Fingerprint analysis of PCB in the environment: an environmental forensics tool for a better knowledge of pollution sources

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Polychlorinated Biphenyls

PCBs are a group of 209 “man-made” chlorinated organic compounds that were widely used in the twentieth century for a variety of industrial uses

PCBs were first produced in 1929 and were manufactured until the 1970s and 80s when their use was phased out due to environmental and human health risks

PCBs are very stable compounds that do not readily degrade, they are POPs and are listed under the Stockholm convention as part of the “dirty dozen”

Polychlorinated Biphenyls

PCB are not produced naturally as single congeners, instead they were artificially synthetized as blends, containing a mixture of different PCB which were sold under trade names based on their chlorine content. The market leader for PCB production was Monsanto who manufactured PCB mixtures called Arochlors

Estimates of Monsanto’s production were around 600.000 tons on a global production estimated to 1.200.000 tons

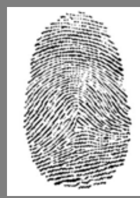
Other major producers of PCB were Bayer AG (Germany) producing Clophens, Kanegafuchi Chemical Company (Japan) producing Kaneclor, Podolec (France) producing Phenochlor and Pyralène and Delor in former Czechoslovakia

Polychlorinated Biphenyls

Monsanto produced nine main Arochlor blends, each were identified with a four digit code.

For example Arochlor 1254 contained 12 carbon atoms and had a mixture of PCB that makes the end product 54% chlorine by weight

Because of the limitations of the Arochlor method in forensic investigations, especially where mixtures of similar sources occur, the high resolution GC/MS-based method is often used



This congener-specific method is used for detailed environmental forensics investigations focused on inference of PCB sources in complex environmental systems

A PCB forensic study involves a sequence of events and activities:

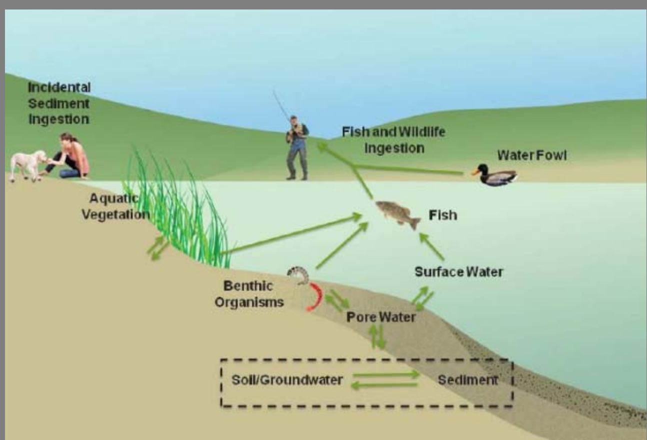
- ✓ Step 1: Develop conceptual site model
- ✓ Step 2: Develop and execute a technically defensible sampling plan
- ✓ Step 3: Conduct rapid characterization
- ✓ Step 4: Conduct advanced chemical fingerprinting
- ✓ Step 5: Data analysis, synthesis and presentation of results

Step 1: Develop conceptual site model

The CSM is a mental “picture” of the site. It includes graphical representation of the contamination and fate and transport processes at the site. CSM development should include the following elements:

- ✓ It should provide an understanding of contaminant fate and transport processes
- ✓ It should include a review of pre-existing information and environmental data to identify contaminants and all of the known or suspected sources or source areas
- ✓ It should support the development of specific objectives (hypotheses or forensic questions) to be evaluated by the study that address the potential PCB sources

Step 1: develop conceptual site model



Step 2: Develop and execute a technically defensible sampling plan

The development of a technically defensible sampling strategy requires a balance between meeting project and data quality objectives within the budget of the project

- ✓ Determine how many samples will be used and the type of analyses to be performed
- ✓ Plan sampling plans for the implementation of the next two steps

Step 3: Conduct rapid characterization

- ✓ Rapid site characterization of PCBs is conducted primarily using immunoassay techniques
  - ➢ Semi-quantitative, non-specific data (cannot distinguish between different Aroclor mixtures or individual congeners)
  - ➢ Cross-reactivity for some classes of contaminants

Step 3: Conduct rapid characterization

- ✓ The benefit of this approach is a cost-effective study design for a heterogeneous matrix such as sediment
- ✓ The goal of the rapid characterization analysis is ultimately to develop a sufficient set of visual or conceptual displays to aid in the selection of samples for next step
- ✓ Physicochemical data, such as the grain size distribution and TOC for sediment, may assist in interpretation of sediment transport and provide useful correlations to PCB concentrations

Step 4: Conduct advanced chemical fingerprinting

Determining the number and location of samples

The analytical strategy and budget will largely determine the number of samples that will be selected. Some guiding principles for the selection of samples are as follows:

1. Select samples that provide ample spatial coverage of the entire study area
2. Select a sufficient number of samples from specific location(s) within the study area that address a specific project objective(s) [source areas and mixing zones], and
3. Select samples that represent the range of the previous step concentrations observed, including those that are (apparently) representative of the background conditions

Step 4: Conduct advanced chemical fingerprinting

Selecting analytical method

The standard methods are focused on compounds identified as “priority pollutants,” (12 PCB) which are generally inadequate to distinguish different sources of otherwise similar contaminants

A forensic analysis for PCBs will typically include the characterization of the 209 PCB congeners

Step 4: Conduct advanced chemical fingerprinting

Interpreting results

- ✓ The first step in source determination is visual congener and homologue profile comparisons
- ✓ An appropriate second step in the data analysis sequence may be the use of exploratory statistical method such as principal component analysis (PCA) or R^2 for similarity and dissimilarity analysis

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Example

In this study, two sites (site 1 and site 2) were considered potential PCB sources to the sediments of a waterway abutting both sites
A first campaign of 90 samples was conducted using immunoassays kits. From these data, a subset of 11 samples representing source samples and waterway sediments were selected for the current evaluation
The data were normalized such that the sum of the congeners concentrations is 100

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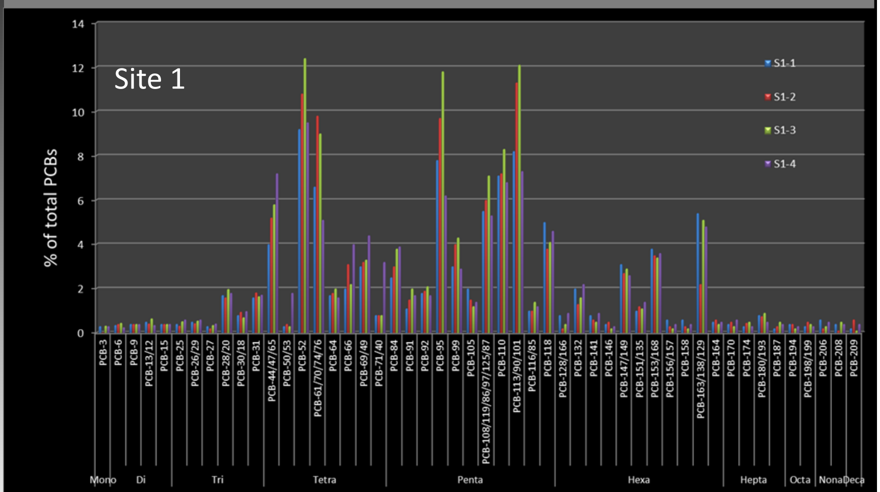

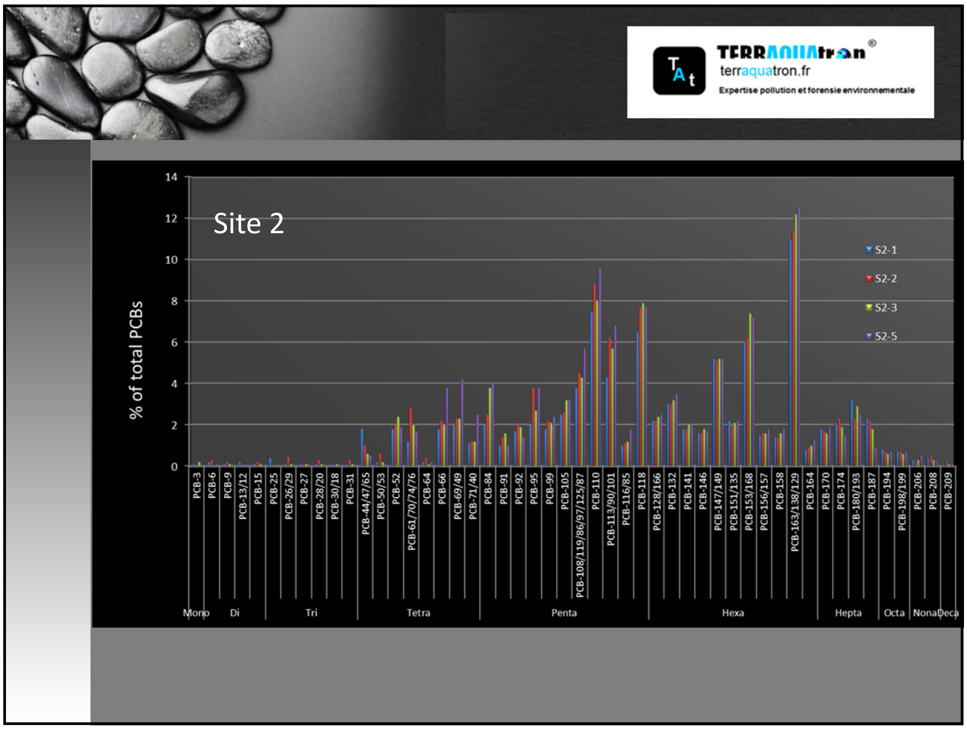
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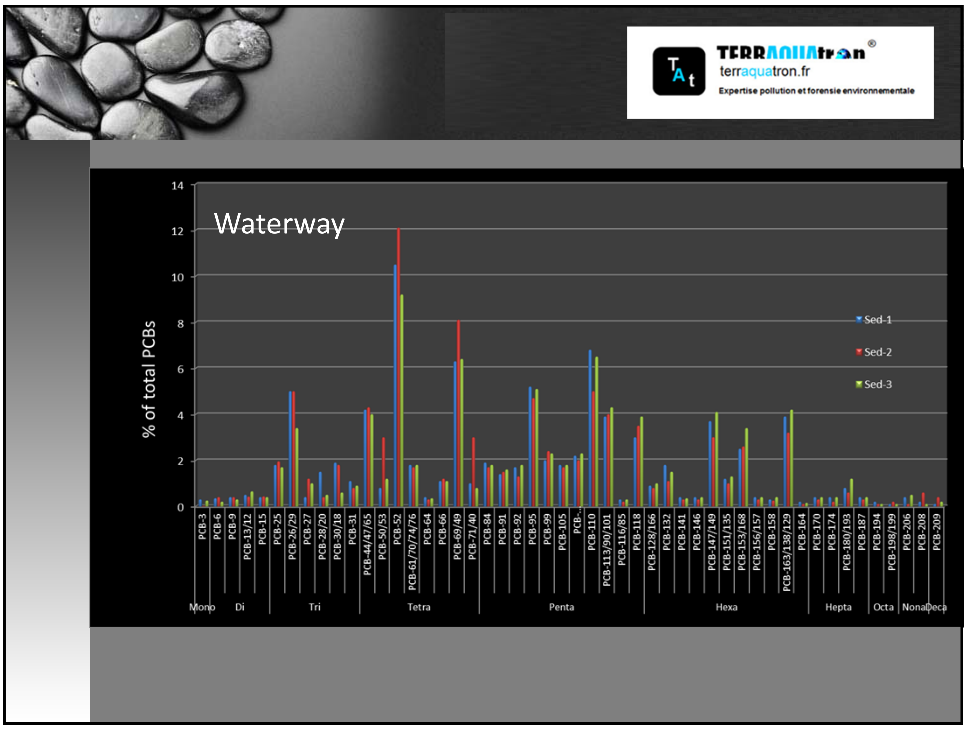
Site 2
% of total PCBs
14
12
10
8
6
4
2
0
S2-1
S2-2
S2-3
S2-5
Mono
Di
Tri
Tetra
Penta
Hexa
Hepta
Octa
Nona
Deca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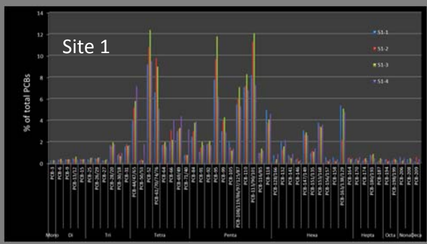
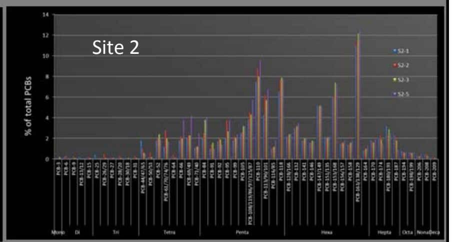
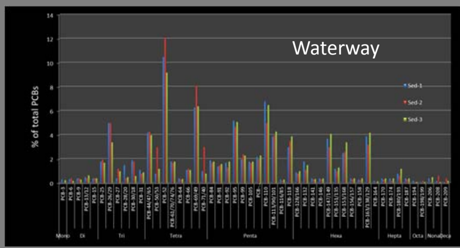
Waterway
% of total PCBs
14
12
10
8
6
4
2
0
Sed-1
Sed-2
Sed-3
Mono
Di
Tri
Tetra
Penta
Hexa
Hepta
Octa
Nona
Deca

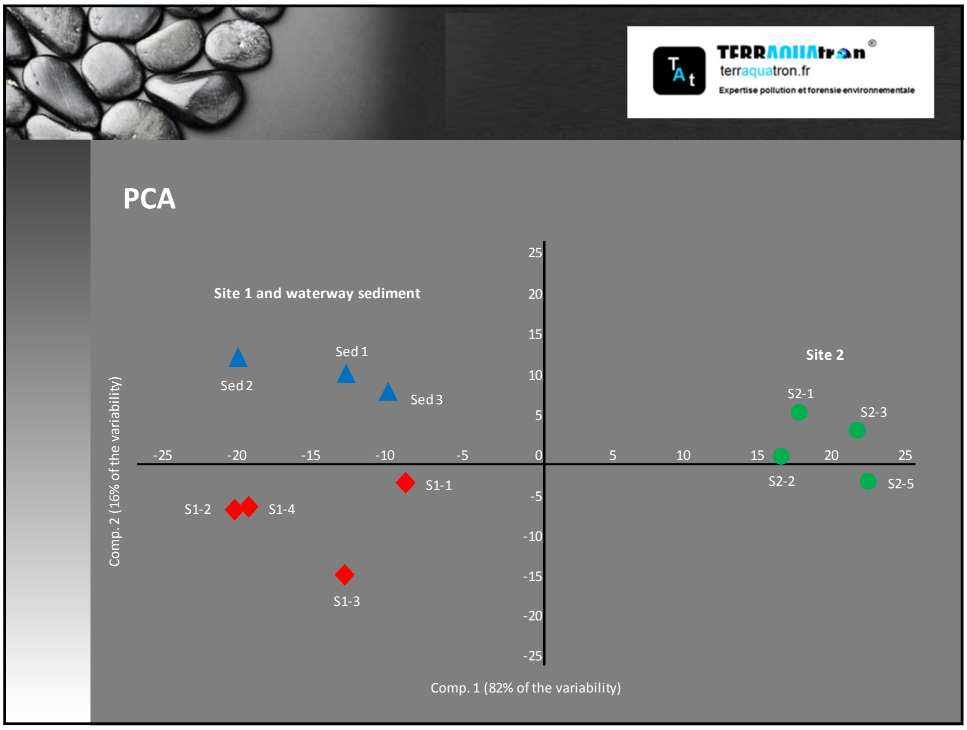






PCA

PCA is a statistical technique that can be used to explore relationships between groups of samples with multiple variables, to determine whether sample profiles resemble one another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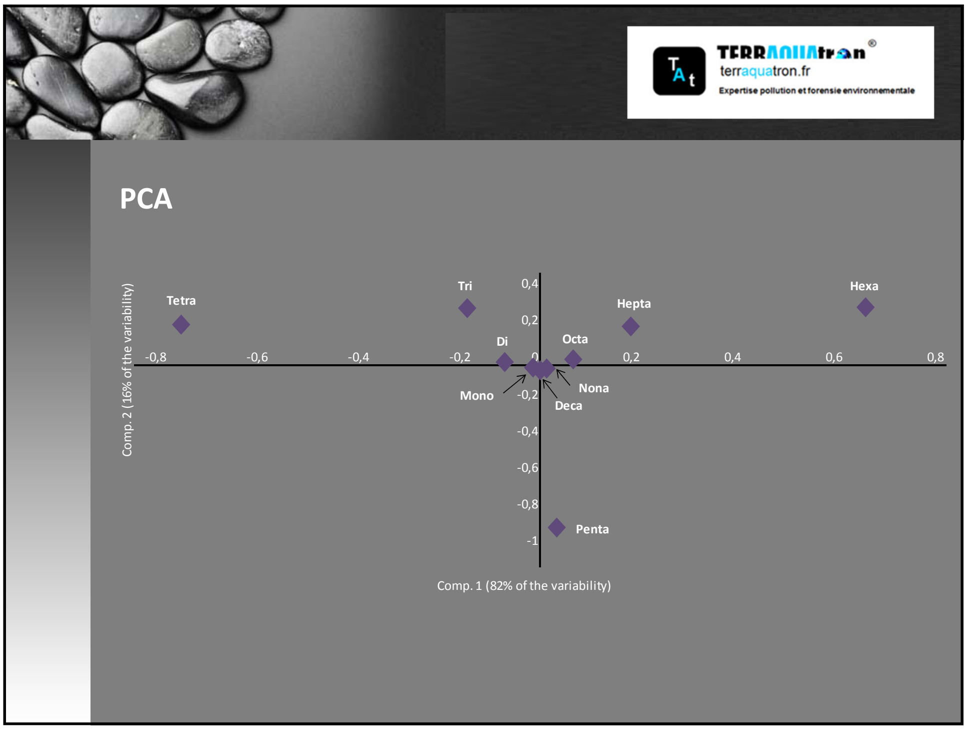
Expertise pollution et forensie environnementale
PCA
Site 1 and waterway sediment
Site 2
Sed 1
Sed 2
Sed 3
S1-1
S1-2
S1-3
S1-4
S2-1
S2-2
S2-3
S2-5
Comp. 2 (16% of the variability)
Comp. 1 (82% of the variability)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Expertise pollution et forensie environnementale
PCA
Tetra
Tri
Di
Mono
Octa
Nona
Deca
Hepta
Hexa
Penta
Comp. 2 (16% of the variability)
Comp. 1 (82% of the variability)

Congener profile comparison using R^2

The similarity between any two congener profiles can be defined through the use of the coefficient of determination R^2 calculated by plotting the congener concentration results of one sample versus the other sample

A R^2 value of 1 indicates a perfect match between profiles, while a R^2 value of 0 indicates no relationship between profiles

✓ A fingerprint match	R^2 is 0,9 or higher
✓ Very similar fingerprints	R^2 is 0,8 to 0,89
✓ Similar fingerprints	R^2 is 0,7 to 0,79
✓ Ambiguous relationship	R^2 is 0,6 to 0,69
✓ Distinctly different fingerprints	R^2 less than 0,6

Congener profile comparison using R^2

Source area profiles: Site 1

For site 1, the range of R^2 between any two samples is from 0,9 to 0,97 indicating matching profiles

Source area profiles: Site 2

For site 2, the range of R^2 between any two samples is from 0,95 to 0,98 indicating matching profiles

Site 1 and site 2 comparison

A qualitative (visual) comparison of the congener profiles associated with site 1 and site 2 source samples showed significant differences. The range of R^2 between all the site 1 and site 2 samples is from 0,18 to 0,63, indicating distinct differences

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Congener profile comparison using R^2

Waterway congener profiles
The sediment samples exhibited similar PCB congener and homologue patterns to each other, with R^2 for congener profiles from 0,92 to 0,97. This indicates that the PCB sources(s) have been fairly constant in composition over time
Congener profile comparison to determine the predominant source of PCB to the waterway sediments
Site 2 and the waterway sediment show a R^2 ranging from 0,18 to 0,5. Site 1 and the waterway sediment samples show many values greater than 0,7 indicating similar fingerprinting profiles

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Conclusion

Multiple lines of qualitative and quantitative analyses were used successfully
Qualitative (visual) congener profile comparisons showed significant differences
These comparisons could be supported by the use of the linear correlation coefficient R^2 and by a PCA
This kind of study is only possible when using the 209 congeners analysis. When using Arochlors or the 12 classical PCB, results are not relevant

THE END

Thank you for your attention

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