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PCB congeners pattern analysis in sediment : attempting to link sources to observations

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Abstract

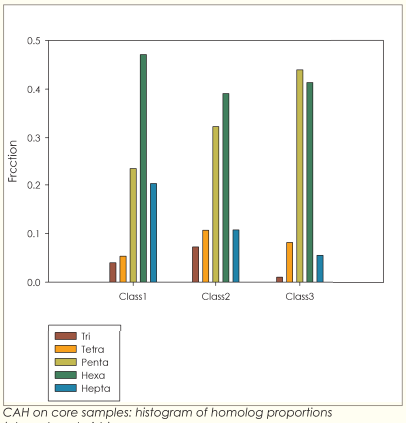
In fall 2005, fish contamination by PCBs above the threshold for fish consumption was observed in the Rhone river, in the vicinity of Lyon (France). This incidental observation triggered a series of investigations on fish and sediments contamination all along the main stream, and is currently extending to tributaries. The data gathered during this still ongoing process should help managers to identify the main sources among the host of potential ones, provided distinct patterns can be identified in relation to these sources. PCB congener pattern analysis in sediments is challenging because weathering processes will modify the original patterns in several ways; moreover, at mid- or downstream sites the various upstream sources will provide mixed patterns. Classical multivariate analyses suffer several pitfalls for such pattern analysis, making it difficult to clearly discriminate among PCB sources. A combination of information about sources or weathering processes, and classification approaches, should nevertheless help to establish relationships between the patterns observed in sediment layers and the sources, yielding an approach helping to sort out priorities for further diagnosis or management actions.

Introduction & objectives

In fall 2005, PCBs were detected in a few freshwater fishes intended for marketing near Lyon (France). Dioxin-like PCBs (DL-PCBs) exceeded the dioxin toxic equivalent (TEQ) threshold for fish consumption, i.e. 8 pg.g^{-1} (FW) (E.C. 2006; E.C. 2006). Step by step, monitoring studies of fish contamination were extended downstream to the Mediterranean sea, as well as upstream close to the Swiss border. Most of the French course of the Rhone was found to be of concern. Sediment samples (surface and cores) were also collected in order to help to locate sources.

As sediments in this system constitute both a type of source among others, and a sink (Babut and Miège 2007), it is interesting to analyze congeners patterns, so as to (i) characterize sources, and (ii) identify fate processes (transport, degradation). Ultimately, this will allow to prioritize management actions throughout the catchment.

Objectives: To perform a preliminary study of existing data on sediments in the Rhone river system, so as to identify an appropriate statistical approach to sources identification. This approach will be applied to the results on an ongoing survey on sediment quality in this system.

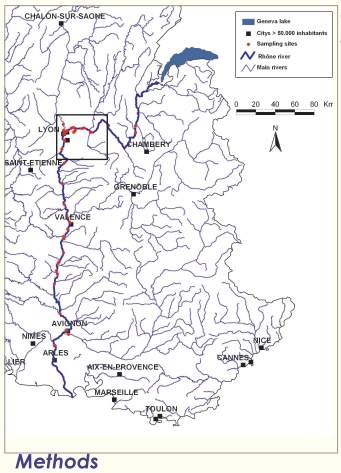


CAH on core samples: histogram of homolog proportions (classes' centroids).

Log ratio of proportion

$$LRp_{ij} = \log\left(\frac{p_{ij}}{g_j}\right)$$

with pij : proportion of homologue i in the sample j ; gj : geometric mean of homologues proportions in the sample j.



Rhone carchment, from Geneva Lake to the Mediterranean sea (design H. Pella, Cemagref)

Rhone and main tributaries near Lyon, France (http://www.geoportail.fr/5061750/visu2D/voir.htm)

Methods

Literature survey

Typically, the analysis of compositional data is complicated by the effect of closure (Miesch 1976); congener proportions have to be transformed prior to any multivariate statistical approach. Suggested statistical methods include PCA and cluster analysis (Howel 2007), or polytopic vector analysis (Huntley, Carlson-Lynch et al. 1998; Barabas, Adriaens et al. 2004). Apportionment models e.g. CMB 8.2 could be an alternative (Li, Jang et al. 2003).

Materials & Methods

- A first set made of cores from 7 locations was sampled in autumn 2006 in the Rhone river. These cores were divided into 22 sub-samples (max. 4 sub-samples per core).
- A second set composed exclusively of surface sediments was made of 43 samples obtained in falls 2006 and 2007; the samples were gathered with a grab operated either from a boat or from the river bank, in sedimentation areas, (i) in a section of the river course close to Lyon, and (ii) along an upstream-downstream gradient covering the whole course of the Rhone in France.
- Sediments were homogenized and freeze dried, and Soxhlet extractions performed with a mixture of toluene/ethanol (30/70, vol/vol). The analysis of 18 PCB congeners was performed according to USEPA standard 1668: gas chromatography (Agilent 6890) coupled with high resolution mass spectrometry (Micromass Ultima Waters).
- Grain size distribution, organic carbon content were available for both sets. Datation by ^{7}Be, ^{210}Pb and ^{137}Cs analysis were performed on core samples.
- Cluster analysis (Ward method) and PCA on log-ratios (Howel 2007) performed with XIstat 2008 ®, Addinsoft.

Results & discussion

Cores

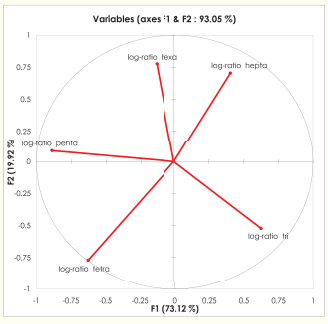
- CAH: class 2 samples have less Hexa- and Hepta- chlorinated congeners, more Tri- to Penta- congeners than Class 1 samples. Sample position in cores (surface versus depth) does not explain the differences.
- Dating was not very consistent for certain cores, suggesting that the deposition regime in this area was frequently disturbed, or deposits modified by dredging.

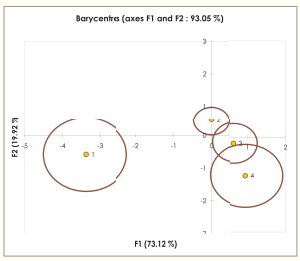
Surface samples

- A few samples collected close to known or suspected sources display distinct signatures. CAH results are complex, with an apparent spatial pattern. Nevertheless sampling sites from the area downstream a well known source are almost equally distributed in 2 different classes.
- A PCA was performed with log-ratios of homologues and the proportion of fine particles (<50 µm) as variables. The proportion of fines is independent from the PCB homologues.
- A FDA (factor analysis based on intra-class variances) was done with sources represented by areas: upstream the T source, Isere catchment etc. Sample sites were assigned to sources classes according to their location in the catchment. Nonetheless, downstream sites are influenced by several sources.
- Samples assigned to class 2, immediately downstream source T, are well classified (predicted); prediction rates for other classes are less satisfactory.
- Further downstream the T source signatures are not easily discriminated, as (i) sources are mixed, and (ii) downstream transport is occurring with floods.

Perspectives

- Some sources at least should be characterized (PCB, PCDD and PCDF analyses/contaminated soils)
- Extend the approach to PCDD and PCDF, which could help to obtain more specific signatures,
- Attempt to apply PVA or source apportionment models
- New sediment cores were collected in 2008, and are currently being analyzed with a higher resolution; rresults will be processed following these approaches.





		Model Clasification				
Classes	Assigned	1	2	3	4	% correct
1	3	2	1	0	0	66.67%
2	17	0	16	1	0	94.12%
3	10	0	4	6	0	60.00%
4	4	0	1	1	2	50.00%
Total	34	2	22	8	2	76.47%

1: Rhone upstream + Bourbre
2: Rhone, downstream source T
3: Isere, and Rhone downstream its confluence with Isere
4: Durance, and Rhone downstream its confluence with Durance

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