior surface also is made of GRP. A schematic sketch of the plant and the sampling points are shown in Fig. 1.

Fig. 1. Schematic sketch of the plant and indication of sampling points for dioxins. The layout of the Amesa sampling system is shown in the bubble.
The purpose of the wet scrubber is to polish the emission levels of HCl and SO2 to comply with the 1/2-hour averages prescribed by the Swedish implementation of the European Hazardous Waste incineration directive. This is achieved by introducing H2O2 to the scrubber liquid, the so called MercOx-process. The H2O2 content in the scrubber liquid also increases the removal efficiency for mercury. The MercOx process has been described in detail by Korell et al. (2003).

Five weeks after the first start-up of the plant with the new scrubber, dioxin levels were measured before and after the scrubber. High concentrations were found after the scrubber even though the concentrations before the scrubber were low. Further measurements during the autumn 2000 confirmed these results. In order to learn more about the dynamic behaviour of the scrubber as to dioxin emissions a continuos sampling device was installed in July 2001. Since then samples have been taken continuously whenever the plant has been in operation. The commercial sampling equipment used has been described by Funcke and Linnemann (1992) and Mayer et al. (2000) and consists of a titanium probe, a XAD-2-cartridge and a control cabinet. (Fig. 1). Flue gases are taken out isokinetically, pass the cartridge and are transferred to the control cabinet where flue gas volume and water content is measured.

The sampling period for each analysis has varied between one to two weeks. Sample preparation and analyses have been made by Eurofins GfA-laboratories in Germany according to EN1948. Eurofins GfA is accredited according DIN EN ISO/IEC 17025:2000 and is participating on a regular basis in international intercalibration studies.

3. Multivariate data treatment

Multivariate data analysis (MVDA) has been used successfully in a number of investigations where complex data sets are to be evaluated, also in the field of dioxin research (Pitea et al., 1994; Buekens et al., 2000; Wang et al., 2003). Multivariate data analysis (MVDA) consists of several methods to extract information from large data matrices. In MVDA the samples (objects k), in our case the weekly dioxin measurements, are seen as points in a multidimensional space with as many dimensions as variables (i) measured on the samples. In principal component analysis (PCA) the points in the multidimensional space are projected down onto a line, a plane or a hyperplane to give the best low-dimensional representation of the data. The data matrix (X) is now approximated by a systematic part (the loading and the score vectors) and a random part (the residuals) which consists of errors in the measurements and imperfections in the approximation. The dimension of PCA is determined by cross validation.

The visualisation of the PCA is normally done in diagram form. The variables are plotted in a diagram with the loading vectors as the axes. The greater the absolute value (positive or negative) of a variable is, the greater impact it has on its loading vector. Variables correlated with a specific vector can thus be identified. The objects are plotted in a diagram with the score vectors as the axes. Objects that have similar patterns will be located near each other and objects with different patterns will be more apart.

Before MVDA was performed on the data set, all data were centered and scaled to unit variance. The calculations were performed on a PC with the software program Simca 7.01 (Umetri AB, Umeå, Sweden). PCA is described in detail elsewhere (Wold et al., 1983; Wold et al., 1984).

4. Result and discussion

The sum of the different homologues for all measurements performed in the flue gas since 1998 are shown as series of time in Fig. 2. The first part shows the measurements made before the wet scrubber and the second part shows the measurements made after the wet scrubber, both short-time and long-time samplings. Each sampling is named according to the time when it was performed with the year and the consecutive week number of that year in the form yyww. When two measurements have been accomplished the same week, the individual measurements have been denoted a and b. Two maintenance stops in April and October 2002 are also indicated in the figure. The TEQ values for the measurements before the wet scrubber varied between 0.003 ng/m3 (W9839a) and 0.033 ng/m3 (W9935). A significant higher level of TeCDDs (0.19 and 0.5 ng/m3) explains much of the rise in 1999. No further investigations have been made in this study as to the cause of the results before the wet scrubber. The values shall be seen in comparison to the results from the measurements performed after the wet scrubber.

In the year 2000 when the wet scrubber was installed, sampling was performed simultaneously before and after the wet scrubber. The results before the wet scrubber as to TEQ values were 0.010, 0.006 and 0.005 ng/m3, which are in the same range as earlier results, i.e. well below 0.1 ng/m3. The TEQ-values after the wet scrubber in the sampling campaigns in year 2000 were much higher, 0.18, 0.10, 0.36 and 0.45 ng/m3. During the first sampling campaign in May (W0021), the difference between the TEQ value before and after the scrubber is about one order of magnitude, 0.01 ng/m3 before the scrubber compared to 0.18 and 0.10 ng/m3 after the scrubber. In the campaign in October (W0040) this difference has increased to almost two orders of magnitude, 0.006 and 0.005 ng/m3 before the scrubber compared to 0.36 and
0.45 ng/m$^3$ after the scrubber. It is clear that the differences in TEQ values before and after the scrubber above all can be explained by the drastically higher levels of low-chlorinated homologues after the scrubber. For example, TeCDD increased from the range 0.02 to 0.14 ng/m$^3$ before the scrubber to 0.1–0.7 ng/m$^3$ after the scrubber, TeCDF increased from the range 0.01 to 0.07 ng/m$^3$ before the scrubber to 3.5–5.7 ng/m$^3$ after the scrubber, and PnCDF increased from the range 0.02 to 0.07 ng/m$^3$ before the scrubber to 1.54–3.11 ng/m$^3$ after the scrubber. OCDD, on the other hand, was in the range 0.03–0.15 ng/m$^3$ before the scrubber and 0.01–0.04 ng/m$^3$ after the scrubber. The same applies for OCDF, which was in the range 0.02–0.19 ng/m$^3$ before the scrubber and 0.01–0.05 ng/m$^3$ after the scrubber.

This change in composition is illustrated in the fingerprint plots in Figs. 3 and 4. Especially the fraction levels of TeCDFs have risen. Before the scrubber the average fraction of TeCDF is 8% and after the scrubber it is 49%. The somewhat deviating pattern for the measurements in 1999 can also be seen. At this time the TeCDF fractions are the most deviating homologue with values of 44% and 52% compared to 5–14% for other measurement periods before the scrubber.

The fingerprint plot in Fig. 4 shows clearly decreasing values with the degree of chlorination. For the PCDFs the average level of the TeCDF is 49% and that is approximately double the amount of the PeCDFs, which is 23%, i.e. more than the double of HxCDFs (9%). HpCDFs have an average fraction of 2% and OCDFs have an average fraction of 0.2%. For PCDDs the trend is similar but to a lesser extent (TeCDD 6%, PeCDD 6%, HxCDD 4%, PnCDD 1% and OCDD 0.2%).

In August 2000, as soon as the results from the measuring campaign in May 2000 were available, an electrostatic precipitator (ESP) used as by-pass for the fabric filter during start-up and shut down was closed since it was suspected that PCDD/Fs were loaded into the scrubber during its operation periods and slowly released afterwards, the “so called” memory effect described in the literature by Kreisz et al. (1997); Wevers and De Fré (1998); Giugliano et al. (2000); Adams.
Fig. 3. Homologue fingerprint for the measurements made before the wet scrubber. This includes both measurements made before and after the scrubber installation. In the years 1998–2000.

Fig. 4. Homologue fingerprint for the measurements made after the wet scrubber in the period May 2000 to July 2001. High ratio of low chlorinated congeners can be observed due to memory effects in the wet scrubber.
et al. (2001). When the ESP was in operation no carbon could be injected so it seemed logical that dioxins were transported to the wet scrubber during these periods. As can be seen in Fig. 2 the dioxin levels were elevated also in the measuring campaign in October 2000 (0.36 and 0.45 ng/m$^3$ TEQ in W0040). When the continuous sampling equipment was installed in July 2001 the TEQ-value after the scrubber was 0.52 ng/m$^3$, which is in the same range as in the October measurement. In Fig. 2 it can be seen that all the homologues except OCDF and OCDD fell from this high level to a level comparable to the levels measured before the scrubber (0.003–0.03 ng/m$^3$). This decline took almost 15 months from the shut down of the ESP. In W0147, which is in the beginning of November 2001 the first result below 0.1 ng/m$^3$ TEQ after the scrubber was obtained. The result was 0.06 ng/m$^3$ TEQ and two weeks later the level had decreased further to 0.04 ng/m$^3$.

During the period of continuous sampling presented here, two dramatically risings of TEQ levels were observed, both in the period just after a maintenance stop of the plant. At the first occasion (W0215) the TEQ value increased from 0.02 ng/m$^3$ to 0.25 ng/m$^3$ and at the second occasion (W0240) the TEQ-value increased from 0.03 to 0.15 ng/m$^3$. It is believed that during the start-up periods high levels of dioxins are generated which normally is not recognized since sampling normally takes place only during stable operating conditions.

The high concentrations just after start-up and the somewhat exponential decline afterwards indicate that dioxins are adsorbed on the olefin plastics in the scrubber and released slowly. Otherwise a sharp peak would be expected just after start-up. It is also typical that the concentrations of OCDD/F do not vary over time since it is known that the absorption for these homologues are much stronger than for the others, (Kreisz et al., 1996). The different absorption pattern for different congeners can be explained by their different vapour pressures. The strong dependence on vapour pressures with the degree of chlorination has been described by Rordorf (1989).

The change in composition can be seen even better when the data is studied using multivariate statistics. The concentrations of the 17 congeners that are used in the calculation of the TEQ value and the results in Fig. 2 were evaluated using PCA. At first a general PCA analysis of the data was made. This model gave little information as to the memory effect, since most of the variation in the data set was used to explain the changes in concentrations between the different sampling periods. If, however, the individual results for every congener was divided by the total amount of all dioxins and furans in that sample, the influence from variations in concentration could be eliminated.

A new PCA model was calculated using the new variables and it was found that principal components 1 and 3 of this model best described the variations in congener pattern that had been observed. The score and loading plots for these vectors are shown in Figs. 5 and 6 respectively.

![Figure 5](image-url)
To the left in Fig. 5, with low values in score vector 1, all the measurements before the scrubber are located (obs. nos 1, 2, 3, 4, 6, 8, 10) and the measurements after the scrubber are located more to the right. Two maintenance stops are located between obs. nos 36 and 37 and between nos 50 and 51. A rapid shift in score vector 1 can be observed during the two maintenance stops. Further it is visible how the observations at the beginning of the continuous sampling period (obs. nos 12–16) are all located close together. During a transition period of four weeks the observations have moved to a new point in the diagram, indicating a new composition in the emission pattern. The emission pattern is then relatively stable until the maintenance stop between observations 36 and 37 occurs.

Observation 12, which is the first measurement with the continuous sampling device, and observation 37 almost have the same score in vector 1 but differ in vector 3. From observation 37, which is the first observation after one of the maintenance stops, the process again moves from high values in vector 1 to lower values over a couple of weeks. The same shift can be seen even better between observations 50 and 51 which is the second maintenance stop during the period covered in this study.

The loading plot (Fig. 6) shows a tendency that the degree of chlorination is described by loading vector 1 and the ratio of PCDD to PCDF is described by loading vector 3. Low-chlorinated congeners have higher loadings in vector 1 and PCDFs are situated toward lower values in loading vector 3. Implementing this in the score diagram it seems that just after a maintenance stop there is a big loss of dioxins and furans with four chlorine atoms. The difference in score vector 3 for the observations 12 and 37 would then indicate that the ratio PCDD/PCDF is higher after the maintenance stop than it was when the continuous samplings were started. The PCA model also shows that there is a shift between PCDDs and PCDFs over time since the loadings for total-PCDD and total-PCDF are situated on one of the diagonals in Fig. 6.

5. Conclusions

- The high PCDD/F emissions found after the installation of the wet scrubber was caused by memory effects due to high formation in the incinerator during start up of the plant.
- The homologue pattern after the wet scrubber differs significantly from the pattern before the scrubber. A relation between the degree of chlorination, the vapour pressure and the emission level for a specific congener was found with the use of multivariate statistics.
- Start-up periods, e.g. after maintenance stops, are the main cause of elevated dioxin emissions from an incinerator. This can only be shown by continuous monitoring where all modes of operation are covered.
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