Process-related patterns in dioxin emissions: a simplified assessment procedure applied to coke combustion in sinter plant

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Abstract

Analyses for dioxins present in the windlegs of sinter plant using coke breeze as fuel which were carried out originally to monitor the 17 targeted isomers have been re-examined in order to establish the variation in isomer profiles with location of the sampling point relative to the beginning of the sinter strand. The analysis has been carried out using peak height as a measure of isomer abundance to allow assessment of a large number of peaks reasonably rapidly. It is found that the isomer profiles of the tetra- to heptachlorodibenzofurans, which dominate sinter plant emissions in the exhaust gases from the majority of the bed are similar. However, analysis shows that whilst some isomers contribute a similar percentage of the isomer group at the beginning of the strand, there are more, which vary significantly from the mean. Ways in which this localised difference in isomer distribution could arise are discussed.

Keywords: Dioxin emissions; Coke combustion; Sinter plant

## 1. Introduction

The formation of dioxins in industrial processes has been the subject of scrutiny for many years [1,2] and operators have been required to obtain samples from plant at regular intervals and provide analyses to indicate compliance with regulations limiting emission levels [3]. Originally, the emissions were dominated by waste incinerators, which burnt substantial quantities of materials which contained not only carbon and hydrogen, but the chlorine also necessary for dioxin formation, plastic items made from polyvinyl chloride being a prime example, under poorly controlled conditions. Restrictions on emission levels from new incinerators have brought the emission levels from incinerators down sufficiently for processes hitherto ignored as minor dioxin emitters to come under scrutiny [4]. One such process is the sintering of iron ore, which is the subject of this investigation.

There are 135 chlorinated dibenzofurans and 75 chlorinated dibenzo-p-dioxins. None of those with less than four hydrogen atoms replaced by chlorine is subject to regulation. Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) with four or more chlorine atoms are collectively referred to as dioxins. Whilst the totals for each degree of chlorination (known as homologue groups) of PCDFs and PCDDs from tetra to octachloro- are obtained during analysis, only those congeners with substitution at the 2, 3, 7 and 8 positions are reported individually. Structurally, each of these congeners is effectively planar, and in practical terms they are less easily metabolised and more likely to disrupt cellular function than the other congeners. Of these 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is considered the most toxic, and is allocated a Toxic Equivalent Factor (TEF) of 1. The remaining 2,3,7,8-substituted congeners are regarded as having lower toxicities than 2,3,7,8-TCDD and have therefore been assigned lower TEFs. The legal requirement thus provides a measure of the toxicity of the emissions from the plant as the total International Toxicity Equivalent (ITEQ). Typically emissions from UK iron ore sinter strands are of the order of 1.2 ng I-TEQ/N m3. This is somewhat higher than the limit of 0.1 ng ITEQ/N m3 set for municipal waste incinerators, and in anticipation of any attempt to reduce the level for sinter plant to a comparable level, a programme of research into means to reduce sinter plant emissions by primary measures is being undertaken by Corus plc [5–12]. At present little is known about the processes leading to dioxin formation in sinter beds. The amount of dioxin in the raw sinter mix is negligible by comparison with the amount found in the combustion gases hence the dioxin emissions from the plant are definitely a product of the sintering process. Addition of small amounts of urea to the raw sinter mix not only results in reduced NOx and SOx emissions [13] but also results in a significant reduction in the levels of dioxins formed. There is an optimum level of urea addition above which the emissions rise again [14]. The effect of urea on these formation processes strongly suggests association of dioxin formation with the combustion process. Experimental investigations of dioxin formation in sinter beds cannot directly provide information about the relationship between the flamefront and the zone where they are formed. Sampling for dioxins needs to be carried out over a period comparable to the time taken for sinter material to travel from one end of the bed to the other in examining formation in a specific location in the material. This requirement together with the travelling bed and (somewhat erratically) travelling flamefront of the sinter plant make sampling in such a way as to obtain samples at a fixed point with reference to the flamefront and the depth of flamefront penetration a virtual impossibility. Indirect methods of obtaining information about the formation mechanism and the region in which formation occurs, by analysis of data derived from samples taken at less closely defined locations, must be used.

## 2. Regulatory compliance analyses for targeted dioxins as a source of data on non-targeted dioxin isomers

Sampling and analysis for dioxins is carried out using a standard procedure described by the United States Environmental Protection Agency [15]. Sampling from gas streams is carried out over a period of typically two hours using a standard sampling train. The sample must be purified before analysis. First, an extraction procedure is used to remove dioxins from the surface of solids in the sample itself or from the polyurethane filter used in sample capture from gases. It is then subjected to a cleanup procedure to remove species, which would otherwise interfere with the analysis. Analysis of the purified extract is carried out by high-resolution gas chromatographic separation with detection by high resolution mass spectrometry. The DB5ms chromatography column used in analyses for regulatory purposes because it gives better separation of the targeted isomers than any other stable column. It is also very stable, i.e. retention times vary slowly with use, so that automatic analysis is feasible. Analyses carried out purely in the pursuit of academic research use other columns, often the SP2331 column, which resolve more peaks. The DB5 column, from which the DB5ms was developed, has been fully calibrated for all tetra- to octachlorodibenzodioxin and -dibenzofuran isomers, as has the SP2331 [16]. Unfortunately, although it is possible to infer the hexachlorodibenzofuran elution sequence of the DB5ms from that of the DB5, the tetra- and pentachlorodibenzofuran chromatograms differ in the number of peaks. The differences between the tetra- and pentaDBF chromatograms is illustrated in Fig. 1(a) and (b). It is also clear from the comparison shown in these figures, that whilst the isomer or isomers considered to contribute to any DB5ms peak can be regarded as restricted to those eluting in a range about an equivalent point on the DB5 column chromatogram, attribution cannot be more definite. Any one isomer could elute earlier or later and there are no rules for predicting direction or magnitude of any change. Whilst it would be preferable to obtain definite attribution of each peak to an isomer or group of isomers, calibration of the column would require evaluation of the retention times of more than 40 isomers out of the total of 66 for the tetra- and pentaDBF isomer groups. Additional calibrations for tetra- and pentaDBD peaks would also be required for completeness. Only a few pure tetra- and pentaDBF isomers are available commercially (at a cost of several hundred ponds each), hence the majority would require separation and purification in order to carry out the exercise. This major exercise is too extensive and expensive to have been incorporated in this project, and indeed, it is unlikely to be carried out (or if carried out, to be placed in the public domain). Tetra- and pentachlorodibenzofuran results are accordingly reported as peak heights in this investigation.

If the sample used for analysis with the DB5ms column has been stored, the extended DB5ms-based analysis can be used in conjunction with a repeat analysis carried out using one of the fully calibrated columns to extend the value of that full analysis to provide trends over the range of samples covered by the DB5ms-based analyses. The results can also identify regions where most isomer concentration variation occurs without further analysis (and performance of unnecessary analyses where trends are minimal can be eliminated).

The chromatograms obtained from analyses for regulatory purposes therefore include information about the concentrations of almost all the tetra- to octaPCDD/Fs. The exceptions arise when the slowesteluting isomer(s) of a given homologue group elute later than the fastest eluting isomer(s) of the next homologue group, since the mass spectrometer is tuned to monitor only for selected PCDD/F ions within a given homologue group within certain time windows. Fig. 1(a) shows the results obtained for one sample for pentachlorodibenzofurans, and illustrates the form of the chromatographic results obtained for each homologue group. The

template shown below the chromatogram in Fig. 1(a) shows how the leading peak is lost due to overlap with the end of tetraDBF analysis. Ten such sets are obtained in each analysis, for tetrachloro- to octachlorodibenzofurans and -dibenzodioxins. The mass spectrometer samples the gas leaving the chromatography column. The various homologue groups elute from the column in specific time windows in order of increasing chlorine substitution, and within each time window the mass spectrometer is programmed to switch rapidly between two major ion peaks of the PCDDs or PCDFs (top two chromatograms in Fig. 1(a)). The corresponding ion peaks of 13C12-labelled CDD/F surrogates that are added as internal standards for quantification of the targeted compounds are also monitored (bottom two chromatograms of Fig. 1(a)). Measurement of the intensity ratio of two parent peaks (all 35Cl and one 37Cl, rest 35Cl) for each compound provides a check that coincident peaks from other species are not misidentified as dioxins. In the scans examined in this work, there was no interference from non-dioxin species in the set of PCDF scans except for the heptaCDFs, which simplified data acquisition somewhat.

PLEASE INSERT FIGURE 1 (a) ABOUT HERE

PLEASE INSERT FIGURE 1 (b) ABOUT HERE

PLEASE INSERT FIGURE 1 (c) ABOUT HERE

The derivation of additional data which might provide more insight into the processes leading to dioxin formation from DB5ms is attractive because of the large number of such records which have been taken, and which can be expected to be stored electronically. These can either be converted to paper copy and read manually, as was the case in this study, or possibly examined automatically if suitable software is available.

We have used the chromatograms obtained to derive targeted isomer abundances along two sinter beds to examine the potential for obtaining information about the nature of the dioxin formation process in the absence of the full DB5ms calibration. In view of the requirement of stability of the columns used in compliance testing, the peak height can, to a reasonable approximation, be used as a measure of the peak area. This allows a larger number of charts to be examined in a more acceptable time than is required for the more rigorous procedure of determination of peak area and without allocation of use of dedicated, expensive equipment. We have examined the extent to which the known consistent, characteristic form of targeted isomer emission profile of the sinter bed (which only represents a small and substitutionally related subset of the whole range of congeners) is repeated in the full range of congeners, using this simplified approach.

## 3. Source of samples examined

### 3.1. The sinter plant

The purpose of the iron ore sinter plant is simply to convert iron ore with the necessary additives mixed in coarse powder form to lumps which when added to the blast furnace to be reduced to iron will not obstruct airflow through the furnace [17]. A typical raw sinter mix contains approximately 75% blended ores (4–7 ores), 3–4% fuel (coke breeze), 14% of various fluxes (limestone, olivine, sand) and up to 5% recycled materials (dry weight basis). The moisture content is typically 6.5–7%. Between 25 and 30% of sinter fines generated in the

screening of the product sinter is added. The chlorine content of the mixture is typically 70 ppm. Briefly, the sintering of iron ore is carried out by spreading moist granules of a mixture of iron ore, coke, and additives on a moving grate typically 2–4 m wide, as a 0.4–0.5 m thick bed of material, which is ignited from above by a natural gas flame. Air is drawn downwards through the bed by a series of extraction fans thus causing the flame front to move steadily down through the bed (Fig. 2). The rate of travel of the strand, which is of the order of 2–3 m/min, is such that the flamefront reaches the bottom shortly before the end of the strand is reached, where the sintered product is tipped off, cooled and screened. The fans drawing the air through the bed do so via a series of ducts referred to as windlegs, typically 15 in number, so that sampling from alternate windlegs provides a profile of dioxin concentration leaving the bed at various stages of the combustion front's progress. One set of results presented here were obtained from alternate windlegs starting at the fourth and ending with the fourteenth (Plant A), while the second set was obtained at a second plant starting at the third windleg and ending with the fifteenth (Plant B). The strands were at different integrated steelworks.

3.2. Sample analysis for targeted isomers and related results

Samples were subjected to standard cleanup procedure, and separation was carried out with a DB5ms chromatographic column with mass spectrometric detection. The system software was programmed to analyse for total congener group concentration and for the 17 targeted isomers. The results of the targeted isomer analyses for one of the sinter beds have been presented elsewhere [6–12], and associated stack emissions and electrostatic precipitator deposit data for the same sinter bed have also been published both for targeted isomers and for the whole range of tetra- to octachlorodibenzofurans [10]. The full analysis of the stack gas and precipitator dust was carried out by repeat analyses using an SP2331 column.

3.3. Full chromatographic data of windleg/windbox samples

In the samples taken from even numbered windlegs in the sinter bed (Plant A) the leading PeCDF peak is observed, whereas in samples taken from the other sinter bed (Plant B) the last TCDF is observed.

As discussed earlier, the DB5ms column calibration for tetrachloro- and pentachlorodibenzofurans is unavailable, and as its calibration would represent an expensive and lengthy project in itself, it has not been attempted. The results for tetrachloro- and pentachlorodibenzofurans are reported here as peak heights referred to a calibration chromatogram. The template for TeCDFs is shown in Fig. 1(b) and that for PeCDFs in Fig. 1(c). In each case, the calibration for the DB5 column is shown, to assist examination of the results. The HxCDF peaks are all identified. The amount of the species in the sample is most accurately derived from the area of the peak obtained on the chromatogram. This is essential where the column retention times and separation characteristics change with age and use, as is the case for some columns used in laboratory investigations of dioxins. However, in the case of the DB5ms, the stability of the column is high, and the peak height can be used to compare chromatograms.

## 4. Results

### 4.1. Total amounts of each isomer group

The total amounts of PCDF and PCDD measured in each isomer group are presented in Table 1. The results show PCDF to dominate dioxin formation in sinter beds, and the remaining discussion centres on PCDF.

PLEASE INSERT TABLE 1 ABOUT HERE

### 4.2. Peak heights—dibenzofurans

An example of a set of peak heights (for windleg 10 for Plant A) is presented in Table 2, as percentages of the total peak height at that windleg for the isomer group (Table 1).

PLEASE INSERT TABLE 2 ABOUT HERE

Some replicate samples were obtained from Plant B: the percentage contributions were found to be in excellent agreement, despite very different recovery levels from the original samples. Comparison of results for TeCDFs from the two strands for windlegs in the middle of the strand (windleg 6 of Plant A and windlegs 5 and 7 of Plant B) is shown in Fig. 3. This illustrates the general similarity between results for the two strands. Standard deviations of the mean derived for each peak in each set of results showed similar resemblances. The examples of the mean standard deviations for each TeCDF isomer for each sinter bed shown in Fig. 4(a) and (b) have evidently similar patterns. Comparison of the standard deviations (SD) with the peak heights showed that in general the highest SD was associated with the most intense peaks, further supporting
the view that the isomer distributions did not in general vary erratically.

PLEASE INSERT FIGURE 3 ABOUT HERE

PLEASE INSERT FIGURE 4 (a) ABOUT HERE

PLEASE INSERT FIGURE 4 (b)  ABOUT HERE

When the standard deviation is compared with peak height, it is noted that whereas for Plant A the value falls with rising peak height, for Plant B it rises with peak height, and is larger than for Plant A in general (insets, Fig. 4(a) and (b)). The results for Plant B were obtained nearer the beginning and end of the strand than for Plant A: to examine whether the variation was affected by removing the first and last sampling station from consideration profiles of the rms variation/mean for each peak was obtained (i) to include all sampling stations, (ii) excluding the first sampling station and (iii) excluding the last sampling station for both plant. These results are shown in Fig. 5(a)–(f). Individual percentage contributions to the isomer group at each windleg in each plant for representative isomers showing large changes in variation with the exclusion of the first sampling station are shown in Fig. 6.

PLEASE INSERT FIGURES 5 (a) to 5 (f) ABOUT HERE

PLEASE INSERT FIGURE 6 ABOUT HERE

### 4.3. Peak heights—dibenzodioxins

As shown in Table 1, the PCDDs are present in concentrations of the order of one tenth of those of the PCDFs. In the case of the tetraCDDs this level is sufficiently low to lead to difficulties in retrieving the data from the chromatogram because of contaminant peaks. Fig. 7 shows the pentaCDD peak variations for Plant B: the variations in peak heights for this group are clearly not restricted to the first and last sampling stations.

PLEASE INSERT FIGURE 7 ABOUT HERE

### 5. Discussion

The overall results of the investigation make it clear that over the whole of the sinter strand, the emissions are of reasonably constant composition. The relative peak heights within each isomer group are also similar for both beds. The variation about the mean contribution by individual peaks varies widely: the increase in standard deviation with peak height observed for TeCDF in the samples from Plant B compared to the fall in variation for Plant A suggests the major differences from the mean occur at the beginning or end of the strand. Comparison of mean variations in TeCDF rms variation/mean obtained on excluding the first and last samples show reductions in the variation/mean value for many peaks for exclusion of the first sampling station for Plant B but little effect owing to exclusion of the last sampling station. The effect for Plant A is much more limited. The same reduced variability on excluding the first sampling station is obtained for the PeCDF peaks in Plant B. Whilst some reductions in fractional variation are also obtained for Plant A the effect is not as marked. A few peaks exhibit reduced variability for the set of windlegs excluding the last, but the effect of this exclusion is also less marked. The same is seen in the results for HxCDFs. The combined variabilities of the three isomer groups shown in Fig. 8 clearly identify the early part of the strand as the main source of variations in peak height.

PLEASE INSERT FIGURE 8 ABOUT HERE

The results of the above evaluation lead to the conclusion that although isomer profiles arriving at the windleg are similar along the majority of the strand, isomer profiles at the beginning of the bed differ from the average significantly more than elsewhere. This does not apply to all isomers— some appear to contribute the same amount to the homologue group at all sampling stations.

Laboratory studies have demonstrated the formation of dioxins by several pathways [18–20]: passing a stream of gas which contains chlorine and hydrogen over carbon heated to several hundred degrees K will lead to dioxin formation (the so-called de novo synthesis path): appropriate organic aromatic precursors (chlorinated phenols, for example) can react to form chlorinated dioxins: and dibenzodioxin and dibenzofuran themselves can be chlorinated. In discussion of emissions from modern industrial plant it must be borne in mind that the emission levels are so low that it is feasible that precursors are present at sufficient levels to form the observed dioxins, but are at concentration levels orders of magnitude below the detection limit of non-specific analysis. It is not therefore possible to discuss the process leading to the formation of dioxins in the sinter bed in other than general terms.

The observation that the isomer profiles away from the ends of the bed are similar would seem more consistent with formation in a small region ahead of the flamefront rather than in a more

extensive region ahead of the flame. Immediately down strand of the ignition hood, the temperature gradient ahead of the flamefront is very steep: much of the bed is cold and moist. Further down strand, the preheated region becomes progressively longer. Part way along all the bed is dry and there is a significant depth of bed heated to several hundred degrees. It seems unlikely that the rates of formation of all the isomers are sufficiently similar for the residence time-temperature history not to affect the isomer abundances if a large amount of the preheat region were involved. The formation of dioxins immediately downstream of the flamefront is consistent with the suggestion by Gullet et al. [19] that reactive chlorine radical formed by combustion-linked reactions from other chlorine containing species dominates chlorination of stable hydrocarbon species in post-flame gases. This limited variation in isomer profiles also indicates that any deposition of dioxin on the unreacted material in the cooler region which has not been significantly preheated is not selective.

If the polychlorinated dioxins are formed close to the flamefront it is necessary that either they are formed by de novo synthesis on the surface of coke particles or they are formed from precursors which are trapped in some way, since free precursors would be volatilised and swept away as the temperature rose. It is possible that precursors are present in closed or relatively inaccessible pores in the coke particles, or are themselves produced in the pores in coke particles. These may include dibenzofuran, which is known to be resistant to decomposition on heating [21]. A wide range of other species are formed during the coke making process [22,23], and may be formed ahead of the sinter bed flamefroint if coking is incomplete. As noted above, the concentrations required to form the observed dioxins are too small to measure without targeted analysis.

The combustion of methane in the ignition hood is a possible reason why the isomer profiles at the beginning of the bed differ from those part way down the strand. The methane used provides a much higher level of hydrogen than the combustion of the coke, which only has a small residual hydrogen content, which could alter the relative rates of the reactions. Particle drying, preheating and ignition of the coke particles in the early stages of passing under the ignition hood will also occur together, i.e. larger and more porous particles will still be drying whilst neighbouring small particles are already ignited and this will lead to differing composition–temperature relationships from those present once a defined flamefront and preheat zone are established.

Positive attributions of the peaks to isomers or groups of isomers need to be viewed with caution because of the possibility of co-elutions which may differ between DB5ms and DB5 columns. Peaks with high variability in intensity which can be identified with specific isomers are Te1 which is 1368-TCDF, and 123479-HxCDF and 1123467-HxCDF.
The remaining attributions require re-analysis using an alternative column, or the unlikely event of the calibration of the DB5ms column becoming available.

6. Conclusions

1. Isomer distributions in the exhaust gases from a sinter strand burning coke breeze fuel have been examined using chromatogram peak height as a measure of isomer abundance.
2. Using this simplified procedure, it has been found that the isomer profiles in the exhaust gases from the mid-bed region of two sinter strands using coke as fuel are closely similar.

3. The isomer profiles for dibenzofurans at the majority of the other sampling stations below each strand are also very similar. However, the isomer distributions at the sampling station nearest to the ignition source differ significantly from those at other sampling stations.

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Figure 1. (a) Example of chromatogram for isomer group: mass spectral intensities for two parent peaks for normal pentachlorodibenzofurans (top), two mass spectral intensities for parent peaks of isotopically labeled standards (middle) and template for reading peak heights, showing peak lost in finishing preceding tetraDBF scan (bottom).
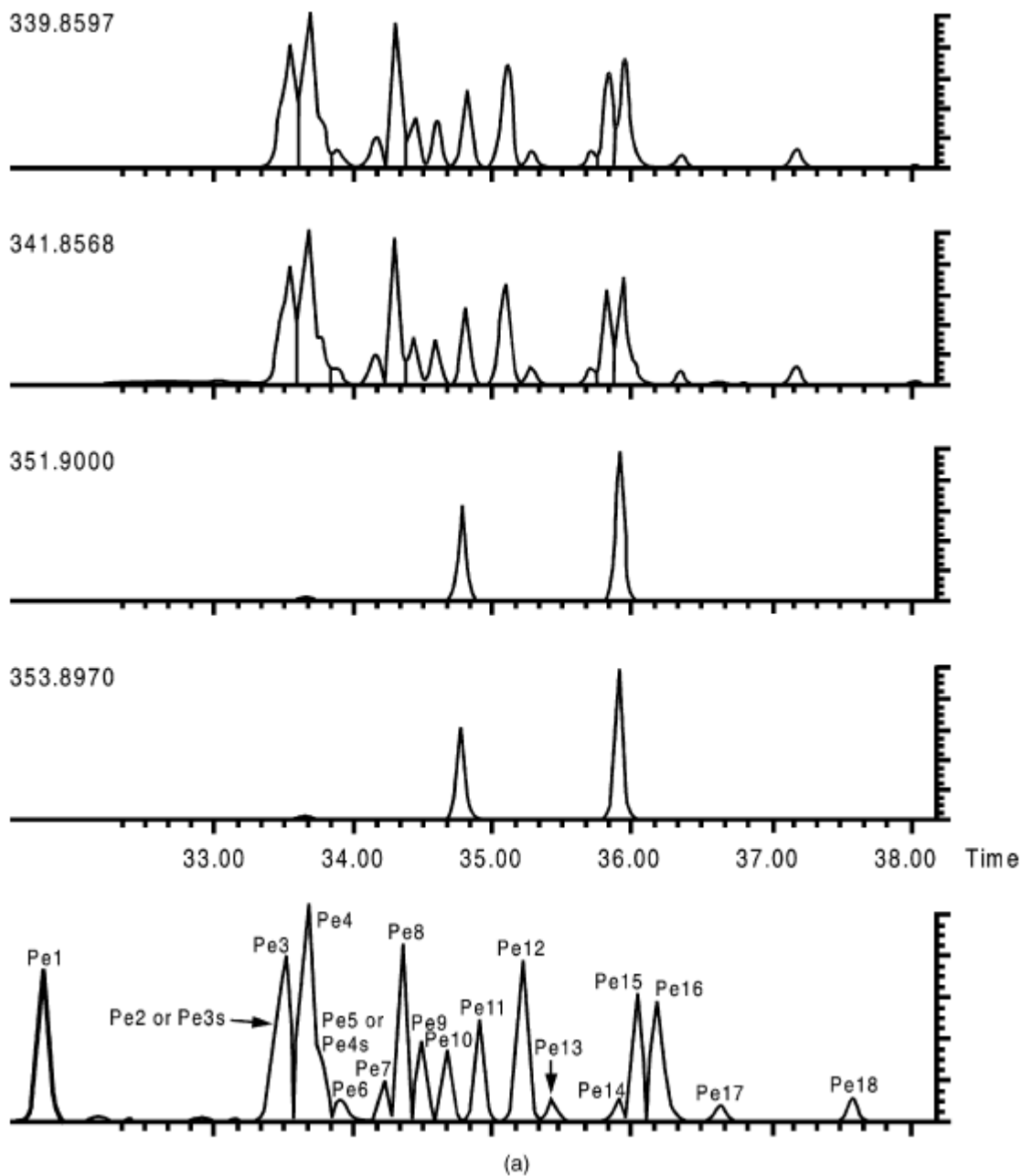


(a)

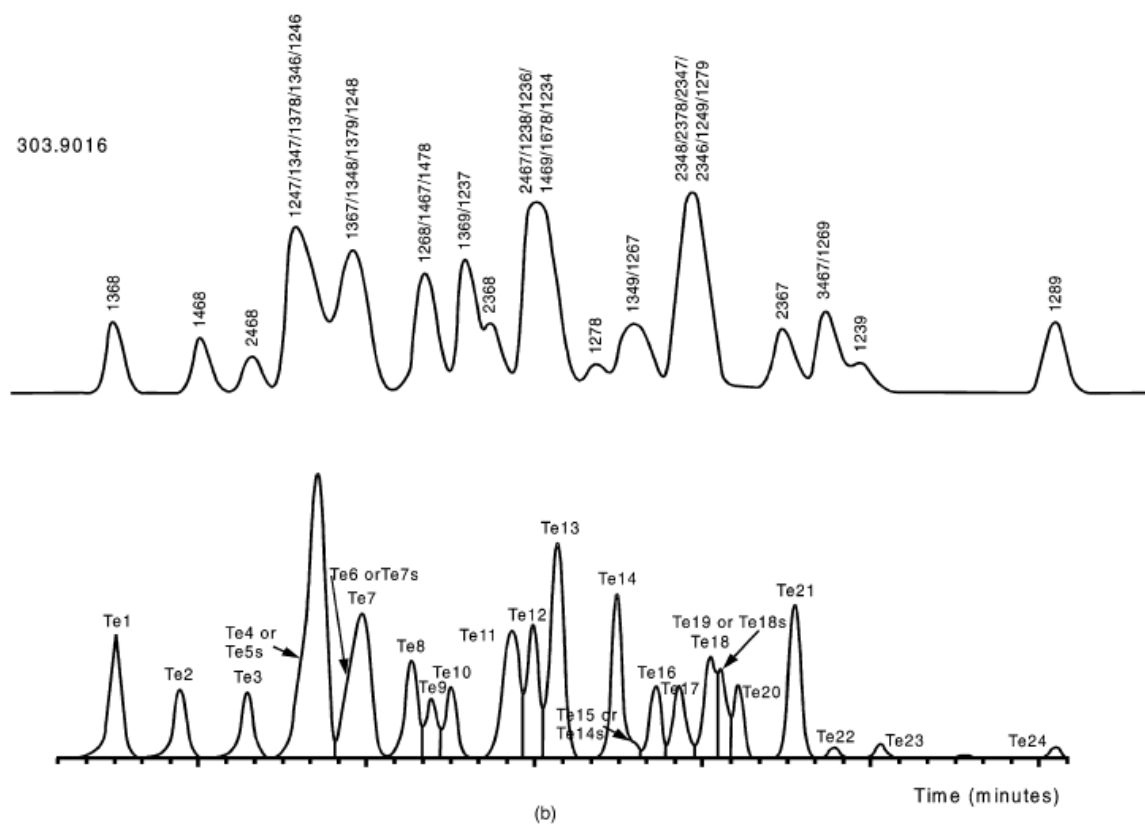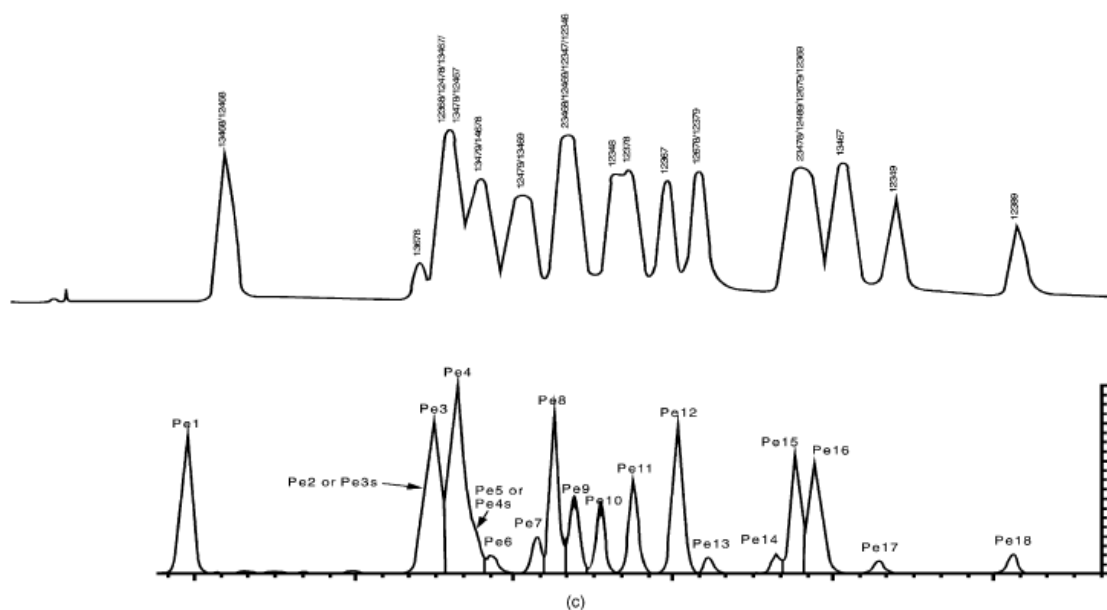Figure 1. (b) DB5 elution sequence for tetrachlorodibenzofurans (top) and template used to read DB5ms peaks (bottom).
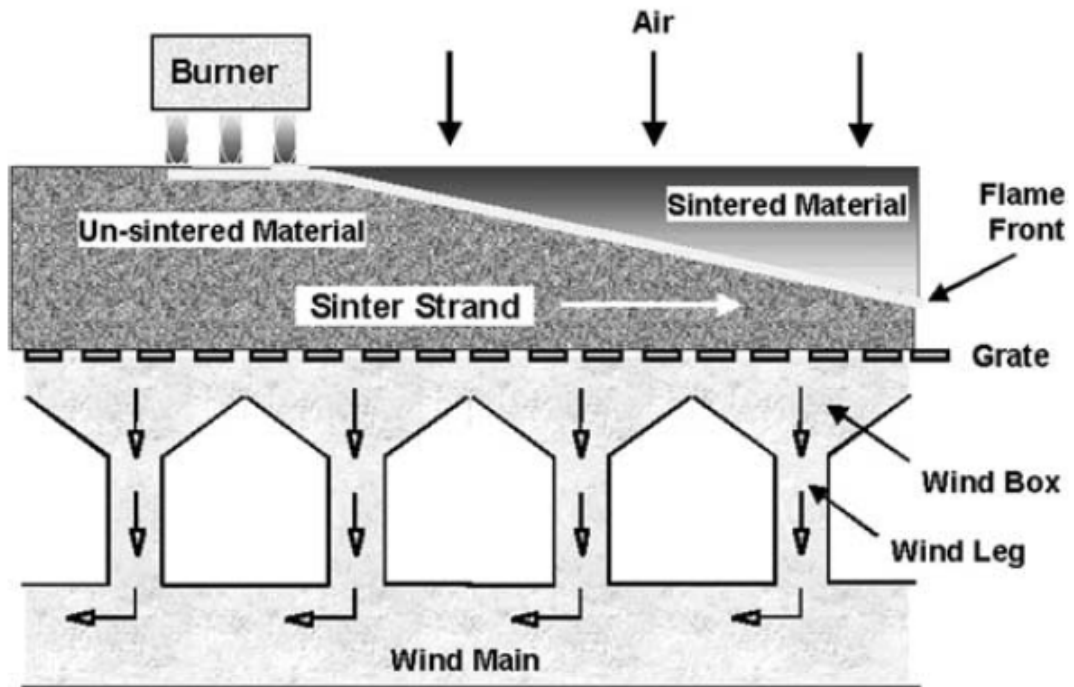


Figure 1. (c) DB5 elution sequence for pentachlorodibenzofurans (top) and template used to read DB5ms peaks (bottom).

Figure 2. Schematic of sinter strand



Figure 3. Comparison of tetrachlorodibenzofuran percentage profiles for windbox 6, Plant B, and windlegs 5 and 7 Plant A
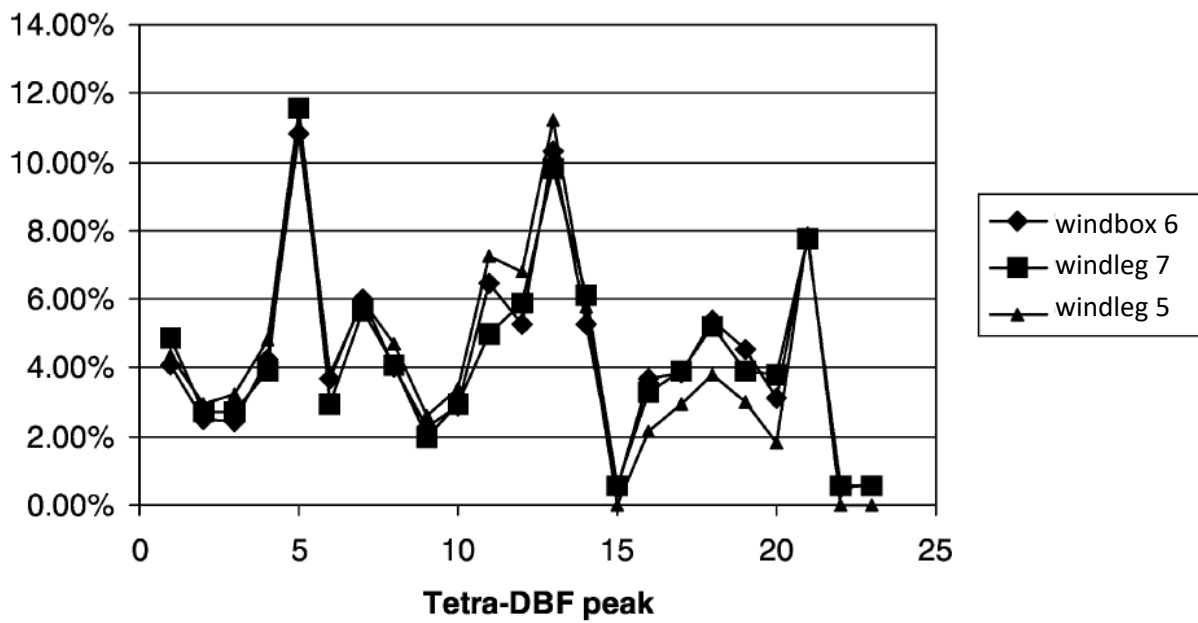
Figure 4. (a) Standard deviations of tetrachlorodibenzofurans Plant A, insets, standard deviations arranged in order of ascending peak height



Standard Deviation of each TetraDBF peak as percentage of isomer group (Plant A)
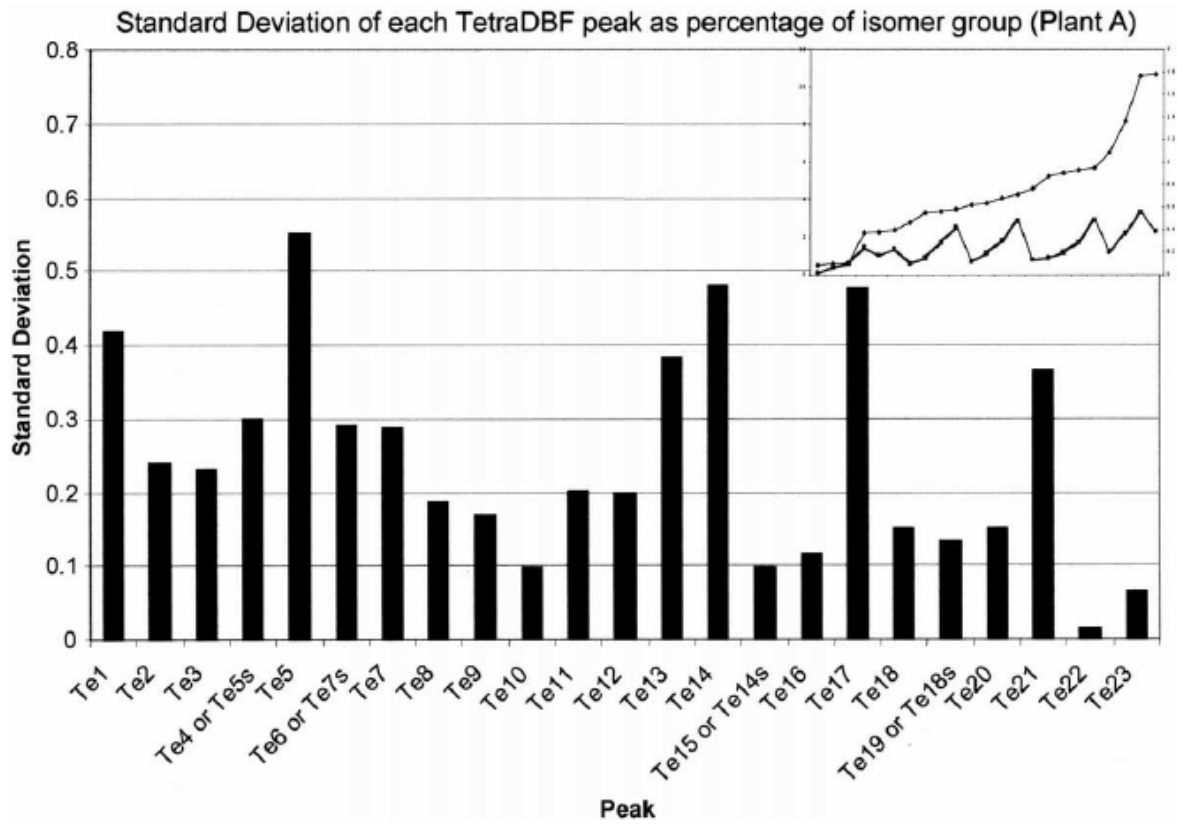
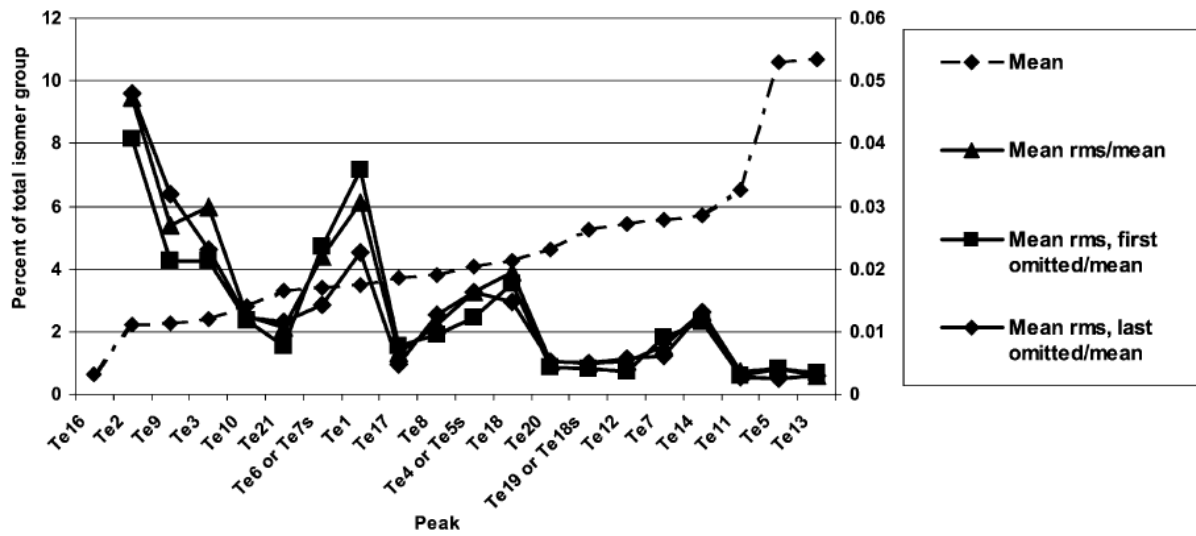Figure 4. (b) Standard deviations of tetrachlorodibenzofurans Plant B, insets, standard deviations arranged in order of ascending peak height
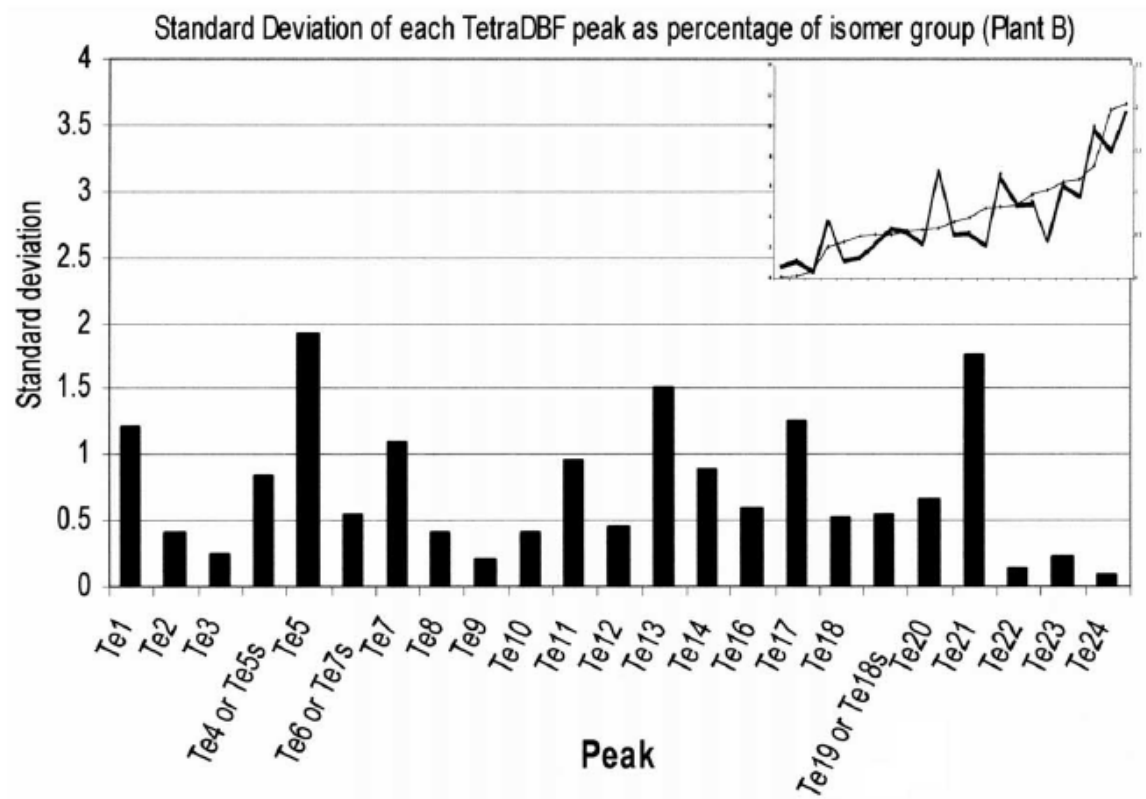
Figure 5. (a) Plant A, tetraDBF mean variation/mean for percentages of total isomer group: all sampling stations included, first station excluded, last station excluded
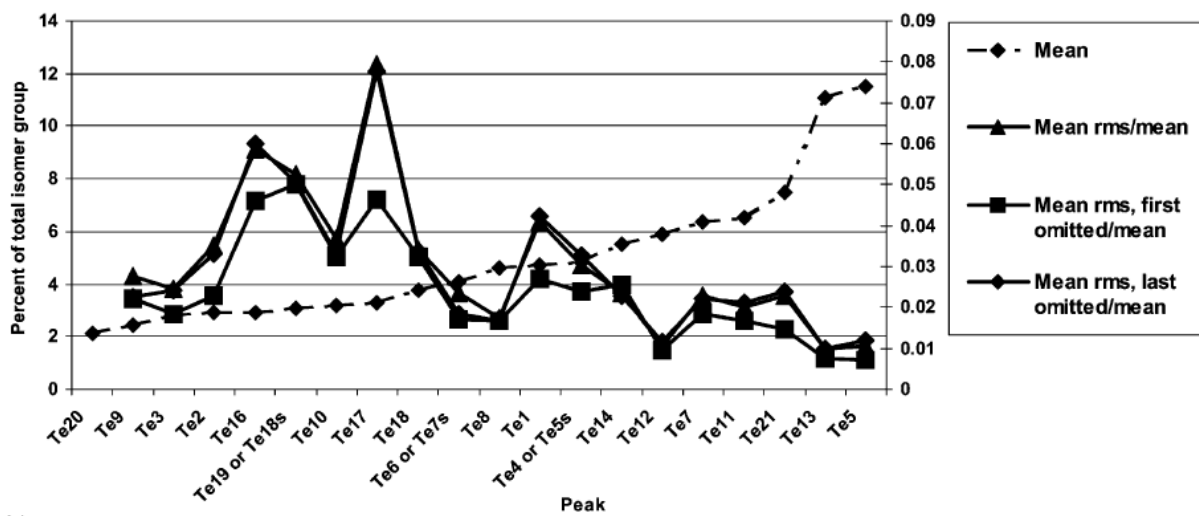


Figure 5. (b) Plant B, tetraDBF mean variation/mean for percentages of total isomer group: all sampling stations included, first station excluded, last station excluded

Figure 5. (c) Plant A, pentaDBF mean variation/mean for percentages of total isomer group: all sampling stations included, first station excluded, last station excluded
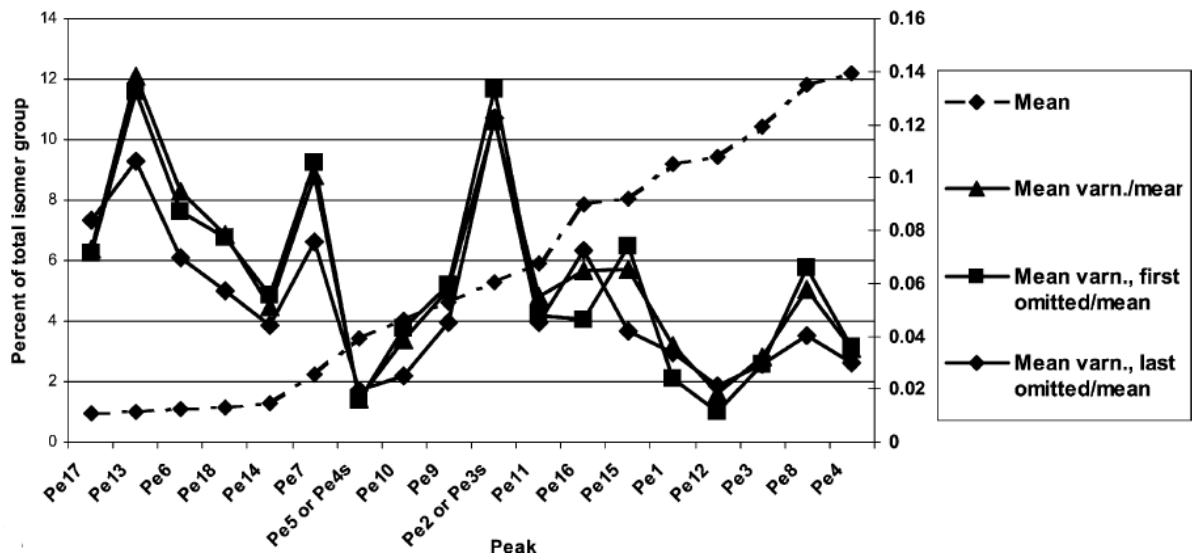


Figure 5. (d) Plant B, PentaDBF mean variation/mean for percentages of total isomer group: all sampling stations included, first station excluded, last station excluded
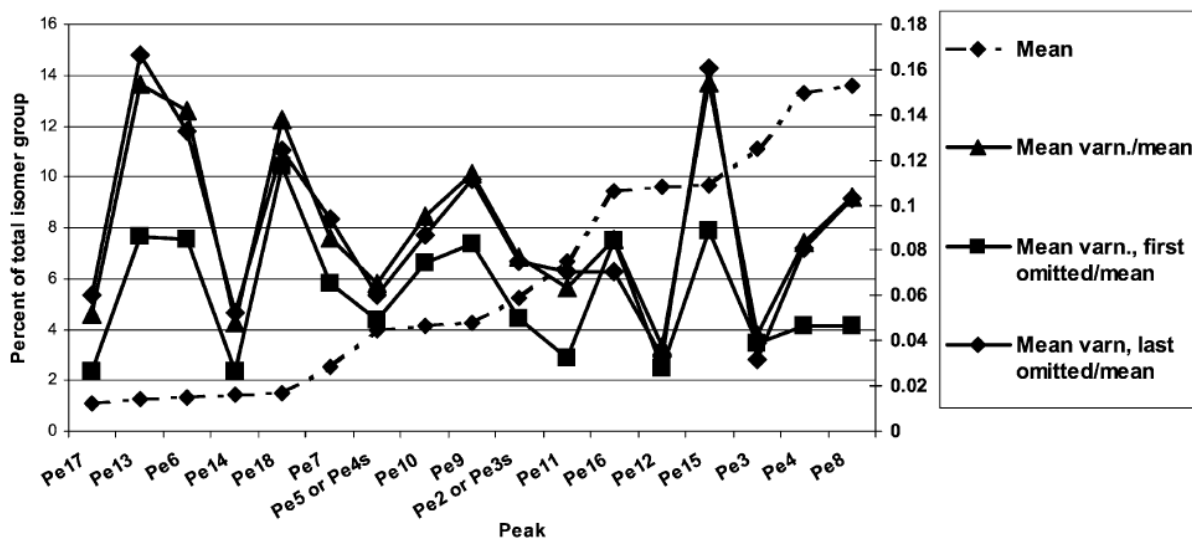
Figure 5. (e) Plant A, hexaDBF mean variation/mean for percentages of total isomer group: all sampling stations included, first station excluded, last station excluded
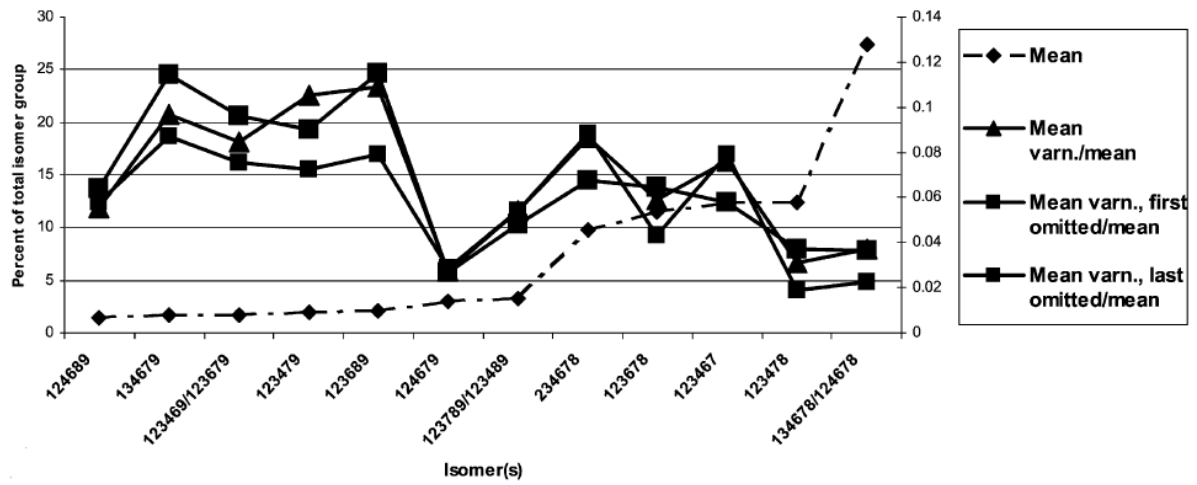


Figure 5. (f) Plant B, hexaDBF mean variation/mean for percentages of total isomer group: all sampling stations included, first station excluded, last station excluded
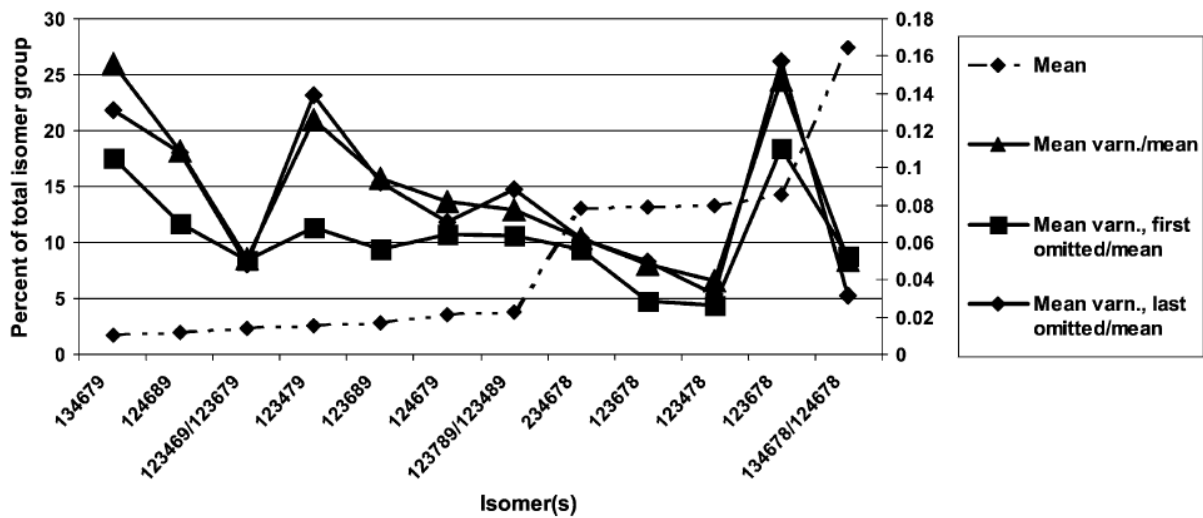
Figure 6. Examples of profiles of variable peaks: variation of percentage due to tetrachlorodibenzofurans Te4 and Te11 with location, Plants A and B
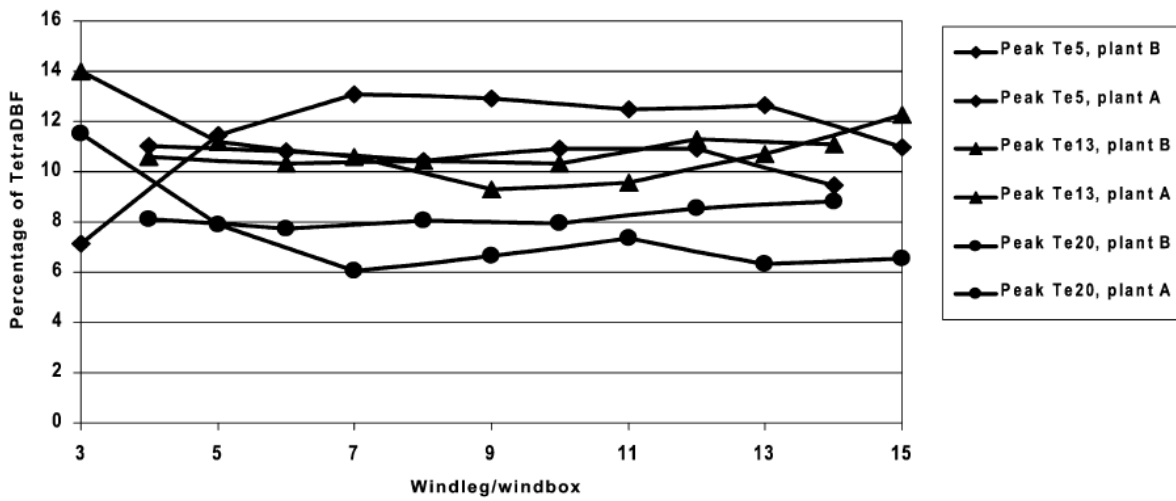


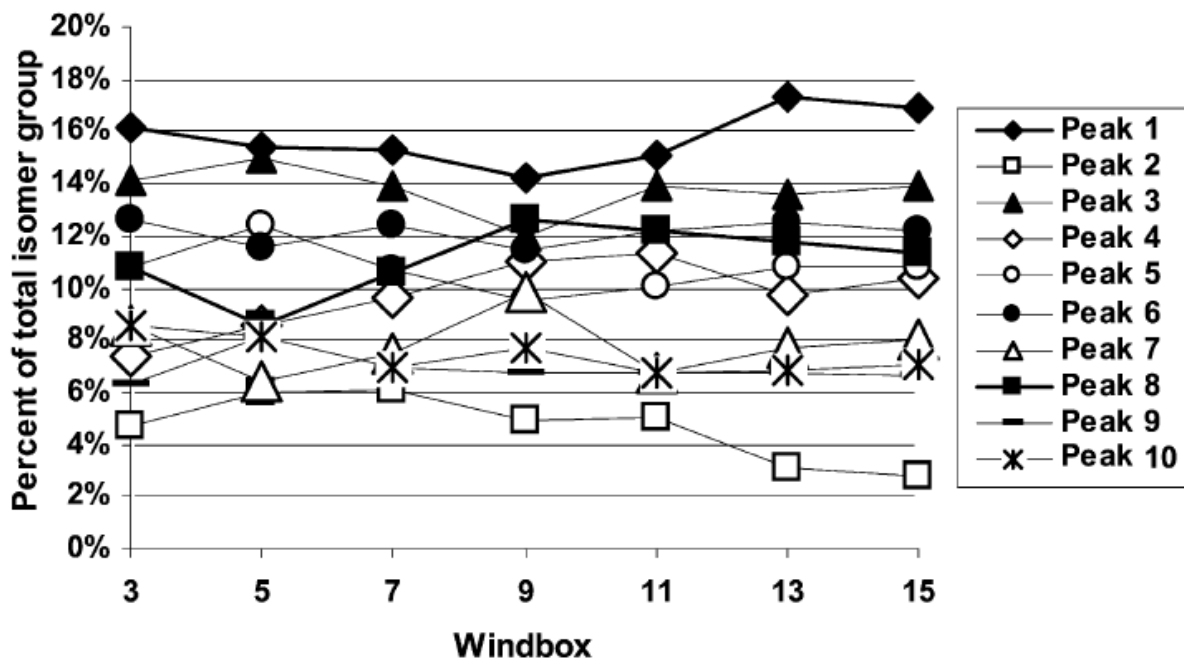Figure 7. Profiles of peak heights of pentachlorodibenzofurans, Plant B

Figure 8. Combined fractional variation of isomer groups at each windleg or windbox
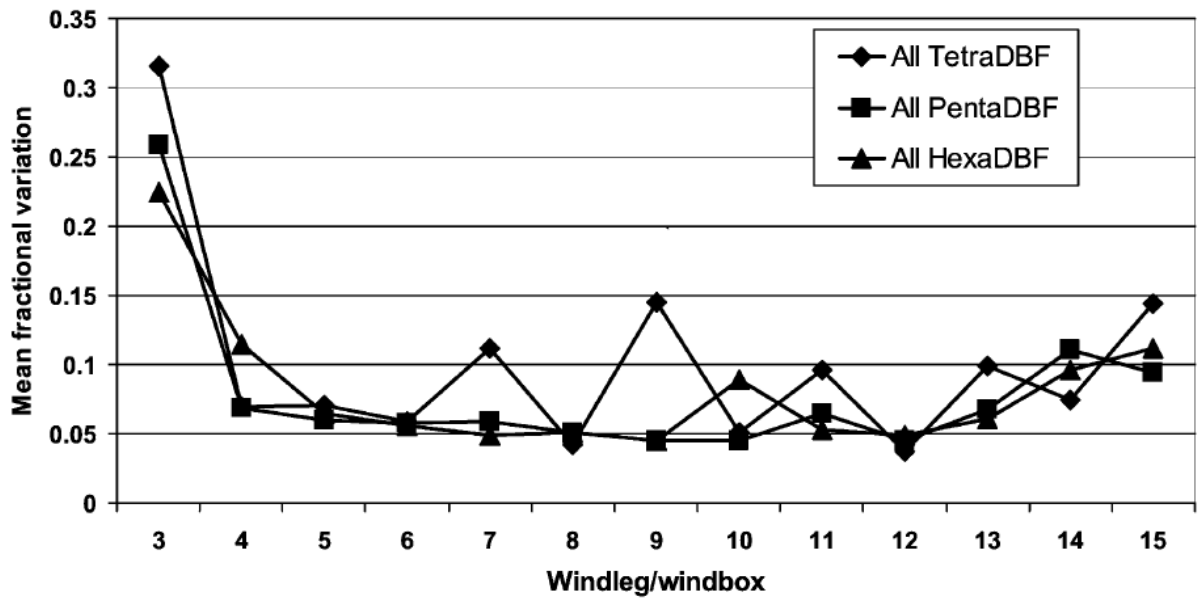
Table 1. Total concentrations of PCDD and PCDF homologue groups in windleg samples from Plant A: (ng/N m$^3$)

| Windleg No. | 4 | 6 | 8 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|
| TetraCDD | 0.14 | 1.49 | 0.91 | 2.45 | 0.59 | 0.85 |
| PentaCDD | 0.42 | 2.50 | 1.61 | 3.15 | 2.03 | 1.74 |
| HexaCDD | 0.63 | 2.53 | 1.31 | 2.40 | 2.49 | 2.68 |
| HeptaCDD | 0.51 | 1.37 | 0.79 | 1.20 | 1.51 | 1.39 |
| OctaCDD | 0.90 | 1.40 | 0.88 | 0.94 | 0.93 | 0.70 |
| TetraCDF | 22.86 | 132.48 | 73.16 | 169.17 | 184.50 | 109.87 |
| PentaCDF | 18.45 | 89.75 | 52.65 | 90.53 | 95.16 | 62.76 |
| HexaCDF | 13.72 | 51.09 | 25.92 | 41.06 | 42.35 | 31.05 |
| HeptaCDF | 4.20 | 13.87 | 6.36 | 9.29 | 8.65 | 8.18 |
| OctaCDF | 1.14 | 3.06 | 1.42 | 2.11 | 2.01 | 1.55 |

Table 2. Example of percentages contributed by each peak to tetra- to heptachlorodibenzofuran chromatogram Plant A, windleg 10

| TetraDBF peak | Percent of isomer group | PentaDBF peak | Percent of isomer group | HexaDBF peak | HexaDBF isomer | Percent of isomer group | HeptaDBF isomer | Percent of isomer group |
|---|---|---|---|---|---|---|---|---|
| Te1 | 3.71 | Pe1 | 9.13 | Hx2 | 123468 | 13.6 | 1234678 | 71.4 |
| Te2 | 2.52 | Pe2 or Pe3s | 6.85 | Hx3 | 134678/124678 | 28.7 | 1234689 | 10.5 |
| Te3 | 2.33 | Pe3 | 10.7 | Hx4 | 123679 | 1.82 | 1234679 | 8.7 |
| Te4 or Te5s | 4.40 | Pe4 | 12.3 | Hx5 | 124679 | 2.99 | 1234789 | 9.4 |
| Te5 | 10.9 | Pe5 or Pe4s | 3.42 | Hx6 | 124689 | 1.33 | | |
| Te6 or Te7s | 3.52 | Pe6 | 1.14 | Hx7 | 123467 | 11.8 | | |
| Te7 | 5.66 | Pe7 | 2.35 | Hx8 | 123478 | 12.3 | | |
| Te8 | 3.77 | Pe8 | 11.1 | Hx9 | 123678 | 10.9 | | |
| Te9 | 2.52 | Pe9 | 4.85 | Hx10 | 123479 | 1.82 | | |
| Te10 | 2.89 | Pe10 | 3.99 | Hx11 | 123469/123679 | 1.49 | | |
| Te11 | 6.48 | Pe11 | 5.85 | Hx12 | 123689 | 1.82 | | |
| Te12 | 5.28 | Pe12 | 9.56 | Hx13 | 234678 | 8.46 | | |
| Te13 | 10.3 | Pe13 | 1.00 | Hx14 | 123789/123489 | 2.99 | | |
| Te14 | 5.47 | Pe14 | 1.28 | | | | | |
| Te15 or Te14s | 0.50 | Pe15 | 7.20 | | | | | |
| Te16 | 3.77 | Pe16 | 7.28 | | | | | |
| Te17 | 4.03 | Pe17 | 0.93 | | | | | |
| Te18 | 5.16 | Pe18 | 1.14 | | | | | |
| Te19 or Te18s | 4.53 | | | | | | | |
| Te20 | 3.27 | | | | | | | |
| Te21 | 7.92 | | | | | | | |
| Te22 | 0.50 | | | | | | | |
| Te23 | 0.50 | | | | | | | |