

Dioxin surrogates - a comparison of approaches

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Aim and scope

- The term "dioxin surrogate" is used to describe substances that show a close correlation to PCDD/PCDF concentration
- This review focuses on surrogates for thermal formation of PCDD/PCDF with the scope to evaluate which approach might be useful for process control

Why use surrogates?

- The standard dioxin analysis procedure by sample collection, sample clean up and HRGC/HRMS is time consuming and expensive
- As a consequence, lack of representativity is a main source of error in many investigations and monitoring schemes

Background

- Already in 1977 Olie, Vermeulen and Hutzinger reported on the simultaneous occurrence of chlorinated dioxins, dibenzofurans, phenols and benzenes in flue gas from municipal incinerators in the Netherlands
- Chlorobenzenes were also the first compounds to be suggested as surrogates (Öberg & Bergström, 1985)

Tentative classification of approaches

1. Observation of feed quality (chlorine content) or operational parameters
2. CO (combustion efficiency) or a thermally stable indicator added
3. Summary parameters, e.g. TOC or VOC
4. Likely precursors or by-products of dioxin formation reactions
5. Non-2,3,7,8-substituted congeners or homologous groups
6. Single PCDD/PCDF congener representing toxicity
7. Multiparametric approaches, e.g. operational parameters or several single compound signals

Correlation

- The linear relationship between variables can be presented as:
 - Correlation coefficients (r), or
 - Coefficients of determination (r^2)
- These measures of correlation does not by themselves tell anything about
 - Statistical significance (size of data set, distribution)
 - Range/domain
 - Predictive ability
- But, in many (most) publications these are the only quality measures presented

Carbon monoxide (CO)

- Has a high thermal stability, and is an excellent indicator for final oxidation
 - Consequently related to all groups of organics present in stack effluents from combustion
- Correlation with dioxins is easily masked if variations are small or if an efficient flue gas cleaning removes high boiling compounds.
 - Hence, investigations of the correlation with dioxins have yielded inconsistent results

Chlorine input

- It is now generally accepted that the chlorine input has an influence on the formation of PCDD/PCDF in thermal processes
- The chemical form of chlorine in the fuel does not matter much, since a major portion is converted to HCl in the combustion chamber

Chlorine input, cont.

- In most practical situations other operational parameters (e.g. temperature and combustion efficiency) are of equal or more importance
- The univariate correlation between chlorine input or HCl and chlorinated organics is weak if:
 - the chlorine content in the feed is stable
 - the combustion conditions are unstable, or
 - an efficient flue gas cleaning is installed

Summary parameters

- Unburned organic carbon (VOC/TOC) is like CO a parameter characterising the combustion quality (efficiency of final oxidation)
 - The same limitations applies as for CO, and a weak correlation was reported from one study
- A more specific summary parameter, semi- and non-volatile organohalogen compounds (SNVOX) showed a much better correlation
 - $r^2=0.75-0.83$ in various MSWI plants

Chlorobenzenes and phenols

- Most of the literature on dioxin surrogates deals with chlorinated benzenes (PCBz) and phenols (PCPh)
 - Many studies report a good correlation between sum or/and individual congeners of PCPh and PCDD/PCDF
 - The correlation with PCPh does however seem to show a large portion of plant-dependence

PCBz and PCPh, cont.

- Many studies are available on the correlation between chlorobenzenes and dioxins in waste incineration, both HWI and MSWI
- The close correlation between PCBz and PCDD/PCDF, and the easy measurability have resulted in the use of these compounds as surrogates in most on-line monitoring systems

PCDD/PCDF congeners

- Several lower chlorinated PCDD/PCDF congeners (Cl₁-Cl₃) have been shown to correlate with the I-TEQ of PCDD/PCDF
- In most thermal processes 2,3,4,7,8-Cl₅DF is a major contributor to the I-TEQ value
 - The correlation was reported to be excellent ($r^2=0.98$) in a study of some MSWI plants

Other compounds

- Chloroalkanes and chloroalkenes are being discussed as surrogates
 - HWI, C_2HCl_3 $r^2=0.65$
 - MSWI, C_2Cl_4 and C_2HCl_3 , $r^2 \sim 0.6$
- Other studies report correlations with PCB, PCN, PAH
 - PAH will of course show the same limitations as CO and VOC

Multiple parameters

- Partial least squares regression (PLSR) have been used to predict PCDD/PCDF from multiple individual congeners of chlorophenols and chlorobenzenes
 - These type of models have been applied to HWI, MSWI and metallurgical processes ($r^2=0.92-0.98$)
 - The congener (chlorination) pattern were shown to account for both variations in fuel composition and flue gas cleaning efficiency
- Plant-specific models reached the same overall precision as direct measurement of PCDD/PCDF

Summing up

Chemical similarity and correlation !

CO, VOC/TOC, PAH, chlorine input, HCl

Chloroalkanes and chloroalkenes

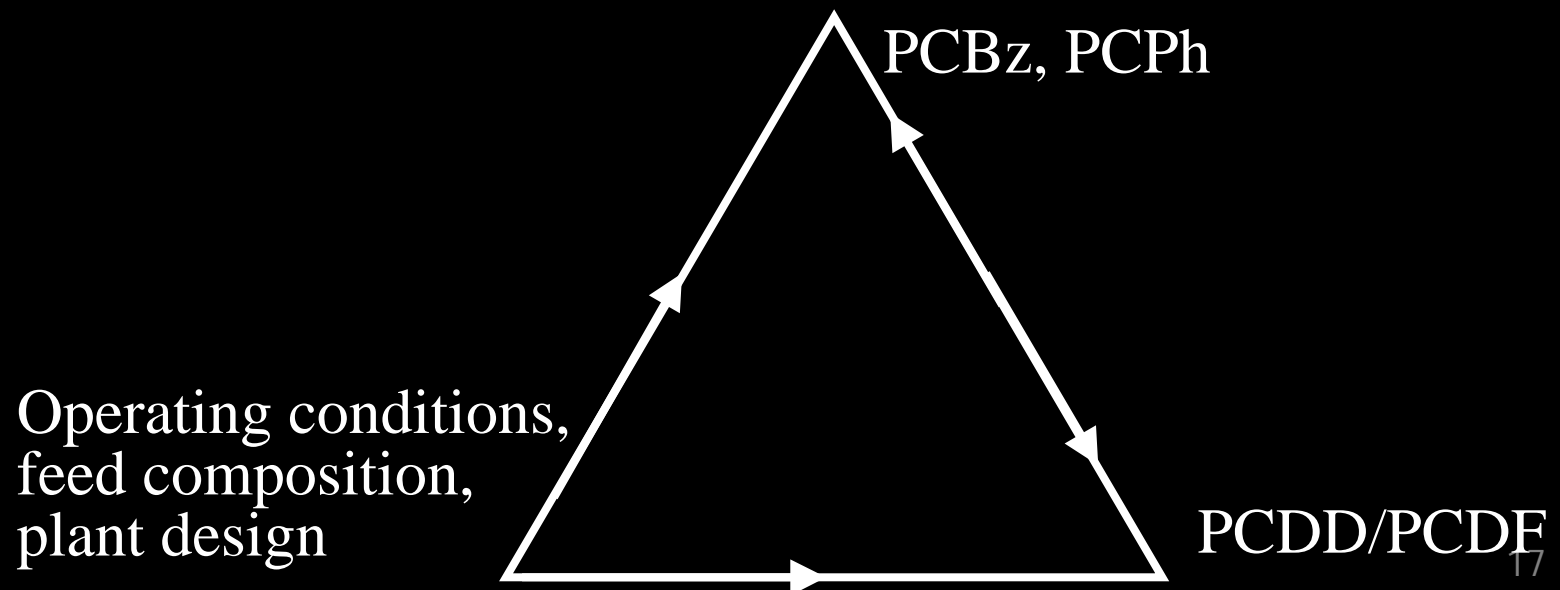
PCBz, PCPh, PCB, PCN, SNVOX

PCDD/PCDF

TEQ

Summing up, cont.

- Reichenbach's Common Cause Principle
 - A correlation between events A and B indicates either that A causes B, or that B causes A, or that A and B have a common cause



Conclusions

- There are a multitude of compounds and other parameters which can serve as indicators for dioxins in combustion stack gases
- However, many of these correlations are plant specific, also depending on operating conditions, feed, sampling points, etc.
- Most promising as surrogates are chemically similar compounds, such as other chloroaromatics (incl. SNVOX)

Conclusions, cont.

- The complexity of thermal formation and other factors influencing emissions indicates that a combination of parameters is justified
- Plant specific models considering multiple parameters have already proved to give reliable estimates
- Application of the surrogate principle to on-line monitoring, process control and optimisation in all kinds of thermal processes is promising and well worth exploring