



Indicator parameters for PCDD/PCDF from electric arc furnaces

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Background

- Sampling and analysis of micropollutants in flue gases increases in complexity and cost as the detection limit is lowered: this applies particularly to ultratrace components such as PCDD/PCDF.
 - The development of indirect measurement methods began in the 1980s. It was then shown that emissions of PCDD/PCDF could be modelled and predicted from analyses of chlorinated benzenes and phenols
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New focus

- A substantial number of papers have been published since then, though most of the work has focused on emissions from municipal waste incinerators.
 - In Europe, however, emissions from waste combustion plants are of less importance today.
 - Instead, much interest and attention is now directed towards other industrial sources, in particular the metallurgical industry.
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Electric arc furnaces

- A recent environmental strategy paper suggested that electric arc furnaces are the only industrial sources with constant or increasing PCDD/PCDF emissions to air.
 - Emissions from electric arc furnaces (EAF) have been monitored on a regular basis in Sweden since the 1980s, and most analyses have encompassed not only PCDD/PCDF but also chlorinated benzenes and phenols.
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Scope

- The purpose of the current investigation was:
 - to extend and update these previously reported models with the new samples from EAF,
 - to describe the main sources of variation,
 - and to compare multivariate calibration with univariate regression.
 - Furthermore, from the outcome it should also be possible to give recommendations for the practical use of these models in process optimisation, control of flue gas cleaning systems and monitoring of emission levels.
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Samples

- The data set evaluated in this investigation consisted of 23 flue gas samples collected between 1987 and 2002 from electric arc furnaces at Swedish steel mills.
 - Four additional samples were included from a study of adsorbents in a pilot scale electric arc furnace at the Metallurgical Research Institute in Luleå, Sweden.
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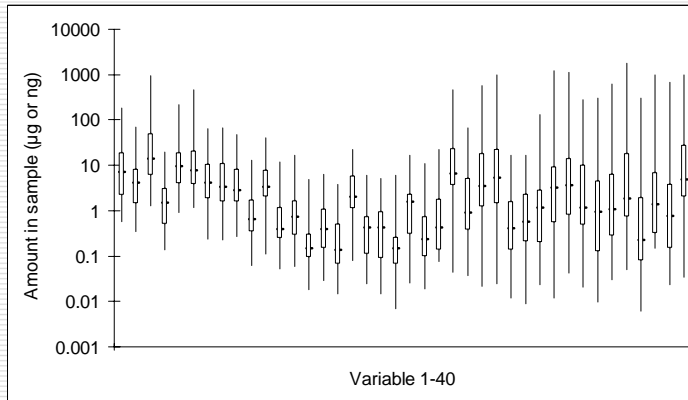
Censored data

- Censored data, with substantial portions of the data below the limit of detection (LOD), are common in environmental applications.
 - In this investigation the LOD values in one sample were often higher than the reported positive identification for the same variable in another sample, and assigning a value related to the detection limit could then add noise, hide data structures and weaken correlations.
 - Data below the LOD were therefore treated as missing values.
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Variables and pre-processing

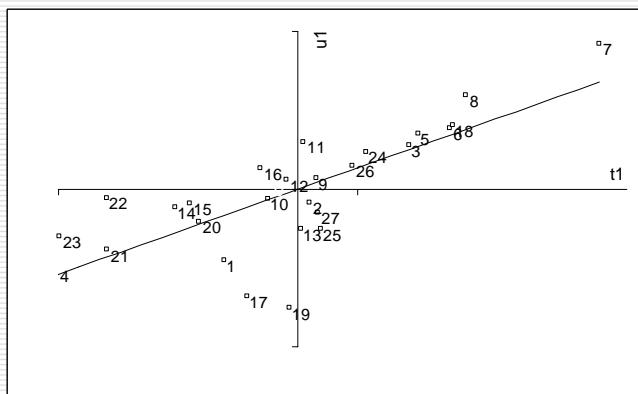
- X-variables:
 - 10 congeners of chlorobenzenes.
 - 12 congeners or group of congeners of chlorophenols.
 - Y-variables:
 - 17 congeners of PCDD/PCDF + WHO-TEQ.
 - Skewed frequency distributions and different scales.
 - Pre-processing: Log-transformed and auto-scaled to zero mean and unit variance.
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Box-Whisker plot



Minimum, 1st quartile, median, 3rd quartile and maximum values, logarithmic scale.

A general PLSR2-model

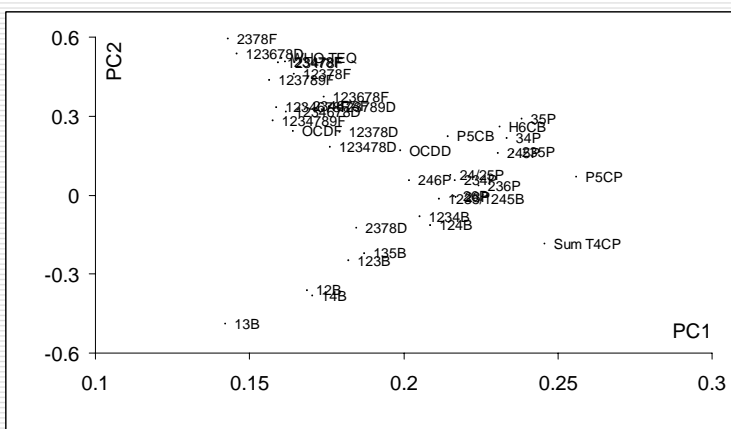


Samples 17 and 19 were from tests with adsorbent injection before flue gas cleaning.

Explained variance

- A model with two significant components explains 68% of the variance in Y and 88% of the variance in X.
- The X- and most of the Y-variables line up with increasing degree of chlorination, and hence also molecular weight and volatility.
- This correlation pattern has been reported previously, and it is a prerequisite for the success of a multivariate calibration approach to this task.

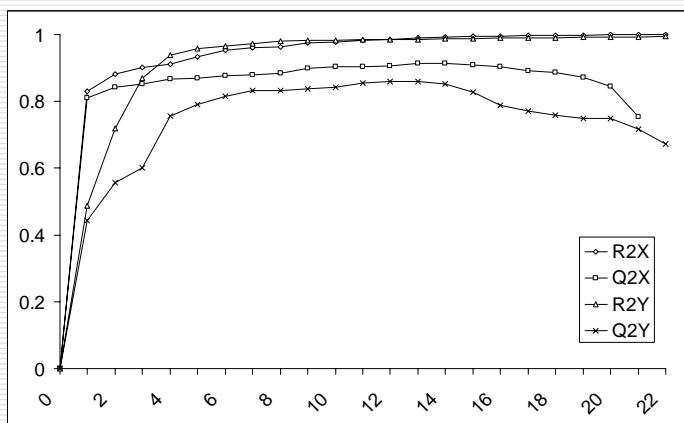
Loading weights and Y-loadings



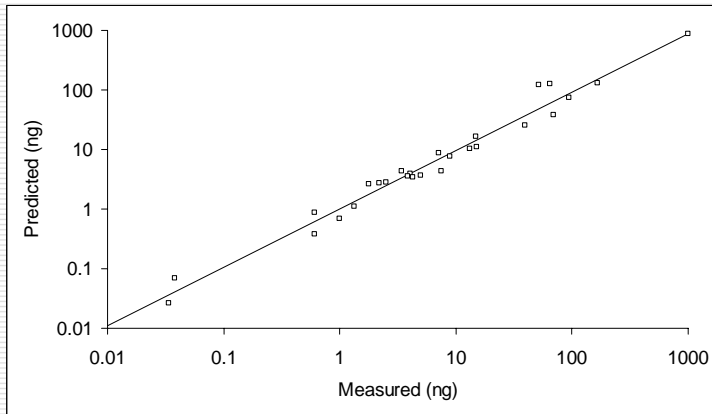
A specific PLSR1-model

- A PLSR1 model often has better predictive ability than a PLSR2 model, and nonlinear structures can sometimes be modelled by including additional factors.
- Focus on one of the dependent variables, namely WHO-TEQ, because it is used for compliance reporting and expresses the environmental significance.
- The optimal rank of the PLSR1 model was estimated to seven components, $R^2_Y = 0.974$ and $Q^2_{Y,LOO} = 0.834$.

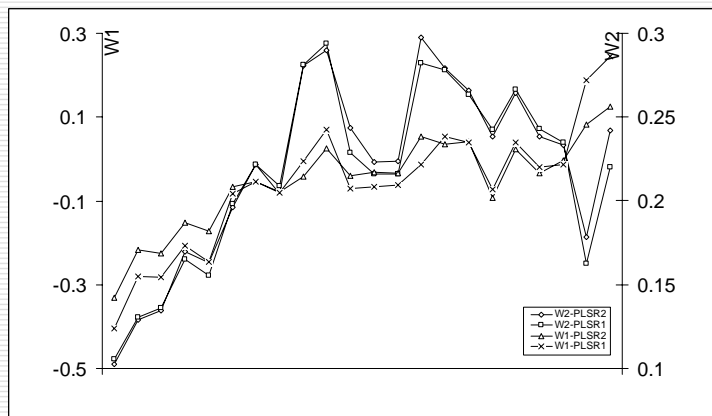
Explained variance vs. components



Five orders of magnitude



Similar structure as PLSR2



Is PLS-regression too complex?

- It has been suggested that PLS regression is an unnecessary complicating step in using chlorinated benzenes and phenols as indicator parameters for PCDD/PCDF.
- Most investigations have instead focused on finding univariate regression relationships to specific congeners, groups or the sum of chlorinated benzenes or phenols.
- The present data set provides an opportunity to compare these different approaches.

Comparison with univariate regression

Univariate linear relationships between WHO-TEQ and some suggested indicator parameters (log-transformed data).

Parameter	n	R ²	Q ²	Parameter	n	R ²	Q ²
DCB	27	0.203	0.057	DCP	26	0.423	0.341
T3CB	27	0.343	0.260	T3CP	27	0.447	0.360
T4CB	27	0.398	0.317	T4CP	23	0.507	0.404
P5CB	27	0.456	0.366	P5CP	24	0.547	0.462
H6CB	27	0.537	0.456	Sum CP	27	0.415	0.308
Sum CB	27	0.264	0.142				

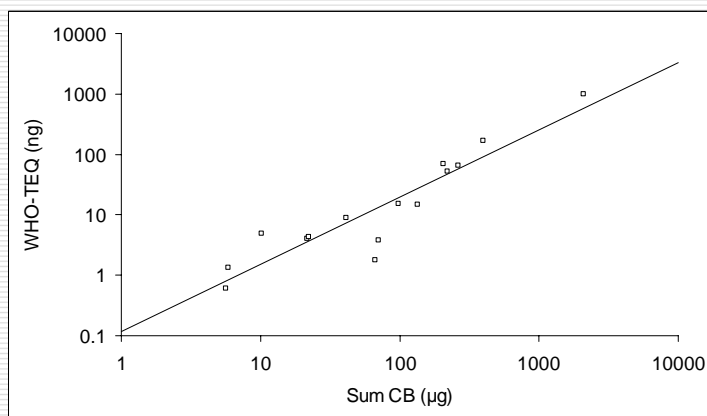
Limitations in univariate regression

- ❑ Hexachlorobenzene was the first variable to be suggested as an indicator parameter for PCDD/PCDF.
 - ❑ It is one of the best univariate relationships for this data set, but is clearly outperformed by the PLSR1 model shown previously.
 - ❑ The variation between plants and processes is due to variations in halogen input and efficiency of flue gas cleaning, and both of these factors affect congener patterns of all chlorinated aromatics in the flue gas.
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In-plant process studies

- ❑ Univariate approaches can be useful in process studies that are performed within a specific plant.
 - ❑ Fifteen of the samples in this study came from the same steel mill, and here the correlation between PCDD/PCDF and the sum of chlorinated benzenes was much better,
 - ❑ A PLSR1 model with two significant components gives only a slightly better performance, with $R^2_Y = 0.938$ compared to 0.852 and $Q^2_{Y,LOO} = 0.815$ compared to 0.811.
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Univariate model in-plant



Conclusions

- The amounts and distribution of various chlorinated aromatic compounds in the flue gases from electric arc furnaces vary substantially.
- It is possible to predict the amounts and congener composition of PCDD/PCDF from the amounts and congener composition of chlorinated benzenes and phenols.
- A multivariate calibration model provide an adequate description of variations in the WHO-TEQ value over almost five orders of magnitude.

Conclusions cont.

- Comparison with univariate regression show that models thus simplified do not give an adequate description of the whole data set.
 - In contrast, measurement data from a single plant show that univariate regression within a limited domain can perform equally well as a multivariate calibration.
 - This is also the likely background to why so much research effort has focused on this approach, i.e. studies performed within single plants.
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Recommendations

- Use of indicator parameters for emission monitoring and evaluation of flue gas cleaning efficiencies are best performed with multivariate calibration models.
 - In process optimisation studies not involving the flue gas cleaning system, univariate regression models usually perform equally well.
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Acknowledgements

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