

Resolving major sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) by use of time trend data and principal component analysis

Lars-Owe Kjeller

Institute of Environmental Chemistry,
Umeå University, S-901 87 Umeå, Sweden

Phone: +46-90 786 6665, Fax: +46-90 186155, e-mail: lok@chem.umu.se

Summary

The content of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in dated environmental samples from sediment, soil and herbage has been related to major sources by use of principal component analysis (PCA). The major PCDD/F sources considered were combustion and catalytic fully chlorinated chemicals as PnCP. All environmental samples are located between the combustion and PnCP in score plots from PCA. The old samples (<1930-50) in each serie of samples are located near combustion source and have only a slight (<10 %) influence of the PnCP. This admixture of PnCP is reasonably apparent and caused by various natural conversions of the mixture of original released PCDD/F composition from combustion, as no other possible sources exist earlier than 1930-50. The most recent samples in each serie have a PCDD/F composition similar to PnCP: proposed that the high chlorinated organics are of higher significance for today PCDD/F deposition than combustion related PCDD/F. Chlorinated organics proposed to be the dominating PCDD/F source today; this is in agreement with earlier hypothesis, however the PCDD/F release of related chlorinated organic compounds seems to be underestimated.

Introduction

Today all major sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are identified. However, some uncertainties still exist concerning the relative size of different PCDD/F sources (1). The confusion depends on discrepancies found in budget calculations between PCDD/F released from known sources, towards PCDD/F deposited in the environment. As major global sources chlorinated organics and combustion should be considered. Then combustion (and eventually other air emissions) is the major released and distribution path for both of these PCDD/F sources, is the ratio between them hard to establish.

The major sources for PCDD/F formation are production of chlorinated aromatic organic compounds by catalytic chlorination as pentachlorophenol (PnCP). Production of such compounds will generate full chlorinated-DD/F molecules. Especially formation of OCDD is favoured, followed by a gradually reduced abundance of lower chlorinated congeners (2,3). Lower

chlorinated T- PnCDD/F will be by-products from production of less chlorinated aromatic compound, however the production volume is smaller. Lower chlorinated PCDD/F congener is also produced from other sources as free chlorination. Secondary formation from Cl-aromatics can occur from many processes as pyrolysis, photo-formation and might be larger than the primary PCDD/F contamination. Another secondary source of PCDD/F is pyrolysis of chlorinated aliphatics. Aliphatic compounds have less capacity for formation of PCDD/F, compared to aromatics. However, some aliphatics have a substantial production volume (4). The other major groups of PCDD/F sources are natural combustion of various items as wood, oil and coal. The PCDD/F composition emitted from these sources is expected to be dominated by low-chlorinated species with a successively declining level of higher chlorinated-DD/F (5). A similar profile is also expected from eventual other PCDD/F sources with origin from eventual other natural free chlorination mechanism.

Method

The source data are compared to environmental time trend data for PCDD/F, e.g. sediment cores and achieved soil and herbage samples. The time-trend data must cover an acceptable period, e.g. a major part of the 20th.C. The advantage with time trend data is that each serie contains its own internal reference. Thus can the PCDD/F composition in old deposit, where natural combustion reasonably is the only dominating source, be used as an internal reference for recent samples. Direct comparison with source composition is complicated by influences on the PCDD/F composition by environmental conversion mechanisms as evaporation, solubility and various degradation by UV-radiations, radicals and enzymes. The intention has been to collect data with 25 PCDD/F values (variables), e.g. congener sums and 2,3,7,8-substituted isomers, at least for sources data. Few series of environmental data satisfy this postulate, however there are thirteen publications covering nineteen different time trends from Europe and north America where at least congener sums or the 17- are toxic congeners are given (6-18). The data have been transformed and scaled to remove differences due to concentrations and normalisation base. Transformation, using a reduced variable sum or geometrical mean, gives essentially the same results. The principal component (PC) calculation is made with SIMCA version 5.1, Umetri, Umeå, Sweden.

Result and discussion

If the available time trends are included in a PC analysis together with natural combustion and PnCP sources the first-PC will express the major difference between the PnCP and natural combustion, Fig 1. This variation corresponds to approximately 23 % of the data variation (sum of squares). The two next PCs express various variations in connection to specific time series, totally 30 % variation, this is likely result of unique contamination, deposition or degradation conditions. The remaining 47 % variation is foremost due to lesser random variation in this rather heterogeneous set of data. If the natural combustion samples are assign to 0 % PnCP, and the pure PnCP product samples are assigned to 100 %, thus is a "scale" created where the environmental samples are located between combustion and PnCP sources, Fig. 2. The minimum of PnCP influences, e.g. samples located nearest natural combustion are all "old" samples dated back to around 1940. With exception for three series there the oldest samples are dated to the period 1950-60, due to core length or non detect. The average of PnCP influences in old samples is 9.4 % (SD 15). The old samples have thus a composition much more similar to combustion, rather than PnCP. The admixture of PnCP is illusive and can be explained by loose of lower PCDD/F congeners towards higher chlorinated primarily by evaporation and solubility, followed by degradation, in agreement with the general theory of PCDD/F behaviour (1). The average of PnCP similarity in

recent samples is 60 %. Thus, the natural background conversion of 10 % can not explain the admixture of PnCP related PCDD/F observed in recent samples for respective time trend, i.e. 1979-93.

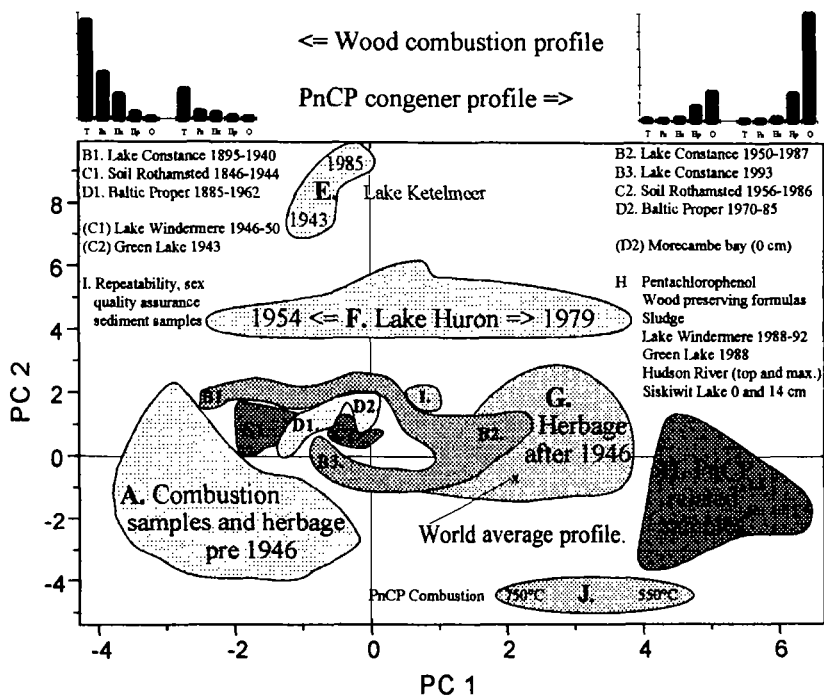


Fig. 1. Example of principal component analysis (PCA) of time trend data for PCDD/F. Not all discussed nineteen trends are included in this figure. PnCP related samples are located to the right, H, and combustion samples to the left, A. The proportion of PnCP-signature increases with time, i.e. a PnCP-signature is superimposed on a continuous present and almost constant combustion-signature. Data A to J are: A: Combustion and Rothamsted herbage before 1946. B: Sediment, Lake Constance. C: Soil Rothamsted (and deep sediment Lake Windermere, Green Lake). D: Sediment Baltic Proper (and recent sediment Morecambe Bay). E: Sediment Lake Ketelmeer. F: Sediment Lake Huron. G: Herbage Rothamsted, after 1946. H: Pentachlorophenol (PnCP), wood preserving formulas, sludge. Recent sediments from Lake Windermere, Green Lake, Siskiwit Lake, and Hudson River. I: Quality assurance sediment J: PnCP pyrolysis.

The average admixture of PnCP among recent samples is 60 % PnCP (SD 35), thus a net increase of in average 51 % PnCP is found. However the recent PnCP influence is highly variable, with some samples around 100 % and other with only 5-10 % above corresponding old samples with combustion composition. Such series are usually from locations where the matrix is mixed, or are suspected to be mixed by various processes as retard transport, bioturbation and ploughing. Thus most of the increase of at least high chlorinated PCDD/F congeners after 1930-50 can be explained by use of chlorinated organics foremost high chlorinated aromatic compounds for the used

locations. Thus one of the reasons to the two-three decades of increased PCDD/F deposition after 1945 is linked to chlorinated organic compounds rather than increased combustion followed by transformation.

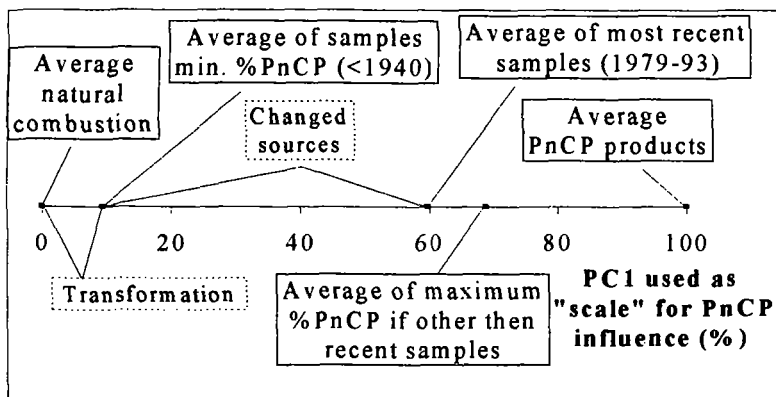


Fig. 2. First PC. Average of combustion and PnCP sources is marked and assigned to 0 and 100 % respectively. For environmental samples the average of minimum PnCP influence (usually samples older than 1946), and average for most recent sample (1979-93) and average of eventual maximum in the PnCP admixture (~1960-80) is marked.

In seven locations the PCDD/F profile has passed a maximum in PnCP influences and is followed by return towards combustion composition. Trends with clear return are collected in areas with a relative vicinity to urban centres. Thus there is no general return towards a natural combustion profile. However, it should be noted that the dating of "most recent" samples span from 1979-93.

References

1. Brzuzy L.P. Hites R.A; *Environ. Sci. Technol.* **1996**, 30, 1797.
2. Hagenmaier H. Brunner H; *Chemosphere* **1987**, 16, 1759.
3. Jiang K. Chen Y.-D. Li L.-J. Schechter A; *Organohalogen Compd.* **1992**, 7, 319.
4. Theisen J. Funcke W. Balfanz E. König J; *Chemosphere* **1989**, 19,423.
5. Bacher R. Swerev M. Ballschmiter K; *Environ. Sci. Technol.* **1992**, 26,1649.
6. Czuczwa J.M. Hites R.A; *Environ. Sci. Technol.* **1984** 18,444.
7. Czuczwa J.M. McVeety B.D. Hites R.A; *Science* **1984**, 226,568.
8. Beurskens J.E.M. Mol G.A.J. Barreveld H.L. Van Munster B. Winkels H.J; *Environ. Toxicol. Chem.* **1993**, 12,1549.
9. Kjeller L.-O. Jones K.C. Johnston A.E. Rappe C; *Environ. Sci. Technol.* **1991**, 25,1619.
10. Kjeller L.-O. Rappe C; *Environ. Sci. Technol.* **1995**, 29,346.
11. Kjeller L.-O. Jones K.C. Johnston A.E. Rappe C; *Environ. Sci. Technol.* **1996**, 30,1398.
12. Smith R.M. O'Keefe P.W. Hilker D.R. Bush B. Connor S. Donnelly R. Storm R. Liddle M; *Organohalogen Compd.* **1993**, 12,215.
13. Smith R.M. O'Keefe P.W. Hilker D. Connor S. Posner E; *Organohalogen Compd.* **1995**, 24,141.
14. Schramm K.-W. Winkler R. Casper P. Kettrup A; *Water Res.* **1997**, 31,1525.
15. Hagenmaier H. Walczok M; *Organohalogen Compd.* **1996**, 28,101.
16. Brzuzy L.P. Hites R.A; *Environ. Sci. Technol.* **1995**, 29,2090.
17. Jüttner I. Henkelmann B. Schramm K.-W. Steinberg C.E.W. Winkler R. Kettrup A; *Environ. Sci. Technol.* **1997**, 31,806.
18. Tyler A.O. Millward G.E. Jones P.H. Turner A; *Estuarine, coastal and shelf science* **1994**, 39,1.