REPORT

Use of congener profiles to trace sources of chlorinated dibenzo-p-dioxins and dibenzofurans in environmental samples

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Report Summary

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Project sponsor

Swedish Forest Industries Water and Air Research Foundation (SSVL), the Swedish Wood Preservation Institute, Avfall Sverige - Swedish Waste Management and the Swedish Environmental Protection Agency.

Author

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The PMF model for Baltic Herring points to three significant sources. One of them is identified to be a background/combustion. One of the other sources is not fully identified but some parts of the pattern are likely flue gas. The last source can not be identified by use of data collected in this project.

Keyword

Dioxins, Congeners, PMF, PCA, Receptor models, Baltic Sea

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Sammanfattning

I denna studie har olika multivariata metoder använts för att försöka koppla dioxiner och furaner i biota till olika källor. De data som använts i studien kom från redan existerande analyser av dioxiner och furaner men även viss data har tagits fram genom provtagning och analys inom projektet. Brist på data, i synnerhet från biologiska prover, begränsade modellering till att omfatta 17 giftiga kongener, bestående av sju dioxiner och 10 furaner. Den dominerar biotiska gruppen är strömming. Två olika typer av multivariata modellerings metoder användes, Principal Component Analysis (PCA) och positive matrix factorisation (PMF) för källfördelning.

PCAn visar att sill från Bottenviken och Finska viken har väldefinierade mönster. Spridningen i mönster är större för strömming som fångas i egentliga Östersjön och Bottenviken. Även åldern på strömmingen har effekt på mönstret, 2-åriga strömmingar är väl grupperade och skiljas från äldre strömmingar. När källprover (rökgaser, förbränning, bakgrund) läggs till i PCAn för biota syns endast en väldefinierade överlapp och det är mellan biota och rökgaser.

PMF-modellen för strömming pekar på tre signifikanta källor. En av dem är identifierad som en bakgrund/förbrännings källa. En av de andra källorna är inte helt identifierade men vissa delar av mönstret liknar det för rökgas. Den sista källan kan inte identifieras med hjälp av data som samlats in i detta projekt.

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1 Introduction

1.1 General background

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are unintentionally formed chemical compounds, among which some are extremely toxic. It was in the 1930s in USA when adverse effects were reported in chemical industry workers producing chlorinated phenols (Butler 1937). The chemical responsible for the effects, 2,3,7,8-tetrachlorodibenzo-p-dioxin, was first reported in 1957 (Kimming, Schultz 1957). The effects in humans included chloracne, a skin disease, and impacts on the hepatic, nervous, endocrine, cardiovascular, gastrointestinal and immune systems (Moses et al. 1984). Animal studies revealed teratogenic effects and evidence to cause cancer at very low doses (Courtney, Moore 1971, Kociba et al. 1978).

1.2 Chemistry and Formation

Chlorinated dibenzo-p-dioxins and dibenzofurans comprise 210 congeners and there are 136 congeners with four or more chlorine atoms. The general structure of the two groups of compounds is shown in Figure 1.

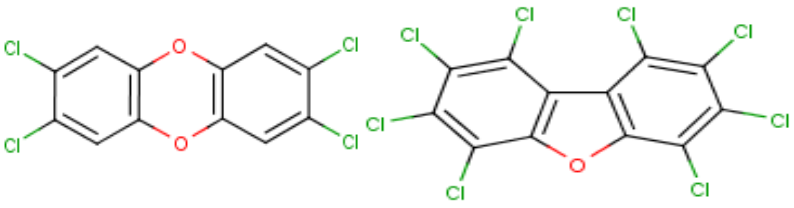

Figure 1 2,3,7,8-Tetrachlorodibenzo-p-dioxin, the most toxic congener (left) showing the critical positions of chlorine substitution and octachlorodibenzofuran, the fully chlorinated furan (right) as representatives of the structural patterns of the toxic chlorinated dibenzodioxins and dibenzofurans.

The substances are formed as by-products in the chemical manufacture of chlorophenols and chlorinated phenoxyacetic acids. They are also formed in a number of high temperature processes including pulp and paper industry, waste incineration and metallurgic industry, in accidental landfill fires and in small and large scale burning of wood. Using elemental chlorine in pulp bleaching produced these compounds (Swanson 1988). Optimal temperatures for formation in incinerators seem to be 300 – 600 °C, but formation occurs in a wider temperature interval (Huang, Beukens 1995). Besides suitable temperatures the requirements seem to be chlorine in either organic or inorganic state and organic material. Trace amounts of metals such as copper and zinc may catalyze the formation (Acharya et al. 1991). Toxic congeners have been shown to form upon enzymic oxidation of chlorophenols using plant peroxidase and lactoperoxidase (Svenson et al. 1989a,b, Öberg et al. 1990).

1.3 Properties and fate

Polychlorinated dioxins and dibenzofurans are poorly soluble in water but dissolve readily in organic solvents and fat-rich compartments. Therefore they sorb to organic structures in soil, water and fatty tissues in living organisms. A great concern is related to the occurence in fat-rich fish species such as herring and salmonids that are used for consumption.

The evaporation is poor due to the low vapour pressure of the compounds. Upon smoking of eel (*Anguilla anguilla*) low chlorinated congeners of dioxins have, however been shown to evaporate (van Leeuwen et al. 2007).

The substances are resistant to biotransformation in microorganisms and higher organisms. The more chlorine in the structure, the more resistant to degradation are the compounds. The substances are not readily metabolized in the mammalian body. When exposed to sunlight the substances may be transformed by direct or sensitized photolysis. Pure chlorinated dioxins and dibenzofurans decompose thermally at temperatures from 800 °C or more, but sorbed to particles they may remain stable at 1150 °C (Esposito et al. 1980).

In general lower chlorinated congeners are more readily transformed microbially. Mono- and dichlorodiobenzo-p-dioxins may be the carbon source and converted by isolated bacteria, whereas trichloro- derivatives were converted in the presence of o-chlorobenzene as cosubstrate (Du et al. 2001). The isolates did not convert congeners with five or more chlorines. Microbial dechlorination of octachlorodibenzo-p-dioxin proceeded in two principally different ways, one conserving the distal 2,3,7,8-substitution and the other removing chlorine from one or more of these positions (Barkovskii, Adiaens 1996). Both aged and newly spiked 2,3,7,8-substituted preparations were dechlorinated.

Aquatic conditions of low redox potential have experimentally been shown to remove chlorine from low-chlorinated dioxins (Beurskens et al. 1995, Ballerstedt et. al. 1997, Vargas et al. 2001). Lesser chlorinated congeners were still detectable after 2-17 months.

Besides dechlorination producing new dioxin and dibenzofuran congeners, dioxygenation reactions also involving ring fissions are known (Neilson, Allard 2008). As lower chlorinated congeners are more readily converted, the congener profiles will change upon modification by these reactions.

Studies on the transfer of these compounds in food webs have shown that whereas the lower substituted congeners were unchanged across the trophic levels, higher chlorinated congeners decreased with increasing trophic level (Ruus et al. 2006, Wan et al. 2005). These congeners were considered not to be as effectively resorbed from the aquatic conditions in the predator gut as the lower chlorinated species (trophic dilution). Octachlorodibenzo-p-dioxin was poorly or not at all taken up in fish upon aquatic exposure (Opperhuizen et al. 1990).

1.4 Toxicity

All toxic congeners are substituted with four or more chlorine atoms. Congeners substituted in the distal 2,3,7,8 positions are the toxic forms and the effects of specific congeners vary. Owing to the relative toxic effects individual congeners have been assigned a toxic equivalency factor (TEF) related to the effect of the most toxic congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (one unit). The toxic factor roughly follows the ligand binding affinity of the congeners to the aryl hydrocarbon (Ah) receptor. There are at least three slightly different definitions of the TEF values,

the one issued by WHO is the most commonly used today (Eadon et al. 1986, van den Berg et al. 1998, 2006). Contributions of analysed congeners in a sample are added and the sum is used as a measure to characterize the sample. Usually contributions from coplanar, non-ortho substituted, polychlorinated biphenyls that exert dioxin-like effects, are included in the toxic equivalent (TEQ) value.

The European Community has set maximum levels for a number of food products (Council Regulation No 2375/2001). Muscle meat from fish may contain at most 4 pg WHO-TEQ of PCDD/Fs/g f.w. Due to the contents in fat fish from the Baltic and the large lakes in Sweden and Finland these countries may exceed the limit value for the period until 2011. The National Food Administration in Sweden has released food intake recommendations for fat fish.

1.5 Tracing sources

Analyses of these chlorine-organic substances in the Swedish environment have been performed in national surveys and a number of separate studies mostly in biological matrices. The results have been gathered in the data-base Miljögifter i Biota hosted by IVL. Analyses in fish from the Baltic have shown that an expected decline in concentrations has ceased the last decade (Roots et al. 2007, Olsson et al. 2008). Important sources for the release of these compounds in Sweden have been the pulp- and paper industry, iron- and steel industry, chemical industry producing chloro-organic compounds and chlorine, waste deposit sites, sewage treatment plants and combustion on a small- and large scale (Anon. 2005a,b).

Different sources of these chlorinated compounds are reflected in the composition of congeners. Earlier sources have been traced by examination of single congeners, usually the most toxic ones. The relative proportions of dioxins and furans have also been used in the search for sources of the contamination. Furthermore homologues, i.e. congeners with the same numbers of chlorine, have been used for this purpose.

1.6 Aim

The project aims at the identification of sources to the appearance of chlorinated dibenzo-p-dioxins and dibenzofurans in environmental samples. This will be done by using congener profiles of sources of the substances on the one hand and profiles of target samples (sinks) on the other hand. Ideally contributions of different sources should be assigned. The focus is on Sweden and specially the Baltic Sea.

2 Methods

2.1 Data collection

Congener-specific analysis profiles of polychlorinated dibenzo-p-dioxins and dibenzofurans in different matrices have been gathered from various published and unpublished sources. Some data has been generated by sampling and analysis within the project.

Data usually generated by gas chromatography – high resolution mass spectrometry transfered to weight concentrations using the appropriate technique at the time of release of results has been

accepted as input data in the modelling. Data of seven 2,3,7,8- substituted chlorinated dioxins and ten chlorinated dibenzofurans have been used.

Non 2,3,7,8- substituted congeners with chlorine in at least four positions were initially intended to be included. Lack of data especially from biological samples limited the modelling to the set of 17 toxic congeners comprised of seven dioxins and 10 furans. Values below analysis detection limits were set as half the limit value. Profiles with more than nine such values were not used in the modelling.

2.2 Modelling

Two different types of modelling methods were used in this project, principal component analysis (PCA) and positive matrix factorisation (PMF) for the receptor modelling.

2.2.1 Principal Component Analysis

A brief description of PCA is given here; more details are given in literature Wold et al. 1987, Martens, Naes 1989, and Esbensen et al. 1996. PCA decomposes a data matrix X according to:

$$\mathbf{X} = \mathbf{TP}^{\mathbf{T}} + \mathbf{E}$$

PCA can be considered a co-ordinate transformation from the original variable space to a model hyper-plane of much lower dimensionality that captures the variance in the data in the most efficient way. The scores, denoted t or T, are the co-ordinates in the new orthogonal co-ordinate system and thus describe the objects (here: chemical substances). The loadings, denoted p or P, describe the relation between the latent variables (principal components) that span the model space and original variables. The matrix E in the equation above contains the residuals, i.e. the part of the data not captured by the model hyper-plane. The substantial dimensionality reduction achieved by applying PCA leads to enhanced interpretation abilities which facilitate classification and clustering of substances. PCA is not a regression method and cannot be used for finding quantitative relationships between descriptors and responses.

The interpretation of the score and loading plots are illustrated in the Figure 2 below.

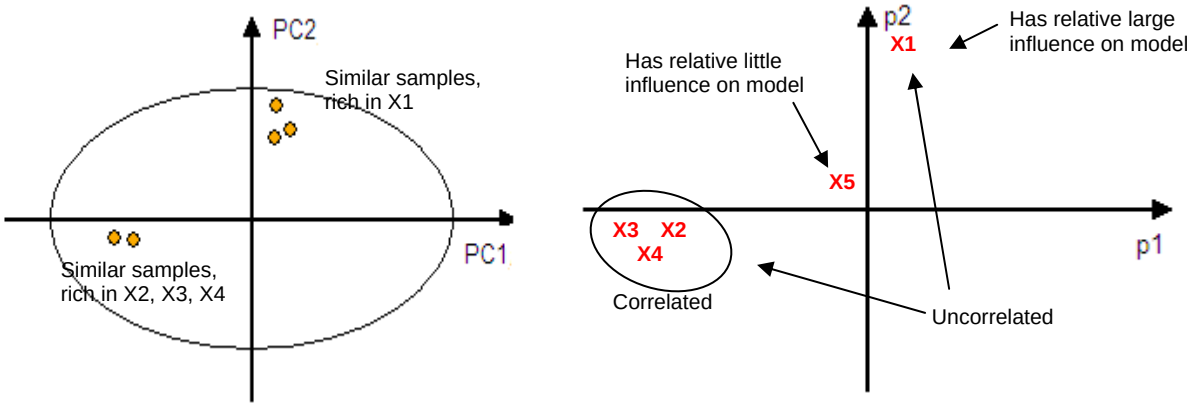

Figure 2. To the left an example of a score plot and to the right an example of the corresponding loading plot.

2.2.2 Positive Matrix Factorization

For analysing the data we also used Positive Matrix Factorization (PMF). The theory and algorithm of PMF has been described by (Paatero and Tapper, 1994; Paatero, 1997). When using the robust mode of PMF means that a limited number of outliers can be tolerated in the data whit out sacrificing the model stability (Paatero and Hopke 2003). Data below the detection limit were treated with the mechanism offered for this purpose by the algorithm. A number of so-called factors are extracted from the data. Each factor represents one or a combination of sources. For each factor, the temporal variation and the relative compositions are determined.

Two types of uncertainty are present in PMF results. The uncertainty that is caused by propagation of the measurement uncertainty is calculated by PMF. The other type of uncertainty, usually denoted rotational ambiguity, is caused by the fact that it is not possible to completely distinguish between sources that do not vary independently. An approximate approach was used to estimate the magnitude of the rotational ambiguities (Paatero, 1997). This method determines a range of mathematically feasible solutions. Some parts of this range may be considered less realistic because of the physical interpretation and knowledge, e.g. about source compositions, but this is not accounted for in the uncertainty intervals determined and presented below.

The approach used for receptor modelling is summarized below:

1. Determine the number of contributing source profiles.
2. Determine the chemical composition of each source profile.
3. Determine the relative contribution of each source profile in each sample.
4. Identify each source profile based on comparisons with known profiles or identify entirely new sources.

3 Results and Discussion

The data collected and used for the modelling are presented in annex 1. An overview of the data is shown in Table 1.

Table 1. Data overview

Type of samples	Amount of samples
Combustion	74
Exhaust	19
Water	54
Air	26
Soil	173
Biota	544
Sediment	106

3.1 Principal component analysis

The PCA was carried out with different sub-sets of the data. To get an overview of the biota data and to see any patterns between the species the first PCA included all biota data from Sweden, see Figure 3. This included Guillemot, several different fish species and sea mussels. Among the fish species the Herring/Baltic Herring was the group with largest amount of samples, coloured red in the figure. One clear observation in the score plot is that the Guillemots are well separated from the other species (coloured blue) The Guillemots have a higher relative contribution of the congeners F123678, F234678 and D123678, se loading plot in Figure 5, then the other spices. The herring have a large spread and are distributed from the lower left to the upper right part. The fish species salmon and salmon trout, caught in lakes, are grouped in the upper right in the plot. This grouping suggests that they all have a relative higher amount of the congeners F2378 and F12378.

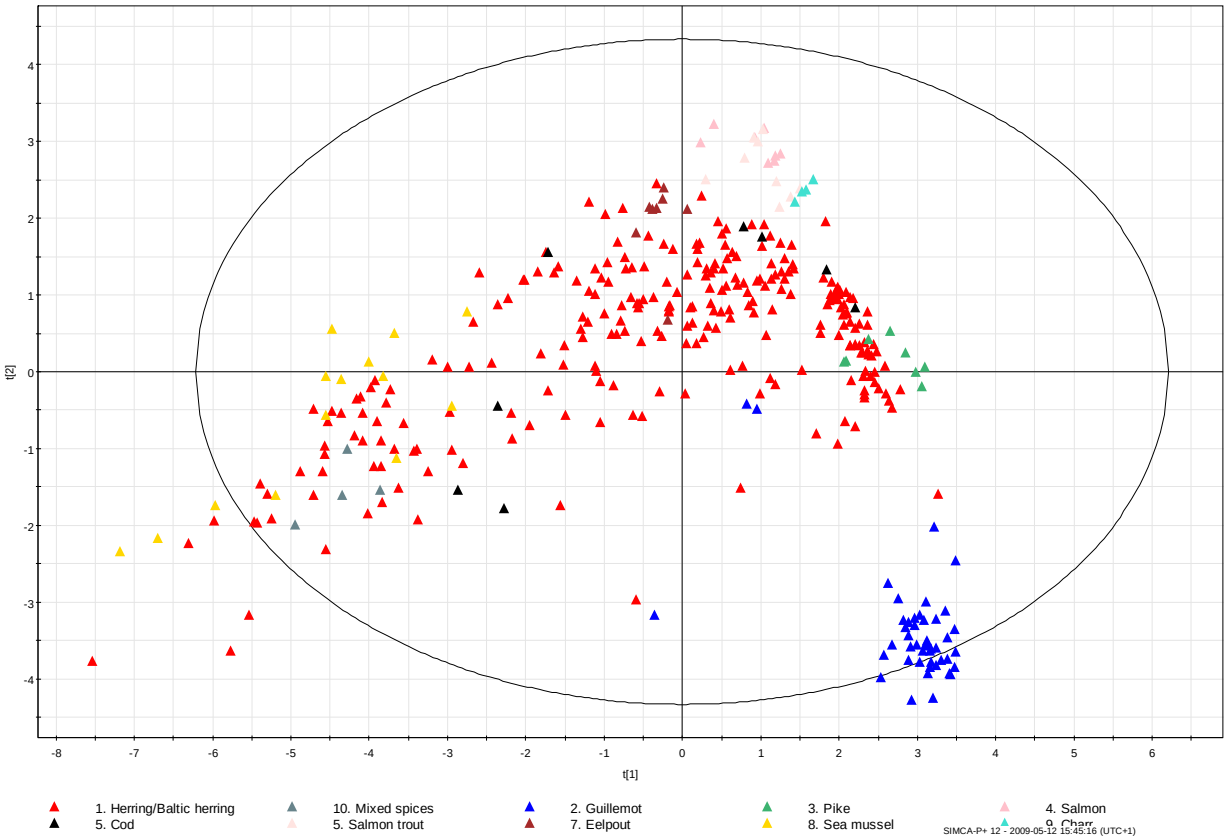

Figure 3. Score plot of biota samples, coloured after species.

There are several different locations of the samples, we have classified them in to 7 different classes and they are presented in Figure 4. This is the same as Figure 3 but coloured by location. The samples from Gulf of Finland and Bothnian Sea, as well as the samples from the lakes Vänern and Vättern, are a well defined group. The other regions are more outspread in the score plot indicating that the congeners profile are not depending on the origin of the sample.

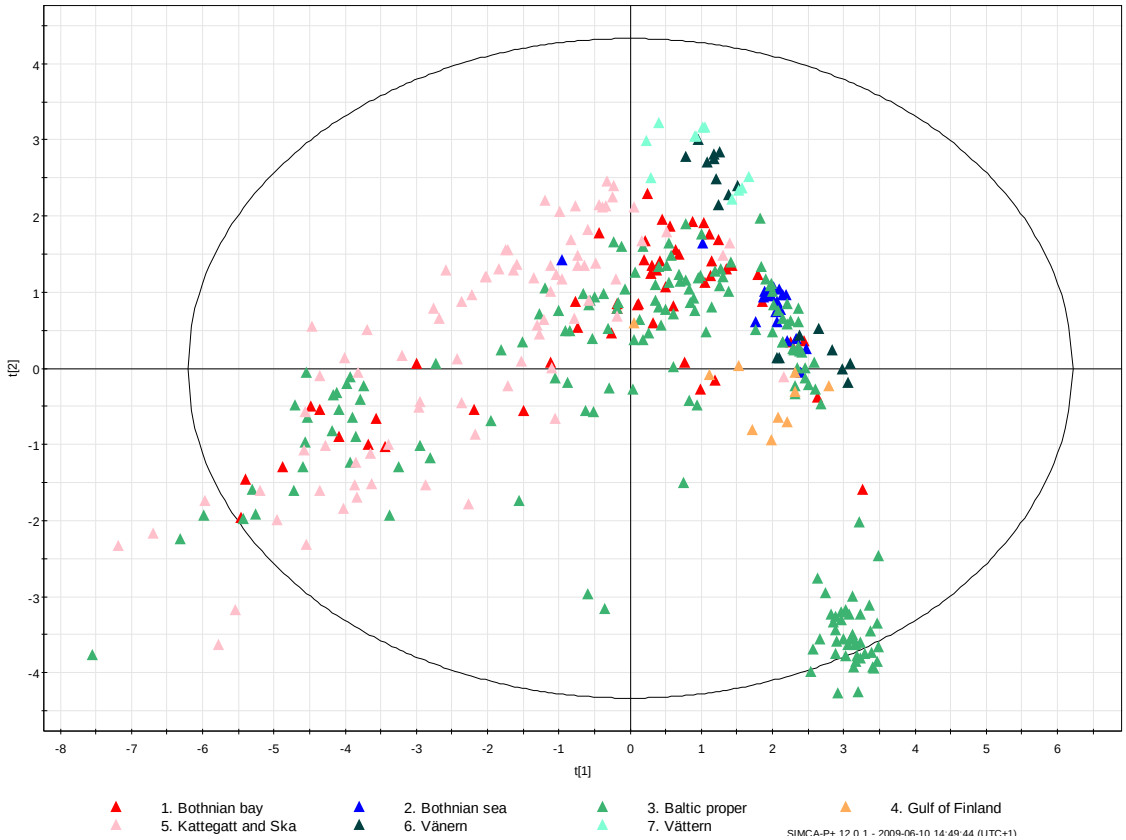

Figure 4. Score plot of the biota samples, coloured by location of catch.

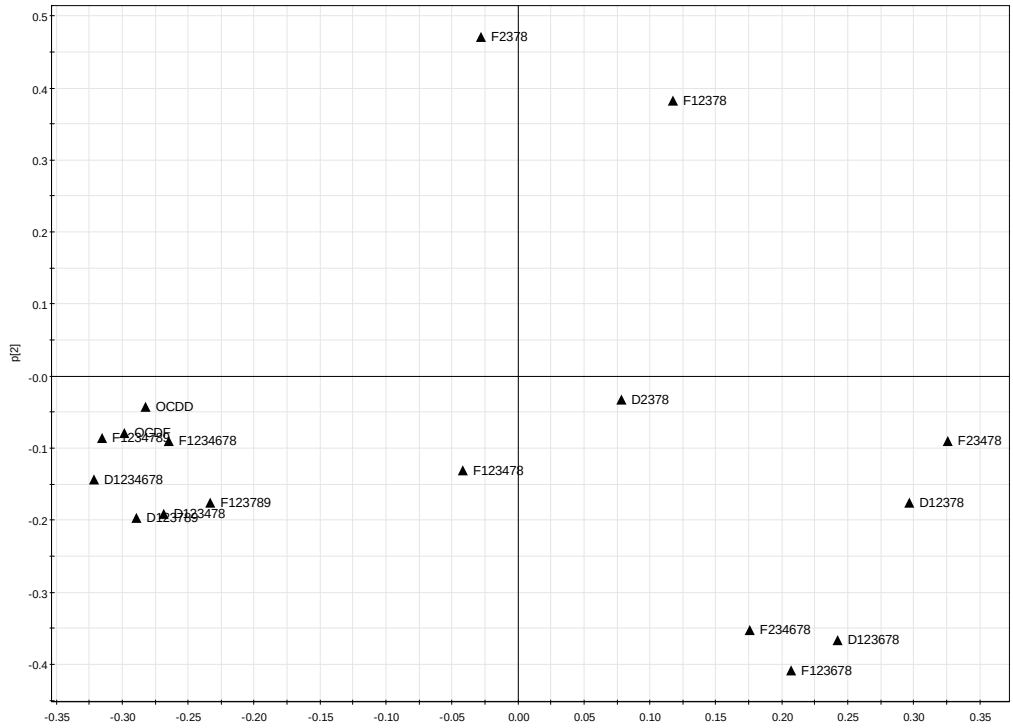

Figure 5. Loading plot for the different furans and dioxins congeners.

The main group of samples is from Baltic herring and there for a PCA was conducted on only these samples. The score plot is shown in Figure 6 below. The pattern is not constant for the Herrings caught in Bothnian Bay and Baltic proper, the samples are spread out through the score plot. Regarding the samples caught in the Gulf of Finland and Bothnian Sea the congener pattern is more or less the same. One possible explanation for the change of congener pattern could also bee that the source pollution has changed over time.

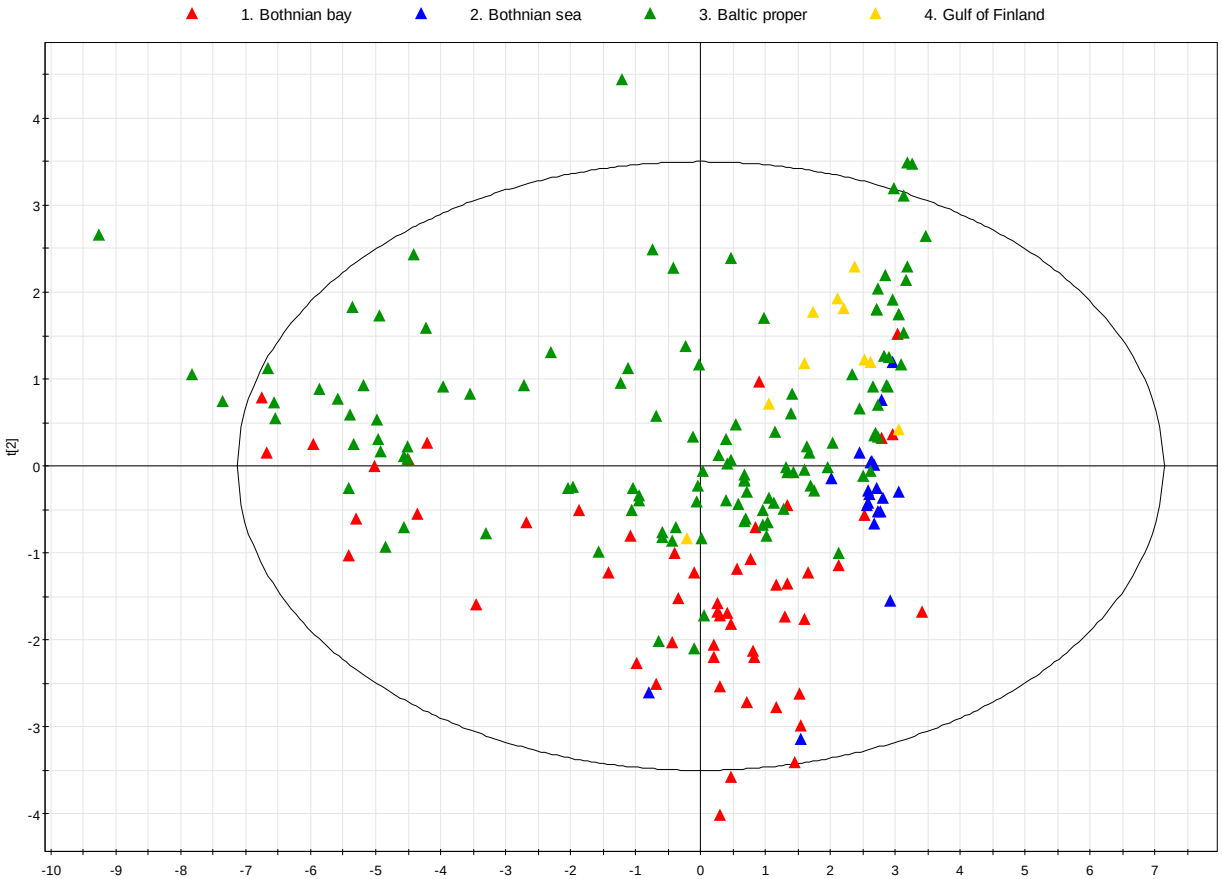

Figure 6. Score plot for only Baltic Hearing samples. Coloured by catch area.

To study this, the samples were tagged with the year they were caught see Figure 7. No obvious time trends are seen but the oldest samples from the 1980s are in the upper right part of the plot, indicating a higher relative contribution of the congeners F123678 and F234678.

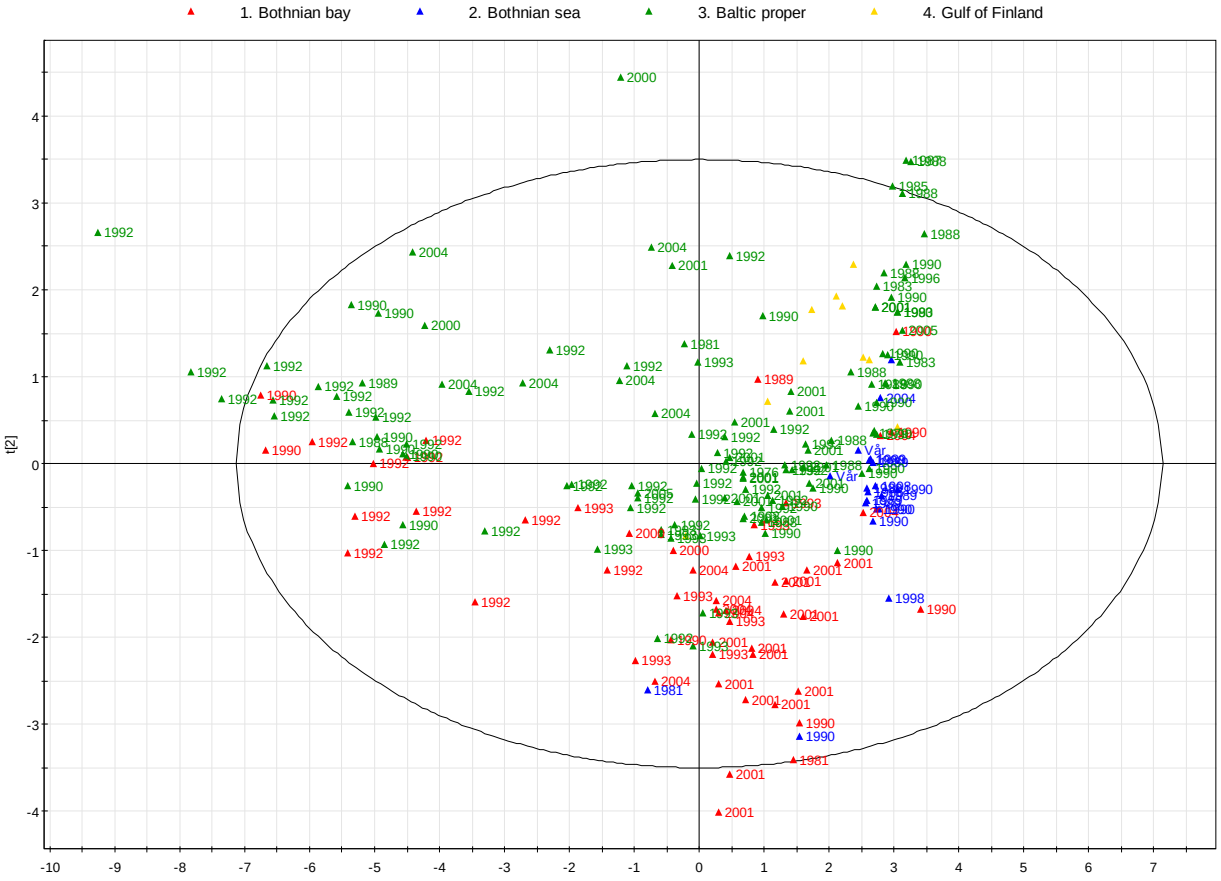

Figure 7. Tagged with the year the fish was caught.

One other possible reason for the difference in congener pattern is the age of the fish caught. In an ideal comparison regarding the source of the PCDD/PCDF all samples should be of the same age. The recommendation in the Swedish monitoring program is that the fish should be 2 years old. The data on the age of the fish used in this study has in some cases not been reported. In Figure 8 the samples are coloured by age.

The 2 years old are grouped well to the left and the older samples more to the right. This indicates that the pattern of dioxins differ between the age classes of Herring, which was already known.

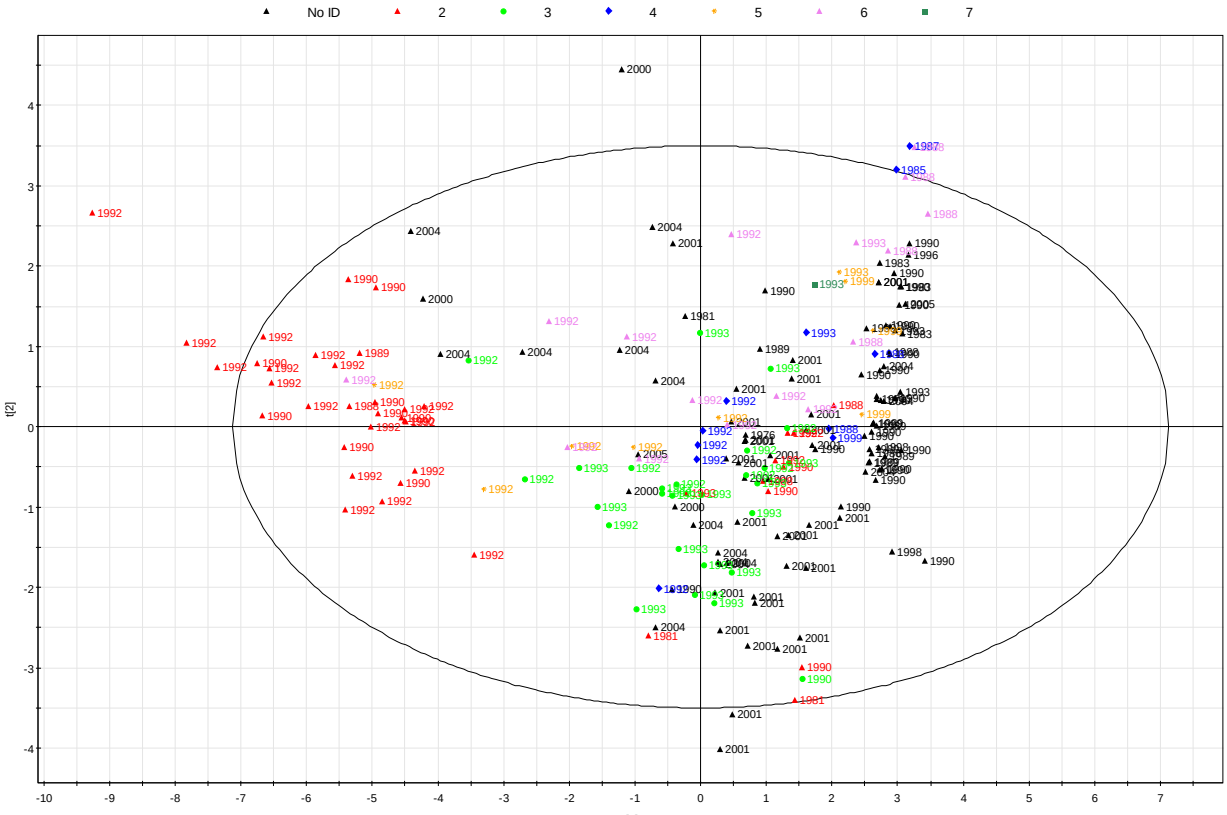

Figure 8. Samples with the age of the fish colour coded and year of catch as observation tag.

The loading plot, see Figure 9, for the above analysis, shows a transformation, marked by the dotted line, from the OCDD and PCDF to the D2378 and F2378 congeners. This means that the observations in the score plot that are located to the left, i.e. the 2 year old Herrings, constitutes of more chlorinated dioxins and furans and a shift in the pattern occurs when going to the right and down in the score plot.

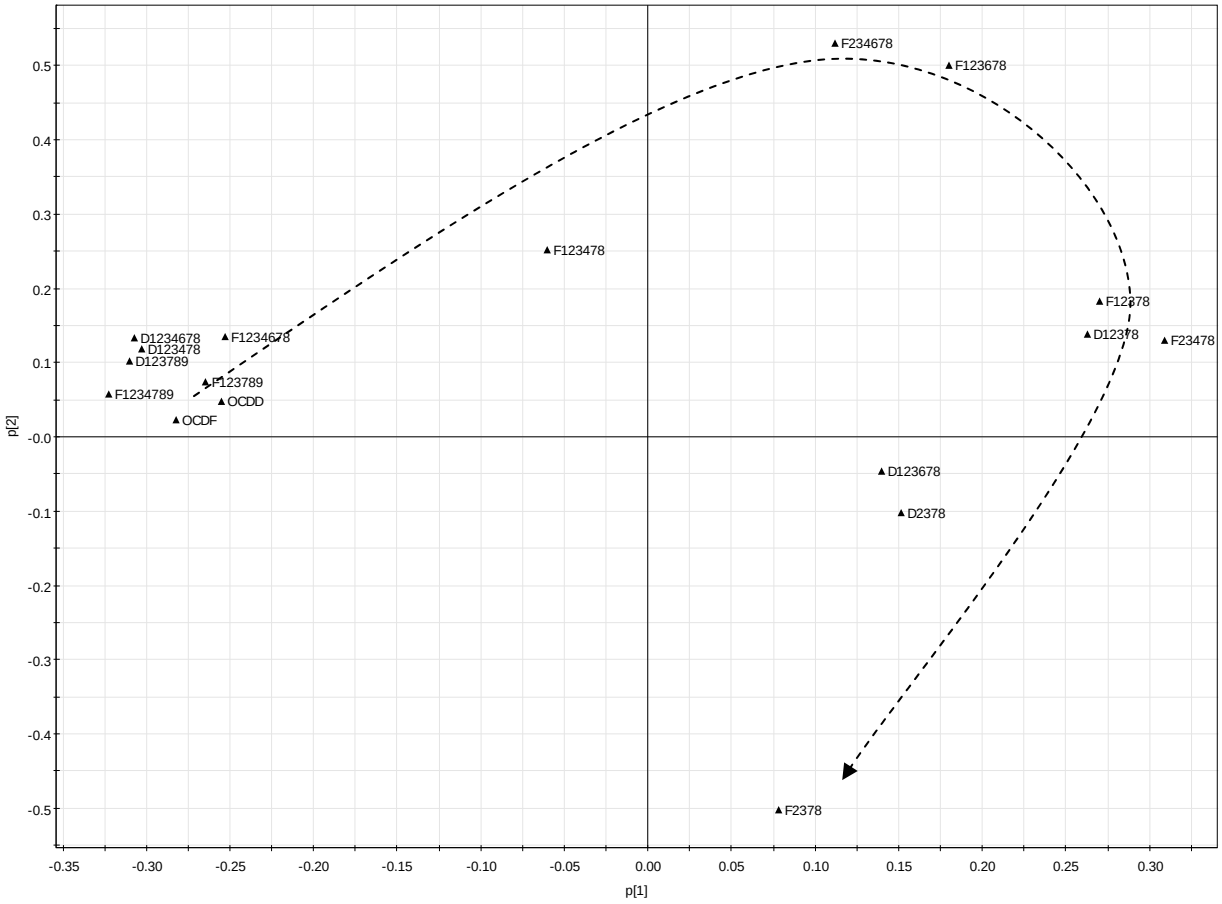

Figure 9. Loading plot for scores presented in figure 5- 7. The doted line show a possible track for changes in pattern of the congeners.

In Figure 10 a score plot where potential sources and biota samples are included in the PCA. The main group of biota samples are found to the right and the sources are spread out in the left part of the plot from the bottom to the top. Some of the source (flue gases) samples are found in the group of biota samples. This indicates that the pattern from these sources is similar to the pattern in the biota samples.

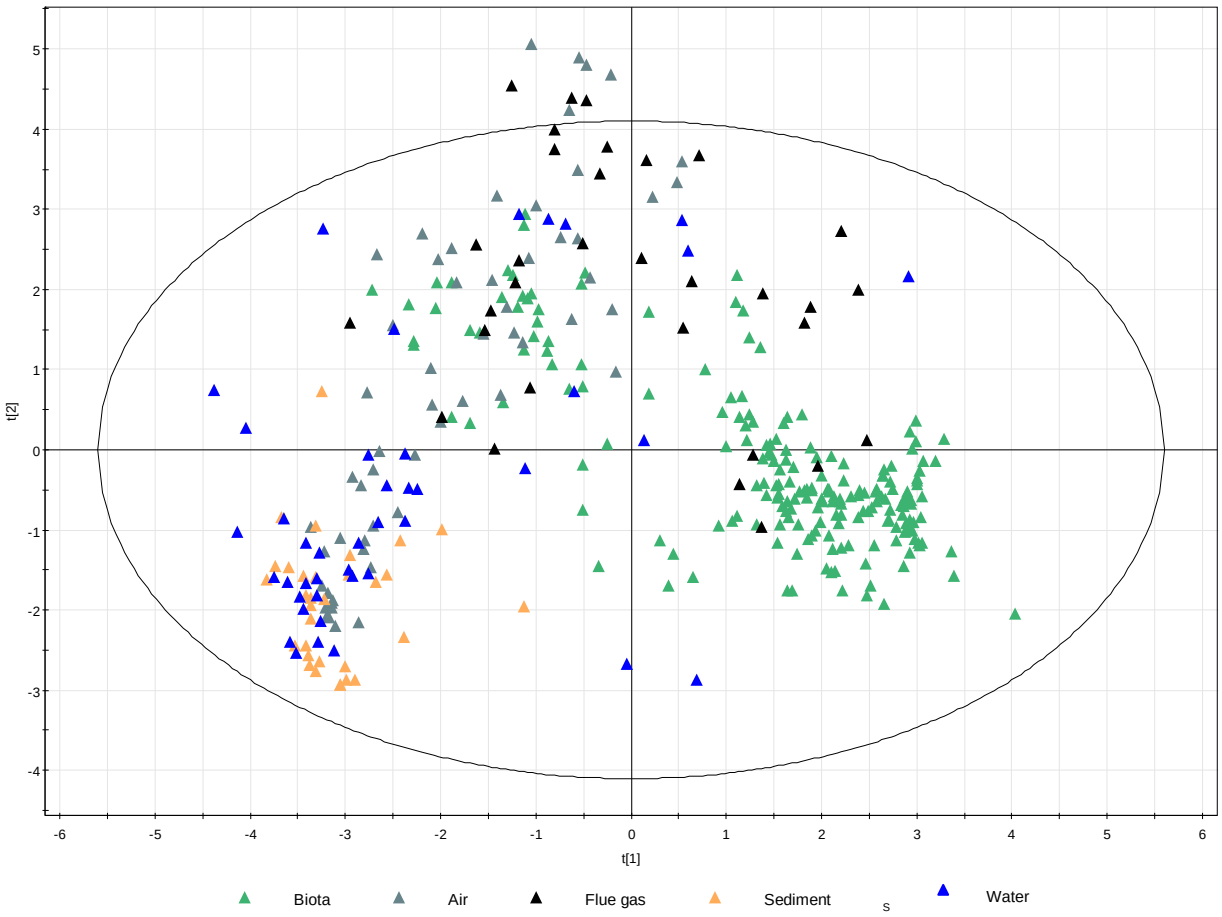

Figure 10. Score plot biota and potential sources.

The loading plot is presented in Figure 11 and a clear shift in the loadings is recognised, marked with a dotted line in the figure, from the OCDD and PCDF to the D2378 and F2378 congeners.

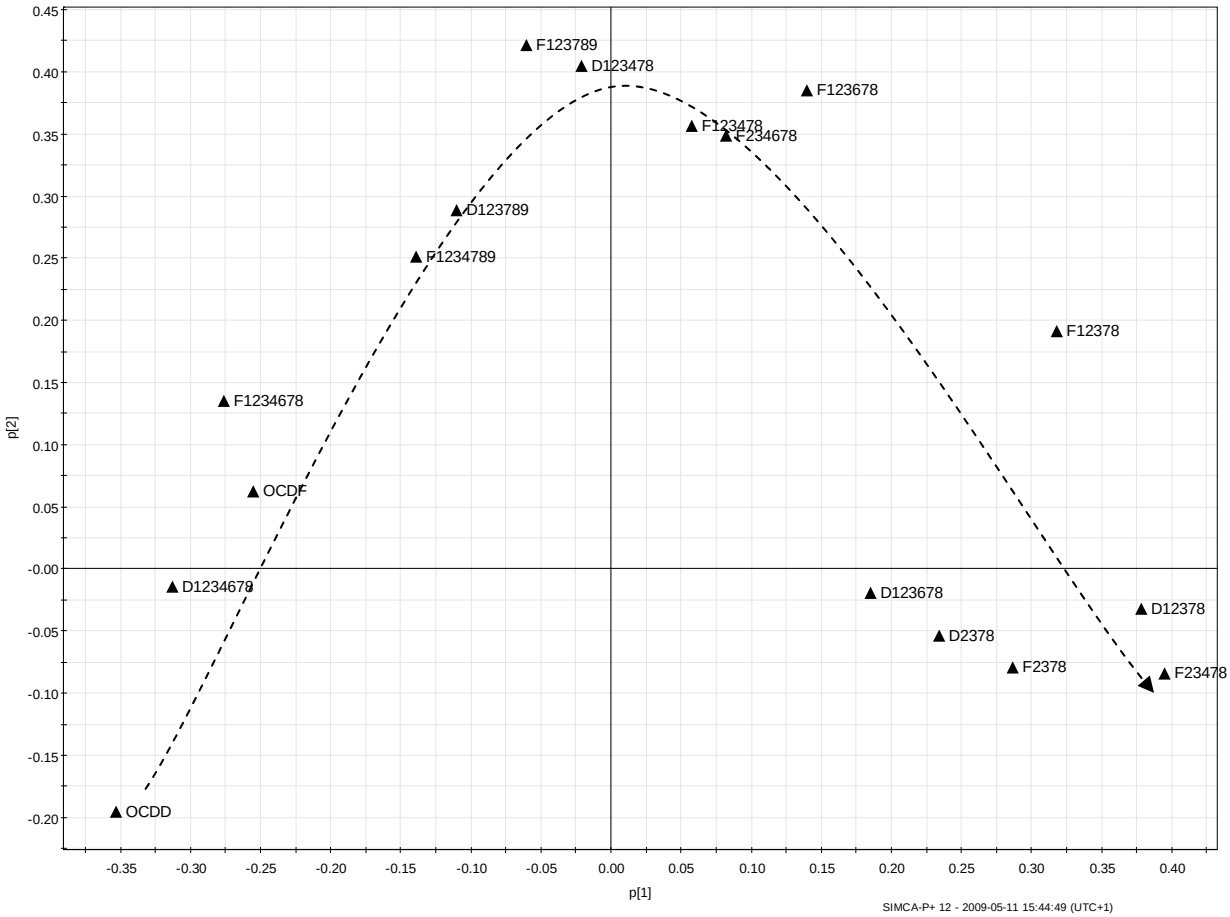

Figure 11. Loading plot for biota and sources.

Since the same data will be used in the receptor modelling this indicate that the sources that are collected in this study partly are matched with the biota samples and not known or not yet identified sources contribute to the patterns.

3.2 Receptor modelling

Three analyses with PMF were made to the data set. The first with data selected from Baltic herring, the second with sediment data and the third with soil data from wood impregnating facilities. To find the numbers of contributing sources several runs with PMF was performed. During these runs the source profile was changed in every run. The results presented below are those who fitted the data best and also could be interpenetrated, more or less.

For Baltic herring the receptor modelling resulted in a 3 factor model. The patterns of the 3 different factors are shown in Figure 12. Factor 1 is dominated by the furan F23478. Factor 2 consists mainly of F2378 and also F23478. Factor 3 is constituted by the most chlorinated dioxins and furans, D1234678, OCDD, F1234789 and OCDF.

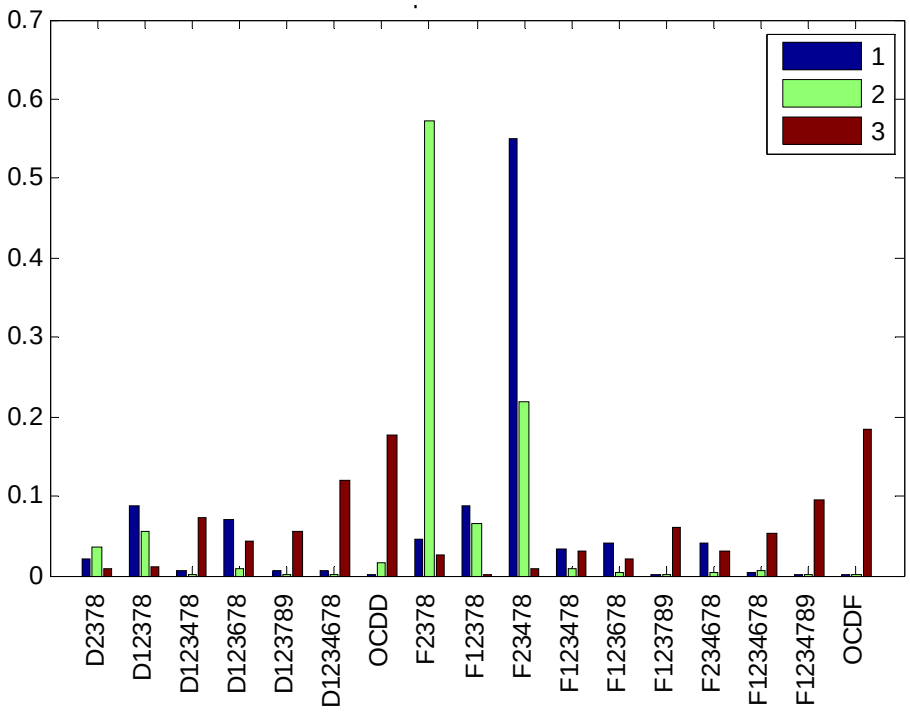

Figure 12. Relative contribution from the three different sources estimated with PMF.

The identification of the 3 factors was performed with help from the dataset collected during the project. Relative contribution plots for all potential sources were compared with the estimated factors above. This matching was done by visual inspection. The most obvious contributor is the "background/combustion" that can be identified in factor 3 above. The profile of factor 3 can be found from several sampling stations that have collected air samples in both rural and urban areas and no obvious point source of dioxins in the relative surrounding area. Factor 2 is dominated by F2378, this profile can be seen in flue gas from some specific combustion sources. But there also a contribution from D2378 and D12378 that not is seen in the flue gas profiles. This can be interpreted that other sources are contributing to this factor but that we do not have data for them and hence not been able to identify them. The pattern for factor 1 has not been identified. The dominating congener F23478 has not been observed as the main contributor in any of our source data. The sources to factor 1 may origin from not known or measured sources and are therefore

hard to identify. Since we have not had access to the newest analysis of dioxins in Herring there is a gap in the data.

The calculated profiles were compared with the measured and the relative errors is presented in Figure 13. The maximum error is about +/- 5 %.

Figure 13. Standardised residuals for the 100 first observations.

The amount of data for the two other target variables, sediment and soil samples, were not that many as for the Baltic herring. For the sediment samples a PMF model with two factors are used for interpretation of the sources, see Figure 14.

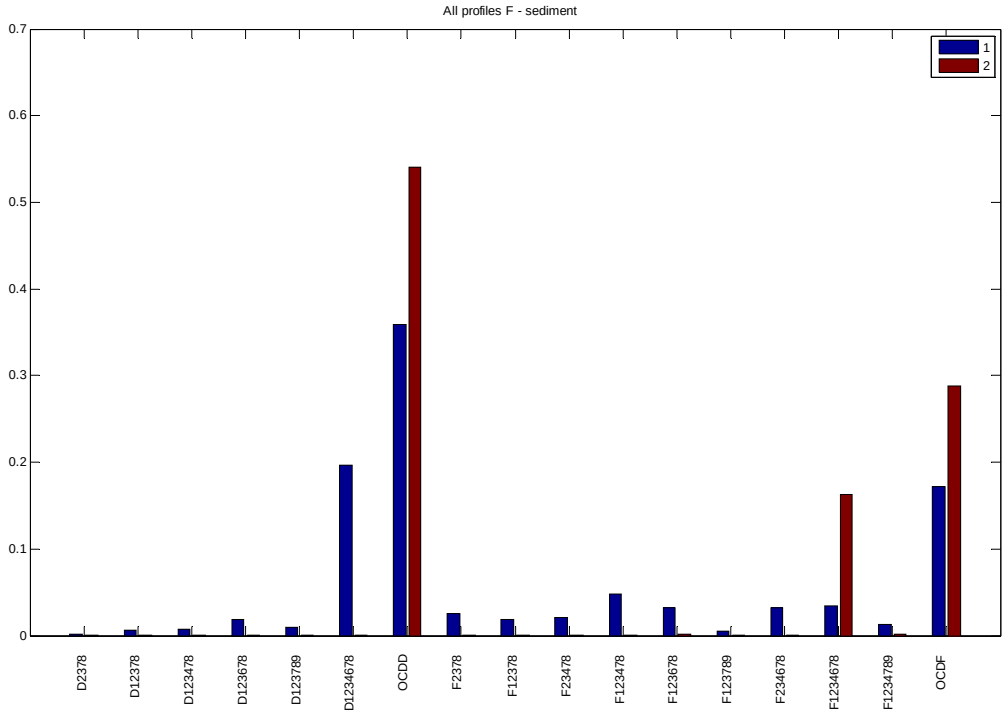

Figure 14. Factors for the PMF model for sediment data.

Almost all of the contribution to the pattern in the sediment is from factor 2. The contribution from factor 1 is almost constant for all the different samples and hence can be interpreted as a common background source. Both factor 1 and 2 patterns are very similar to the combustion- and the atmospheric background profiles, which are dominated, mainly by OCDD and then OCDF, F1234678, D1234678 congeners.

For the soil samples a one factor model is shown in Figure 15. The source for the dioxins in the soil should only be from the historical activities on this sites and the one component model also show this.

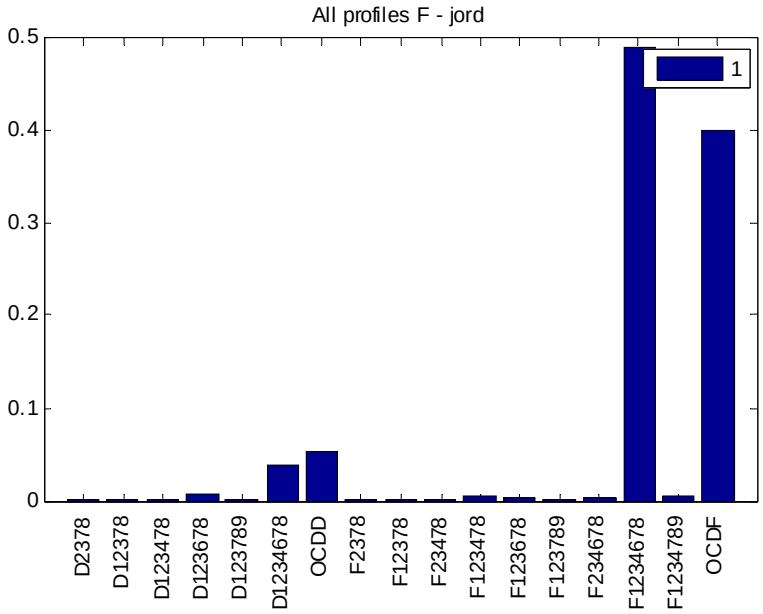

Figure 15. The profile of the only factor calculated by PMF for the soil samples.

Both the PMF models for the sediments and soil is calculated, as mentioned above, on few data points. Regarding the soil samples more observation will not alter the resulting model but for the sediment samples that could be true.

4 Conclusions

The pattern of dioxins and furans in Baltic Herring has been studied by PCA and some general conclusions can be made from this.

Herrings from the Bothnian Bay and Gulf of Finland has well defined pattern. The spread in pattern is larger for the Herrings caught in The Baltic proper and Bothnian bay. Also the age of the Herring effect the patterns, 2-year old Herring are well grouped and separated from older Herrings.

To investigate if biota and source samples (flue gas, combustion, background) have overlapping characteristic, a PCA model with these two kinds of samples were included. We found that the only sources in our data that were overlapping were biota and flue gas samples.

The PMF model for Baltic Herring points to three significant sources. One of them is identified to be a background/combustion. One of the other sources is not fully identified but some parts of the pattern are likely to be flue gas. The last source can not be identified by use of data collected in this project.

Unfortunately we do not have access to the recent analysis of dioxins and furans in Baltic Herring. Including those data in the PCA and PMF studies would certainly give more information about the pattern and trends in data.

To map sources to the Herring is a hard work and method development is needed in the receptor modelling to include biological transformation in the fish. It would also be god to have some kind of validation of such modification to the PMF model by use of process water containing dioxins in fish test.

Further work is also needed for better identification of potential sources. The focus of sources in this work has been from Sweden but a survey should be done on an international level.

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