Unscrambling contaminant mixtures to determine their chemical fingerprints and origin

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Introduction

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Apportionment of environmental liability and allocation of response costs among two or more responsible parties are frequent issues in liability dispute settings

Introduction

Typical approaches to quantify relative amounts of released contaminants between parties include:

1. Chemical loading estimates based on operations
2. Contaminant fate and transport models
3. Chemical fingerprinting and statistical analysis

Introduction

The latter approach includes a variety of quantitative "Chemical Source Models" that have been developed and published in the literature, and applied in legal proceedings

These Chemical Source Models are also called "receptor" models, with "receptors" referring to environmental media, such as sediment or soil, that received contamination, and for which contributions from different sources are being determined

What are Chemical Source Models?

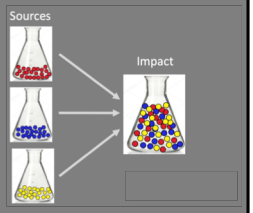
What are chemical source models?

Chemical Source Models quantify source contributions to environmental samples based on chemical fingerprints of the environmental and source samples.

Chemical Source Models focus on the chemical profiles of environmental and source samples to calculate contributions from a mixture of sources.

What are chemical source models?

Mixing models rely on the user-identified chemical source profiles to mathematically mix those profiles in varying proportions until the best match to each environmental sample is obtained.



What are chemical source models?

Mixing models

Model	Example Applications	
	Environnemental media	Contaminants
Chemical mass balance (CMB) - EPA	Airborne particulate matter, sediments	PAHs, PBDEs, PCDD/Fs
Partial least squares (PLS)	Sediments	Petroleum hydrocarbons
Multiple linear regression (MLR) may be combined with other statistical techniques	Airborne particulate matter, sediments	PAHs, PFCs

PBDEs : polybrominated diphenylethers
PFCs : per- and polyfluorinated compounds

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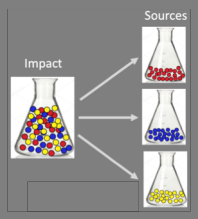
What are chemical source models?



Unmixing models begin with the environmental samples and use the measured environmental chemical data in each sample to determine a set of potential source chemical profiles

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What are chemical source models?

Unmixing models

Model	Example Applications	
	Environnemental media	Contaminants
Positive Matrix factorization (PMF)	Airborne particulate matter, sediments, soils	PAHs, PCBs, PCDD/Fs, PBDEs, PFCs, metals
Unmix	Airborne particulate matter, sediments	PCBs, PAHs, PFCs, metals
Polytopic vector analysis (PVA)	Sediments	PCBs, PCDD/Fs

PBDEs : polybrominated diphenylethers
PFCs : per- and polyfluorinated compounds

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What are chemical source models?

	PVA	PMF	UNMIX
Pros	Intuitive and simple to operate, produces comprehensive text-based output files, able to reproduce good results from synthetic data, assist in determining the number of sources	Free from US EPA, provides the most accurate results from the synthetic data, has a community support forum, flexible with many sources solutions possible, supports XLS files, workflow is readily apparent	Free from US EPA, has a community support forum, produces figures for inspection within the package, supports XLS files
Cons	Not available commercially, although routines exist for other mathematical packages, the results are not as accurate as those from PMF	Relatively intensive in processor time, does not assist in determining the number of source	Inflexible and will produce solutions based only on set criteria, the user interface looks dated, with "buttons" missing, does not always work

Modelling steps and interpretation

Most of the time, the following three steps are included where Chemical Source Models are applied:

1) Establish the number of probable sources to the affected environment
2) Determine their chemical fingerprints
3) Estimate the proportions at which these sources have affected the receptors

Prior to conducting the unmixing of sources with the environmental dataset, the data are analyzed by principal components analysis (PCA) to determine the most likely number of sources and the major chemicals in each source.

PCA also allows for a degree of data validation, as unusual samples will be highlighted and can be investigated as necessary

Polytopic Vector Analysis (PVA)

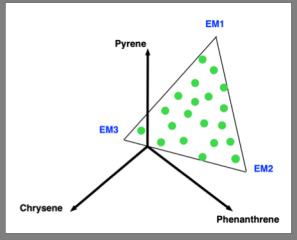
Polytopic vector analysis

When there is an unknown number of sources as well as background condition, Polytopic Vector Analysis (PVA) can be used to determine the number of end members or potential sources in a dataset.

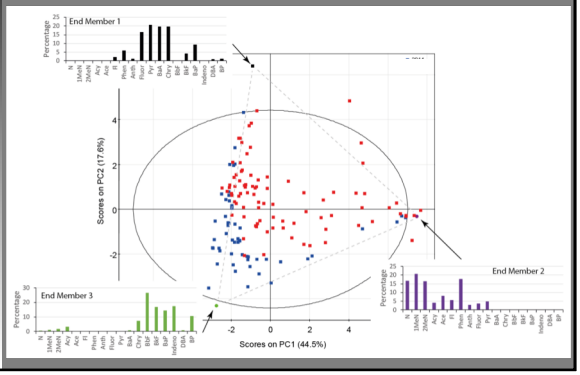
The approach fits a shape with the fewest corners necessary to encompass all of the measured data.

Polytopic vector analysis

A polytope is a shape with one less dimension than the number it is plotted in.



Polytopic vector analysis



Polytopic vector analysis

Corners can be added until an adequate fit is obtained, within the constraints and uncertainty of the data.

This approach will also identify the composition of the end members (sources) at the corners and what the mixing proportions of the sources are necessary to reconstitute any sample.

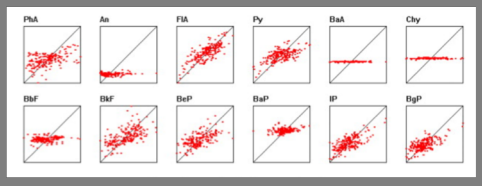
Polytopic vector analysis

To determine the correct number of end members in a data set, the correlation between the observed and predicted proportions can be used.

As the number of end members increases, the fit to the data improves.

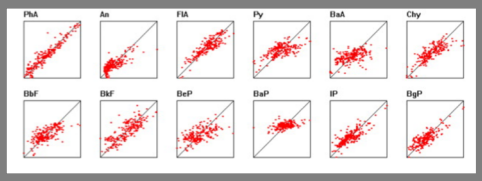
Polytopic vector analysis

Observed vs predicted with two sources



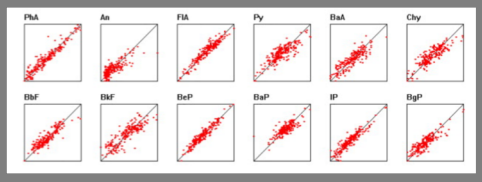
Polytopic vector analysis

Observed vs predicted with four end members



Polytopic vector analysis

Observed vs predicted with six end members

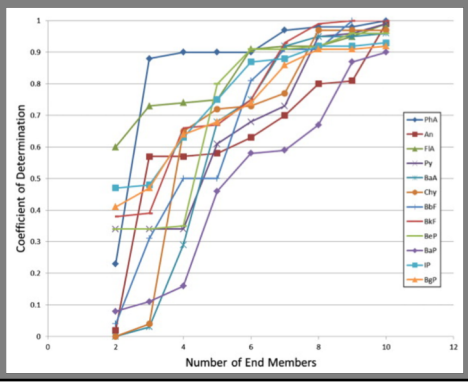


Polytopic vector analysis

It is possible to put all of this data onto a single figure by plotting the fit to the data for each compound with each end member.

The data displayed can be seen with all end members and compounds included.

Polytopic vector analysis



Summary

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All statistical methods rely on having sufficient quality data of the appropriate type It is not possible to have a robust defensible result with poor data and so effort should be directed to ensuring data quality all the way through the sampling and analysis program.

The stages may be summarized as:

Summary

Summary (cont.)

1. Identify the question that requires an answer *before* collecting any samples
2. Determine the most appropriate sample types and location for analysis and the most appropriate chemical compounds to analyze. Don't only analyze for the toxic compounds if the question relates to source apportionment

Summary

Summary (cont.)

3. Ensure quality and consistency throughout these aspects and verify the dataset before conducting statistical methods
4. When applying the multivariate methods outlined here, normalize the data to remove the concentration effects and develop strategies for zeros and for including or excluding compounds

Summary

Summary (cont.)

5. Chose the most appropriate statistical analysis for the data and answer the question. Consider performing several statistical tests to ensure they all indicate the sample result for improved confidence in the answer.

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