

SAMPLING INCINERATOR EFFLUENTS FOR PCDDs AND PCDFs : A CRITICAL EVALUATION OF EXISTING SAMPLING PROCEDURES

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Abstract

The chemical analysis of PCDDs and PCDFs is nowadays considered to pose no longer a serious problem. Much larger errors can be made during the sample collection in the stacks of incinerators. In this paper, the potential artefacts that can occur are summarized and a very simple sample collection procedure is suggested, which minimizes the possibility of chemical artefacts and ensures a complete recovery of sampled organochlorinated compounds.

Introduction

After PCDDs and PCDFs had originally been demonstrated in a number of fly ash samples from below electrostatic precipitators of municipal waste incinerators, scientific interest focused on the analysis of fly ash, the more because this could be collected more conveniently. As a result, dioxin emissions were initially believed to be mainly associated with the solid phase (1,2) and for many years the emitted particulates rather than the total emissions were being studied. Collection of a representative particulate matter sample from the stack necessitates an isokinetic and isoaxial sampling technique. Non-isokinetic sampling conditions result necessarily in non-representative particulate matter samples, the error being greatest for particles larger than $5\ \mu\text{m}$ (3), which contribute significantly to the weight of emitted particles. Smaller particles (e.g. soot) tend to follow the deviations of the gas stream and sampling errors will be small. Organic emissions in the solid phase are predominantly associated with particles having a diameter below $5\ \mu\text{m}$ but the largest surface. Beyond that, isokinetic sampling procedures assume an ideal laminar flow. Benarie (4) states that in a non-laminar flow, a non-isokinetic sampling of particulate matter does not provoke any significant concentration differences nor differences in size distribution. Very often, sampling conditions cannot be regarded as ideally laminar because of the bent ducts, the presence of induced draft fans, etc. In view of these non-ideal sampling conditions, the error introduced by a non-isokinetic sampling will be relatively small.

Before 1980, no attention had been paid to the gas/solid distribution of these compounds, in spite of the elevated temperatures encountered at the sampling site. At that time, Cavallaro et al. (5) reported them to be present predominantly in the vapor phase. Their results supported our preliminary findings (6) and we decided to concentrate our sampling efforts on the vapor phase. Since gaseous species are distributed uniformly over the cross-sectional area of the flue, their concentration is the same everywhere and less severe constraints are imposed upon the sampling procedure. Consequently, a less cumbersome and less expensive technique can be used.

A second important aspect is the possibility of artefacts, that may alter both the physical and chemical composition of the sample while being collected. Several authors described a number of experiments, that were intentionally conducted to provide evidence for the strong catalytic potency of fly ash. These experiments point in our opinion to the possibility of serious artefacts to occurring in situ during the sampling of the hot effluent.

In this article, the existing sampling techniques and the methods of validation will be surveyed. The arguments in support of our approach will be presented and discussed.

Scientific experience from model experiments

A systematic evaluation of occurring arteficial phenomena during the sampling requires either carefully designed and rather complex on stack experiments or laboratory tests under similar conditions. Sonnichsen et al. (7) tried out the two approaches. They injected various "tracers", isotopically labelled polyaromatic hydrocarbons, at a controlled rate through a heated probe in the effluent gas of coal-fired boilers, to evaluate the recovery of their sampling procedure. Under field conditions, recoveries were in general very poor and discrepant (from zero up to over 1400 %, gas and solid phase combined). There was a significant scatter in the data obtained from laboratory experiments as well, although average recoveries approached a 100 %. This fully justified their conclusion "that the use of tracers as a means of correcting sample losses is not recommended, until these phenomena (i.e. the occurring artefacts) are better understood". This is at present certainly not the case.

More recently, Hagenmaier et al. (8) and Rappe et al. (9) experienced the same difficulties when attempting to validate their sampling methods for PCDDs and PCDFs under field conditions (municipal waste incinerators). They added isotopically labelled standards to the filter before the sampling was started, an approach that is inferior to the previously described one. In spite of the poor results, some authors (9, 10) still advocate the application of such standards to compensate for the rather large yet unexplained losses during the sampling.

The validity of such a correction procedure can be questioned seriously. First, it takes no account of the distinct interaction forces that prevail between organic compounds sorbed onto co-entrained particulates during the transport within the ductings of the plant and organics that are simply deposited on the filter material. Second, added standards have a longer residence time on the filter as compared with the average residence time of the emitted PCDDs and PCDFs. Third, losses will be different for different congener groups and classes of compounds. Finally, we think that this approach can only be adopted with confidence if the fate of the lost compounds is known, which is not true at present.

Alternatively, laboratory experiments have been carried out. However, the actual on stack situation is very complex, involves many parameters and is difficult to control or imitate. Furthermore, the unique composition and morphology of particles generated during high temperature processes in general and during the combustion of municipal waste in particular impose important restraints on most laboratory conducted experiments: these are usually carried out with electrofilter fly ash.

Indeed, the peculiar properties of a given particulate sample constitute an important parameter that is beyond the scientist's control but that may vary considerably from sample to sample. Still, for practical reasons most researchers use electrofilter fly ash instead of on stack collected particulate material, assuming that the surface chemistry of larger particles is similar to that of the finer fly dust (11). However, fly ash is an average particulate matter sample containing particles with relatively large and widely ranging size, which has been reported to reach up to 850 μm (12).

The sample-to-sample divergence is clearly illustrated by the following experimental observations:

- the wide variability in sorption capacities of different polymeric carbons (13);
- the large differences in the oxidation rates of polyaromatic hydrocarbons when distinct coal fly ash samples are used (11);
- the dependence on the source of the relative distribution of organics among various size fractions of fly ash (12);
- the varying yields of PCDDs produced out of P₅CP using fly ashes from different sources (14, 15);
- the different extraction efficiencies obtained for different samples from the same incinerator (own data, to be published elsewhere);

- the varying increase in concentrations of PCDDs and PCDFs upon oxidation in air for fly ashes from different origins (16).

All these factors limit the validity of laboratory experiments simulating conditions similar to those in stack sampling. This should be kept in mind when interpreting the data from such experiments. Furthermore, the conditions used should be verified in detail, because a small deflection from the actual on stack circumstances may have important repercussions on the results.

Artefacts concerning the sample's integrity

Physical integrity

Artefacts that may alter the physical composition of a particulate matter sample during the collection are either loss, elution of sorbed organics out of the solid material retained on the collection medium, or the opposite process, sorption of gaseous compounds present in the flue gas by the particulate matter or the collection medium material. The general term sorption is used here to emphasize the complexity and variety of possible interaction mechanisms between solid carrier and gas molecule. Both processes strongly depend on the same physical and physicochemical characteristics of the effluent (temperature, pressure, sampling velocity, composition), collected particulates (surface area and composition, porosity, sorption characteristics), organics studied (vapor pressure, concentration, volatility, interaction ability with the solid phase) and on the sampling technique (collection efficiency for fine particles, pressure drop over the collection medium, reactivity of the materials used).

In both incinerators studied, the flue gas temperature at the sampling point is between 250 and 300 °C, which are the temperature limits for the operation of this type of electrostatic precipitators. The vapor pressures of the compounds studied under stack conditions are sufficiently high to allow a sizable fraction of these compounds to be found in the gas phase. However, care should be taken with such a straightforward approach : it takes no account of the non-equilibrium nature of the processes involved nor of kinetic effects nor of the sorption forces between particle and organic compounds. On the basis of adsorption experiments with polyaromatic hydrocarbons on both coal and municipal incinerator fly ash, Eiceman et al. (17) concluded that at least two basically different sorption mechanisms are occurring. The first is an exceptionally strong, irreversible chemi-sorption, which would lead to a reduction or even inhibition of extractability of the sorbed compounds. The second is a weaker, reversible adsorption on the surface of the particulates, which would result in severe losses by thermal elution. The latter mechanism is determined mainly by vapor pressure-controlled condensation.

The occurrence of evaporative losses of semivolatile organic compounds (e.g. aliphatic and polyaromatic hydrocarbons) out of airborne particulate matter loaded on a filter during the sampling at ambient and at stack temperature was frequently suggested in the literature (18, 19). This artefact was unambiguously demonstrated by Van Vaeck (20). Similar experiments at higher temperatures confirming the thermal elution of PCDDs were carried out by Dickson et al. (21). However, a substantial volatilization is obtained only if the contact between effluent and fly ash is intimate. Vogg et al. (22) placed a large amount (20 g) of fly ash in a crucible and, when heating this, they observe only at a temperature of 400 °C that PCDDs and PCDFs vaporize and are found in the air passing through the furnace.

The occurrence of the opposite process, sorption of gas phase organics, is more probable at lower temperatures. Natusch (23) investigated coal-fired power plants and reported the polyaromatic hydrocarbon concentration (expressed in ng/m³) associated with the particulate matter emitted, to increase significantly following emission into the atmosphere in spite of the evident dispersion. This was explained by a sorption of co-entrained organics in the gas phase, which was unfortunately not sampled, onto emitted particles with the temperature decrease.

A considerable decrease in temperature also occurs if a particulate collection device mounted outside the flue is used for the sampling, even if this device is heated. Consequently, condensation of water vapor and volatile organics may occur. While cooling down, these organics may form condensation particles or may adsorb on the surface of the already collected particulate matter or collection material, tubings, the probe

walls, etc. As a result, the observed gas/solid distribution will not reflect the actual distribution of the stack emissions. Moreover, important losses may occur.

Chemical integrity

The influence of chemically active compounds in the gas phase (e.g. SO₂, NO_x, HCl) on the integrity of analytes present in the collected sample (either particulate matter, condensed liquid or loaded gas trap) during the sampling period is a major concern. Beyond that, the specific properties of this solid matrix may cause serious artefacts : fly ash is not an inert substrate, but conversely it may promote or inhibit various types of chemical reactions of sorbed organics. Electrofilter fly ash from municipal waste incinerators has been tested extensively by the research groups of Eiceman and Karasek. Originally, these experiments were set up to demonstrate that certain chemical reactions can occur between an organic molecule and a chlorine source (usually HCl). However, the conditions used in these laboratory tests depart too wide from the actual situation in stacks to allow balanced conclusions. First, an expanded bed of fly ash is used. Second, the reaction times are considerably longer than the residence time of fly ash and dust in the combustion chamber, in the ductings or in the hot zone of the electrostatic precipitator. Third, most experiments are conducted only once, hence it is impossible to distinguish between the role of certain organic compounds sorbed onto fly ash and the role of certain elements with catalytic properties.

These reactions can roughly be divided in two major types : chlorination reactions (24,25,26,27,28) and thermal dioxin formation/destruction reactions (8,14,15,16,22,27,28).

Avoiding artefacts

From the discussion above, it will be obvious that it is impossible to freeze the on stack gas/solid distribution. Any change in temperature induced by the sampling equipment necessarily alters the physical composition of the effluent. The collection of particulate material from hot flue gases will inevitably lead to thermal elution losses of semivolatiles compounds, provided that they are already present in the solid phase under such circumstances. Beyond that, important chemical artefacts that may resemble the actually occurring formation/destruction reactions of PCDDs and PCDFs possibly occur during the sampling of particulate matter at temperatures between 100 and 300 °C, which are typically prevailing on stack or if a heated sampling probe is used. At nearly ambient temperature however, these artefacts are far less important - if occurring at all.

It is obvious that the major objective of the sampling procedure should be the avoiding of chemical alterations rather than trying to overcome the inevitable thermal evaporative losses. Given the fact that hot fly ash (or dust) thereby plays an essential role as catalyst, the contact time between high temperature particulates and flue gas constituents on the one side and the compounds under study or their possible precursors (either sorbed onto fly dust or in the gas phase) on the other, should be as short as possible to simulate the actual emission conditions.

This can be achieved in two ways :

- a drastic and sudden cooling of the collected particulate matter in a way that resembles the cooling of the hot effluent upon discharge into the atmosphere. This implies that an out-of-stack particulate collection and, in view of the high sampling velocity, a sufficient cooling must be provided. Such a sampling device (e.g. the Strohleim apparatus) is quite complex and costly;
- a separate collection of the fly ash on a filter while still hot and of the gaseous compounds. The effluent of the combustion chamber should normally contain only low concentrations of organics. While the temperature shortly after the electrostatic precipitator remains between 250 and 300 °C. Under these conditions, the probability of condensed particle forming on stack is rather small, leaving most compounds in the vapor phase or sorbed by weaker forces on the surface of co-entrained particles (3).

A drastic cooling of the effluent has several practical disadvantages :

- the major part of organics will be sorbed on the fly dust, which thereby acts as a thin bed of solid sorbent, the sorption capacities of which are not characterized; condensation particles, which tend to coalesce, will form. The solid matrix thus generated is difficult to extract;
- the required sampling equipment is rather complex;
- important losses may occur due to the adherence of particles and the condensation of gaseous compounds on the walls of the cooler devices and connections of the sampling train; these losses may be sizable because the more complex the sampling equipment is, the more difficult to recuperate quantitatively the compounds are;
- to ensure a complete trapping of all organic compounds, a gas phase collection device has to be provided even if the temperature is reduced to ambient.

Hence, we preferred the second approach, which will now be described in more detail.

Description of the sampling device

Our simple collection device consists of a stainless steel filter holder carrying the glass fiber filter (diameter 2 cm), placed on stack, and a Tenax® gas adsorption trap, installed in series out of stack. Condensation/expansion flasks, a suction apparatus and a gas meter are also provided. Typically, only 1 m³ of flue gas is sampled at a sampling rate of about 6 l/min under approximately isokinetic conditions, thus avoiding obstruction of the filter.

After each collection period, the condensation flasks and the gas tubing preceding the adsorption trap, which is deliberately very short, are thoroughly rinsed with n-hexane and the samples (loaded filter, condensed water with rinsing solvent, Tenax® trap) are stored in the dark. The filters are packed in aluminium foil; the gas adsorption trap is stoppered and kept at - 18 °C.

Results and discussion

Samples were collected at the Ghent and Merksem incinerator.

Table 1 shows the average observed gas/solid distribution for all available and complete samples for the PCBzs, PCPs, PCDDs and PCDFs (abbreviations, see Table 1). Samples containing a total concentration (gas and solid phase combined) near the limit of detection are not included. Within each sample, the relative vapor pressure correlates fairly with the gas/solid distribution, although intersample variations may be large. Since the vapor pressure decreases with the increasing degree of chlorine substitution within one class of compounds (29), the fraction of lower chlorinated congeners present in the solid phase will be smaller as compared with the fraction of higher chlorinated ones. The few exceptions observed can be explained by other sorption mechanisms : Dickson et al. (21) already suggested that the vapor pressure may be a major but not the only factor that determines the gas/solid partitioning.

The data presented do not pretend to reflect the true gas/solid distribution in the stack. They merely indicate what fraction of organics is collected in the heated (250 to 300 °C) portion of the train and illustrate the effect of the relative vapor pressures on the gas/solid partitioning. Under these sampling conditions, the fraction of organics remaining in the solid phase is on the whole very low. This is particularly true for the PCBzs and PCPs, which have been suggested to be potential precursors of the PCDDs and PCDFs, and for the lower chlorinated PCDDs and PCDFs, congener groups that contain the most toxic isomers. Occasionally, the fraction of higher chlorinated congeners present in the fly dust is substantial. Hepta- and octachlorinated congeners are the least toxic ones and are less affected by a possible in situ chlorination artefact.

In view of the specific sampling conditions (elevated temperature, relatively low particle load, fast sampling velocity, moderate HCl concentrations) we do not believe the previously described chemical artefacts to be responsible for these observations. We believe that they can be explained by a thermal

elution and/or the actual gas/solid distribution in the stack effluent. Which of either two phenomena is the most prominent one cannot be derived from these data.

Table 1 : Average fraction found in the particulate phase ($\pm \sigma_{n-1}$, number of observations between brackets)

Compound	Sample origin	
	Ghent	Merksem
T ₄ CBz	0.2 ± 0.5 (21)	0 (12)
P ₃ CBz	1.9 ± 4.3 (21)	0.1 ± 0.2 (12)
HCBz	4.3 ± 11.3 (21)	0.3 ± 0.3 (12)
DCP	0 (21)	0 (10)
T ₃ CP	0 (21)	0 (12)
T ₄ CP	1.6 ± 4.9 (21)	1.5 ± 3.2 (12)
P ₃ CP	4.8 ± 12.2 (21)	5.9 ± 8.6 (12)
T ₄ CDD	0 (11)	-
P ₃ CDD	0.2 ± 0.6 (15)	-
H ₄ CDD	2.7 ± 7.2 (18)	0 (5)
H ₃ CDD	8.7 ± 16.5 (19)	11.3 ± 31.0 (10)
OCDD	18.1 ± 26.5 (19)	15.7 ± 29.5 (10)
T ₄ CDF	0.5 ± 0.6 (18)	0 (3)
P ₃ CDF	1.0 ± 2.1 (18)	0 (6)
H ₄ CDF	3.1 ± 6.3 (18)	0 (5)
H ₃ CDF	2.4 ± 5.1 (17)	12.5 ± 35.0 (8)
OCDF	9.8 ± 14.1 (19)	11.8 ± 33.1 (9)

.. : no data available

Experimental verification of the safe sampling volume

At the Ghent incinerator, the safe sampling volume under field conditions was checked by sucking a total volume of 10.629 Nm³ of flue gas over a series of six short (about 2 cm) consecutively placed individually packed gas adsorption traps, connected by all glass joints. The adsorption traps 1 to 6 contained 0.456, 0.547, 0.551, 0.553, 0.471 and 0.478 g of Tenax[®] respectively; the average sampling rate amounted to ca 6 l/min.

The proportional concentrations of the compounds of interest in each subsample are shown in Table 2. In normal practice, all extracts from the cooled part of the sampling train are combined to increase the amount of analyte in the sample.

Some very interesting and useful conclusions can be drawn from these results.

- In spite of the presence of huge amounts of other organic compounds and of the adverse sampling conditions, a collection volume of 1 m³ can be considered as reassuringly safe at ambient temperatures. Under these conditions, none of the compounds under study are lost by breaking through the gas adsorption trap. Over 80 % of the compounds reaching the gas trap (including the most volatile ones) are even found on the first cartridge, over 99 % on the first three cartridges, which when added equal the amount of sorbent of a normally used gas trap. The reduced column length did not lead to serious losses in the first trap, which could be caused by inefficient packing or channelling of the sampled gases.
- The moisture, the inorganic and corrosive constituents of the effluent, do not significantly degrade the porous polymer material or its sorption capacities, even if a five- to tenfold excess of effluent volume is sampled.
- All PCBzs are predominantly (over 80 %) found on the first gas adsorption trap; the more volatile ones can also be demonstrated in the second and -to a lesser extent- in the third cartridge.

4. A sizable fraction of PCPs, PCDDs and PCDFs is found in the condensed liquid and rinsing solvent; this increases with the mounting degree of chlorination (or the decreasing vapor pressure) in every class of compounds. Only a minor fraction of hepta- and octachlorinated isomers actually reaches the gas trap. This can be attributed to condensed particle forming, coprecipitation with the condensing moisture or condensation on the walls of the different cooler parts of the sampling train of the least volatile compounds. It also indicates that condensation of semivolatile compounds out of stack actually occurs when the temperature drops and that losses due to the adherence on the colder walls or connections of the sampling train may be substantial if a more complex equipment is used. This holds to a lesser extent for the lower chlorinated congeners.
5. An adsorbent back-up cartridge is indispensable. Even if the effluent is cooled to ambient temperature and the condensed liquid is sampled, an important fraction of particularly the PCBz, PCPs and the lower chlorinated PCDDs and PCDFs may escape collection.
6. The fraction collected in the heated portion of the sampling train, i.e. the filter, either present in the particulate phase or sorbed during sampling, can be neglected. Whether this is (partly) due to an effective elution by the hot effluent or not, cannot be concluded from this experiment. However, this does not exclude possible losses by chemisorption, since chemisorbed compounds are difficult - if not impossible - to extract.

Table 2 : Proportional concentration of organochlorinated compounds in the different samples of the safe sampling volume test.

Compound	Filter	Condensed liquid	Sample						Total concentration (ng/Nm ³)
			Tenax 1	Tenax 2	Tenax 3	Tenax 4	Tenax 5	Tenax 6	
1,2-CBz	0.3	0.7	80.7	15.0	2.6	0.4	< 0.1	< 0.1	1,383
1,3-CBz	0.8	1.7	81.7	12.1	2.9	0.3	< 0.1	0.4	1,260
1,4-CBz	0.9	2.1	84.9	8.1	2.3	0.2	< 0.1	0.2	801
DCP	n.d.	38.7	51.0	5.3	5.0	n.d.	n.d.	n.d.	820
T ₂ CP	n.d.	42.2	56.8	0.7	0.2	n.d.	n.d.	n.d.	3,304
T ₄ CP	n.d.	61.1	38.6	1.9	< 0.1	< 0.1	n.d.	< 0.1	3,106
P ₂ CP	n.d.	72.2	27.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	2,150
T ₂ CDD	n.d.	35.5	63.9	0.6	n.d.	n.d.	n.d.	n.d.	3
P ₂ CDD	n.d.	60.7	38.5	0.8	n.d.	n.d.	n.d.	n.d.	9
H ₄ CDD	n.d.	77.6	21.5	0.2	n.d.	n.d.	n.d.	n.d.	31
H ₂ CDD	n.d.	88.7	11.1	n.d.	n.d.	n.d.	n.d.	n.d.	46
OCDD	n.d.	94.6	5.4	n.d.	n.d.	n.d.	n.d.	n.d.	36
T ₂ CDF	n.d.	28.7	70.8	0.5	n.d.	n.d.	n.d.	n.d.	19
P ₂ CDF	n.d.	62.1	37.0	0.9	n.d.	n.d.	n.d.	n.d.	26
H ₄ CDF	n.d.	79.6	20.2	0.2	n.d.	n.d.	n.d.	n.d.	45
H ₂ CDF	n.d.	95.6	4.4	n.d.	n.d.	n.d.	n.d.	n.d.	73
OCDF	n.d.	95.9	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	35

n.d. not detected; limits of detection are below 0.1 % except for HxCDD (0.2), HxCDF (0.1), OCDD (0.3) and OCDF (0.3) (approximate value between brackets).

< .. traces observed, lower than the value indicated

CBz = chlorobenzene; CP = chlorophenol;

References

1. K. Olie, P. L. Vermeulen, O. Hutzinger, *Chemosphere*, 6, 1977, 455-459
2. R. M. M. Kooke, J. W. A. Lustenhouwer, K. Olie, O. Hutzinger, *Analytical Chemistry*, 53, 1981, 461-463
3. G. A. Junk, C. S. Ford, *Chemosphere*, 9, 1980, 187-230
4. M. M. Beaurie, *Atmospheric Environment* 11, 1977, 527-529

5. A. Cavallaro, G. Bardi, G. Iuvernizi, L. Luciani, E. Mongini, A. Gorri, *Chemosphere*, 9, 1980, 611-621
6. J.Janssens, L. Van Vaeck, P. Schepens, F. Adams, in *Physico-Chemical Behaviour of Atmospheric Pollutants, Proceeding of the Second European Symposium, Varese, Italy*, ed. B. Versino/ H. Ott, Reidel, Dordrecht, 1981, 29-39.
7. T. W. Sonnichsen, M. W. Mc Elroy, A. Bjorseth, in "Polynuclear Aromatic Hydrocarbons : Chemistry and Biological Effects", A. Bjorseth and A. J. Dennis (eds.), Battelle Press, Columbus, Ohio, 1980, 617-632
8. H. Hagenmaier, H. Brunner, R. Haag, M. Kraft, K. Lutzke, *Waste Management and Research*, 5, 1987, 239-250
9. C. Rappe, S. Marklund, M. Tysklind, *Waste Management and Research*, 5, 1987, 295-300
10. B. Jansson, G. Bergvall, *Waste Management and Research*, 5, 1987, 251-255
11. W. A. Korfmacher, D. F. S. Natusch, D. R. Taylor, G. Mamantov, E. L. Wehry, *Science*, 207, 1980, 763-765
12. F. W. Karasek, R. E. Clement, A. C. Viau, *Journal of Chromatography*, 239, 1982, 173-180
13. W. L. Fitch, D. H. Smith, *Environmental Science and Technology*, 13, 1979, 341-346
14. F. W. Karasek, L.C. Dickson, *Science*, 237, 1987, 754-756
15. L. C. Dickson, F. W. Karasek, *Journal of Chromatography*, 389, 1987, 127-137
16. H. Vogg, M. Metzger, L. Stieglitz, *Waste Management and Research*, 5, 1987, 285-294
17. G. A. Eiceman, V. J. Vandiver, *Atmospheric Environment* 17, 1983, 461-465
18. L. Van Vaeck, G. Broddia, W. Cautreels, K. Van Cauwenberghe, *The Science of the Total Environment*, 11, 1979, 41-52
19. T. Alsberg, U. Stenberg, *Chemosphere* 8, 1979, 487-496
20. L. Van Vaeck, PhD thesis, University of Antwerp, 1981
21. L. C. Dickson, O. Hutzinger, F. W. Karasek, V. Ozvacic, *Int. Journal of Environmental Analytical Chemistry*, 24, 1986, 55-74
22. H. Vogg, L. Stieglitz, *Chemosphere*, 15, 1986, 1373-1378
23. D. F. S. Natusch, *Environmental Health Perspectives*, 22, 1978, 79-90
24. G. A. Eiceman, H. O. Rghei, *Chemosphere*, 11, 1982, 833-839
25. H. O. Rghei, G. A. Eiceman, *Chemosphere*, 13, 1984, 421-426
26. H. O. Rghei, G. A. Eiceman, *Chemosphere*, 14, 1985, 167-171
27. H. Hagenmaier, M. Kraft, H. Brunner, R. Haag, *Environmental Science and Technology*, 21, 1987, 1080-1084
28. J.G.P. Born, R. Louw, P. Mulder, *Chemosphere*, 19, 1990, 1629-1633
29. B. F. Rordorf, *Chemosphere*, 14, 1985, 885-892