A new model for the inference of population characteristics from experimental data using uncertainties. Application to interlaboratory studies.

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QUASIMEME Project

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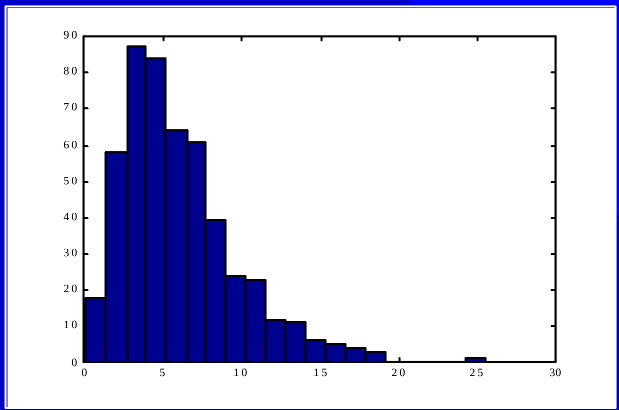
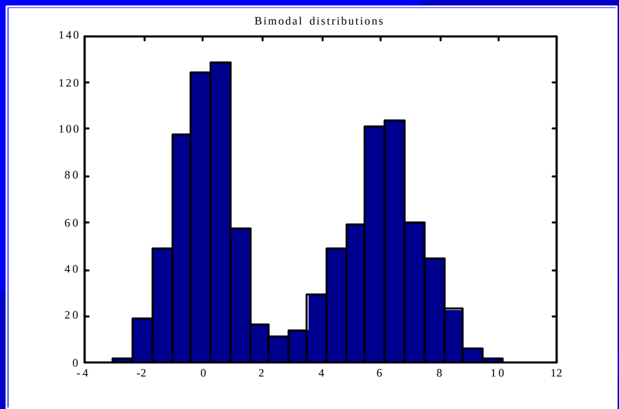
Why search for a new model?

- Currently, either models using outlier tests (thus assuming a certain distribution for the data) or robust statistics are used
- These existing techniques have difficulties to cope with many datasets encountered in practice (bimodal, strongly tailing,…)

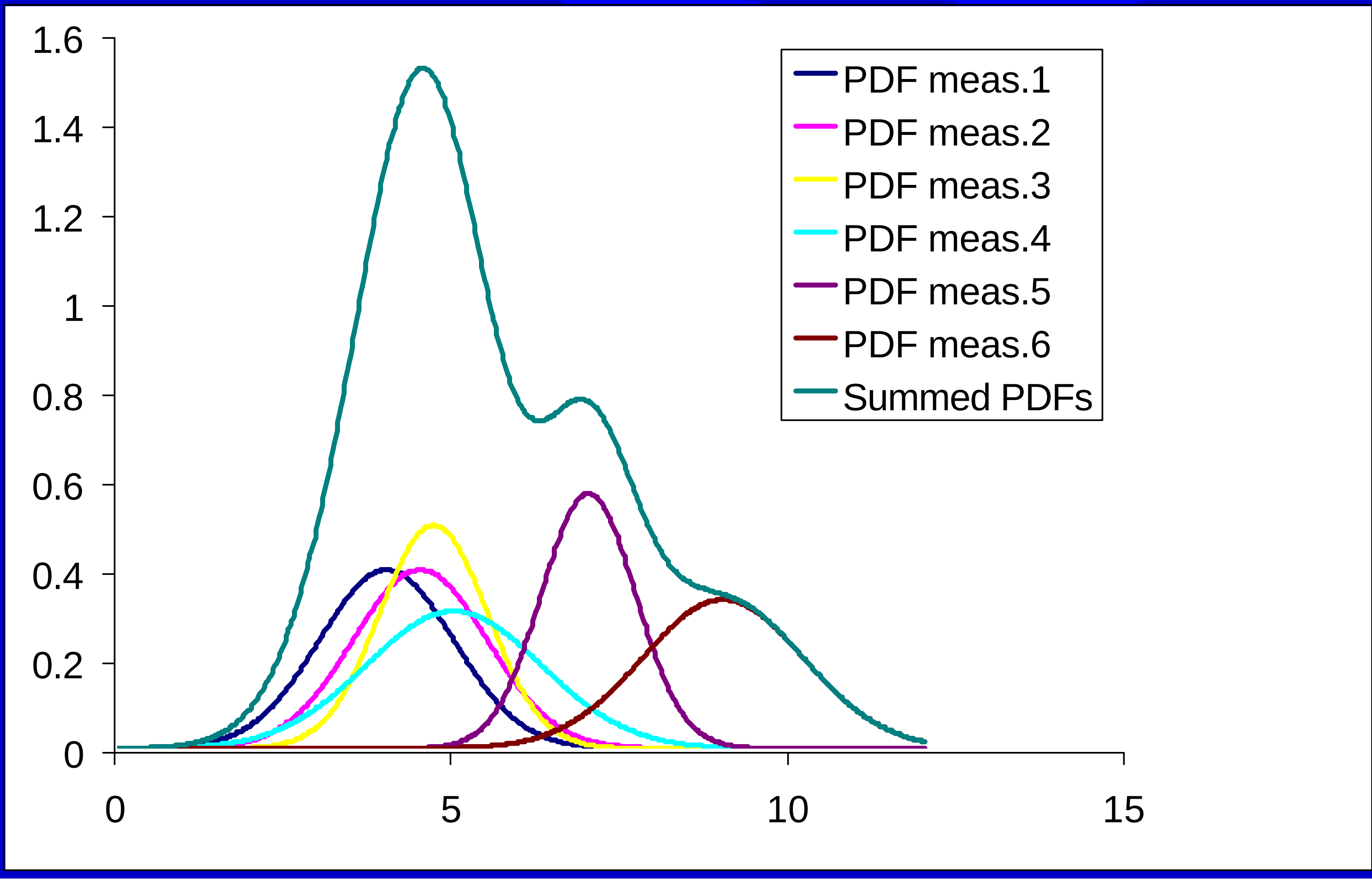


Tailing distributions



Bimodal distributions

The concept of the model – replace datapoints by probability density functions, look for maxima in overall PDF



The model-Quantum chemistry as analogon

- Stationary states of system (e.g. an atom) have wavefunctions Ψ which are solutions to the Schrödinger equation $H\Psi=E\Psi$
- $|\Psi|^2$ is a probability density function

- Molecular orbitals are constructed from atomic orbitals using matrix algebra:

$$\Psi_j = \sum_i c_{ij} f_i$$

coefficients are determined by finding minimum energy

- Our knowledge of measurement processes enables us to to estimate probability density functions of labs/datapoints
- the square root of the estimated pdf for a lab/datapoint can be used as a 'wavefunction' (**Observation measurement function** OMF ϕ)
- A '**Population measurement function'** PMF $\Psi(x)$ is defined as

$$\Psi_j = \sum_i c_{ij} f_i$$

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The model- continued (I)

- The coefficients c_i are obtained by
  - in words
    - ➔ *selecting the largest number of laboratories/data which 'agree'*
  - mathematically
    - ➔ *maximising the probability of the (unnormalised) population measurement function, i.e.*

$$\int \Psi^2 \, \mathrm{d}x$$

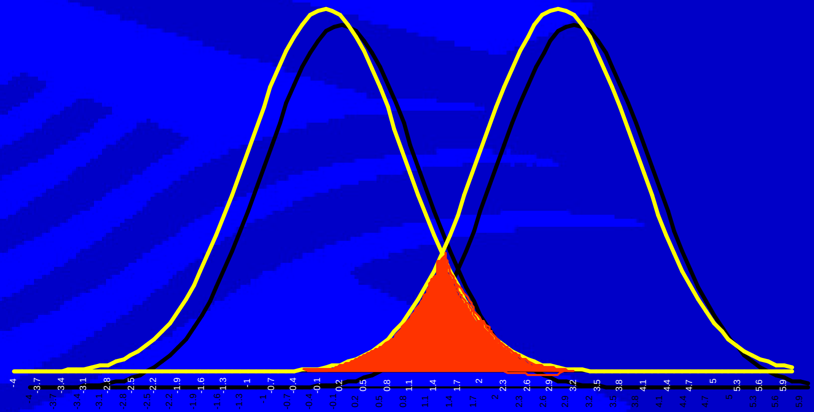
Ψ *being given by*

$$\Psi = \sum_i c_i f_i$$

using the method of Lagrange multipliers subject to the constraint that the sum of the coefficients equals 1

Overlap as central concept

- The results of two laboratories/datapoints (may) overlap
- The magnitude of overlap is a measure for ‘how well the laboratories/data agree’
- The overlap is calculated as follows:



Red: Area of Overlap

$$\int f_i f_j dx = S_{ij}, 0 < S_{ij} < 1; \quad S_{ii} = 1$$

The model - continued (II)

- The mathematical approach amounts to solving the eigenvalue-eigenvector equation,

$$Sc = l\,c$$

- the eigenvector c_l with highest eigenvalue λ gives the pursued coefficients
- the eigenvalue λ_i is a measure for the probability of the interlaboratory measurement function Ψ_i

The model - continued (III)

- The expectation value and variance of the population measurement function Ψ_i is calculated as

$$\bar{x}_i = \int x\Psi_i^2 dx / \int \Psi_i^2 dx,$$

$$s_i^2 = \int x^2\Psi_i^2 dx / \int \Psi_i^2 dx - \bar{x}_i^{\,2}$$

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The model requires uncertainties – how do we get these? Example for laboraties

- Estimation of a reasonable value for the parameter/concentration level based on e.g. previous interlaboratory studies, standards, expert judgement, literature,…
- Making use of prescribed performance characteristics
- Making use of performance characteristics of reference method
- Using a model
- Asking participants to report measurement uncertainty according to a well defined format *(information will become available as ISO 17025 is used more commonly)*

An implementation of the model (the normal distribution approximation) has been developed to cope with situations were no estimates of uncertainty are available

The model summarised

- Model needs estimate of uncertainties of laboratories and an estimate of the type of probability density function of the laboratories/data
- The model can use with different estimates for the probability density function of labs/data (*examples: normal, Student-t, symmetric triangular, rectangular*)
- No assumptions are made regarding the distribution of the population of labs/data
- In addition to the variance, a new measure for the degree of intercomparability is obtained (λ, a measure for the probability of the population measurement function)
- The model provides powerful graphical tools to obtain insight in the data structures

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Examples

- Illustration of merits model on different distributions
- Bimodal: Pb in marine sediment
- Strongly tailing: Cd in plaice tissue
- ‘Regular’: BCR certified reference material CRM 349
- Investigating method dependencies: RIZA interlaboratory study
- Dealing with less than values (preliminary results)

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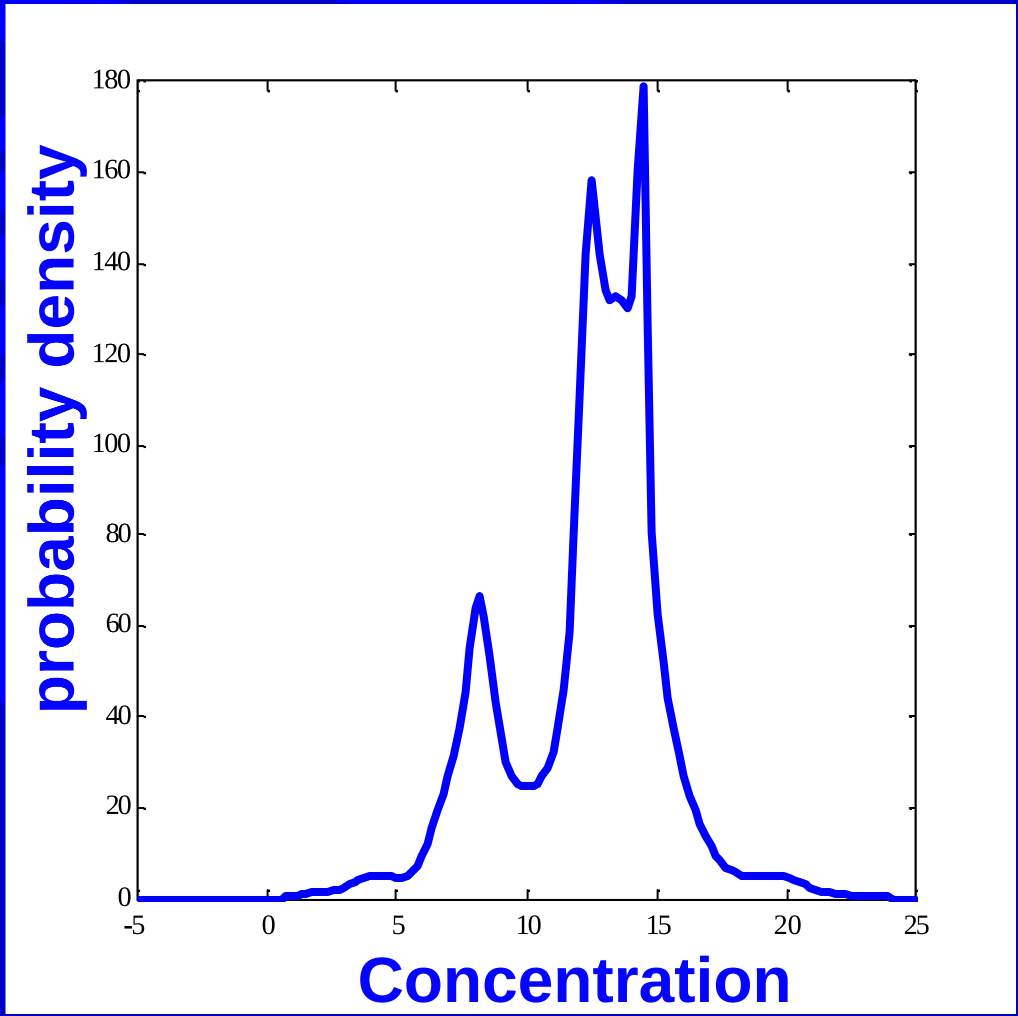
Pb in marine sediment

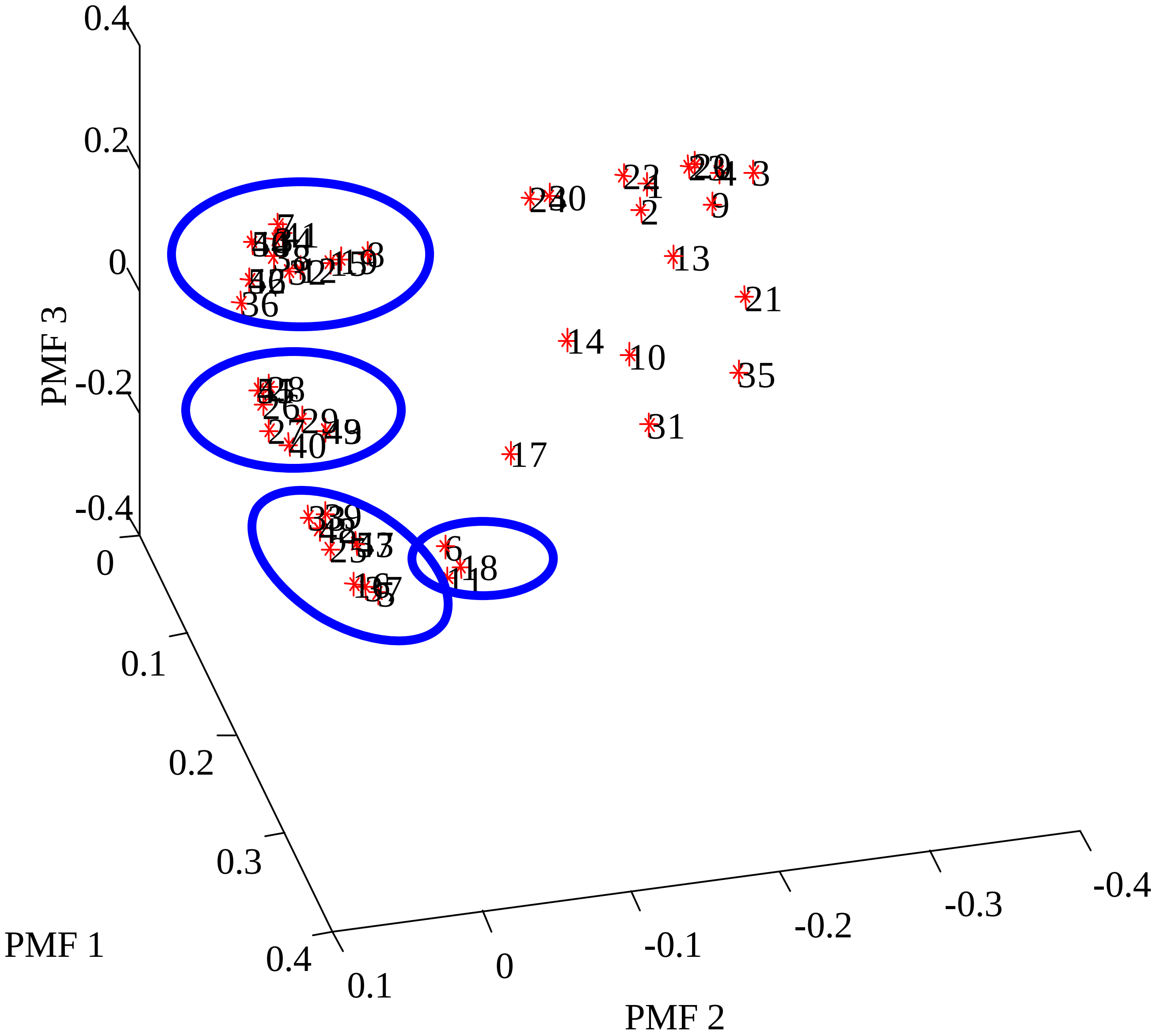
- Laboratories analysed with both ‘total’ (e.g. HF) and ‘partial’ (e.g. aqua regia) methods
- 6 replicates
- Bimodal distribution



Pb in marine sediment
Results of statistics (mg/kg)

	All data N=53			'Total' methods N=29			Partial methods N=24		
	x	s	%	x	s	%	x	s	%
Robust statistics , UK-AMC									
	11.8	**4.2**		**14.2**	**2.0**		**8.7**	**3.5**	
This model									
IMF1	**13.4**	**1.6**	*35*	**14.0**	**1.3**	*52*	**8.7**	**1.6**	*34*
IMF2	**8.7**	**2**	*17*	**14.2**	**2.7**	*13*	**11.0**	**2.0**	*22*

Tri-plot showing structures in data,
Clustering may point to systematic effects



Cd in plaice mussel tissue

- Extremely low concentration
- Strongly tailing distribution
- No experimental estimates for laboratory-uncertainties available
- From literature and other PT schemes: a within lab RSD of 15% is considered appropriate, each laboratory has been allocated an uncertainty (standard deviation) equal to 15% of the median of the dataset
- Assigned value established with a limited number of reference laboratories: 6.1 ug/kg

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Cd in plaice mussel tissue

	Full dataset N=37		Trimmed dataset N=27	
	x (ug/ kg)	s (ug/ kg)	x (ug/ kg)	s (ug/ kg)
Robust statistics , UK-AMC	8.79	6.0	5.78	2.0
This model, IMF1	5.42	1.4	5.42	1.4

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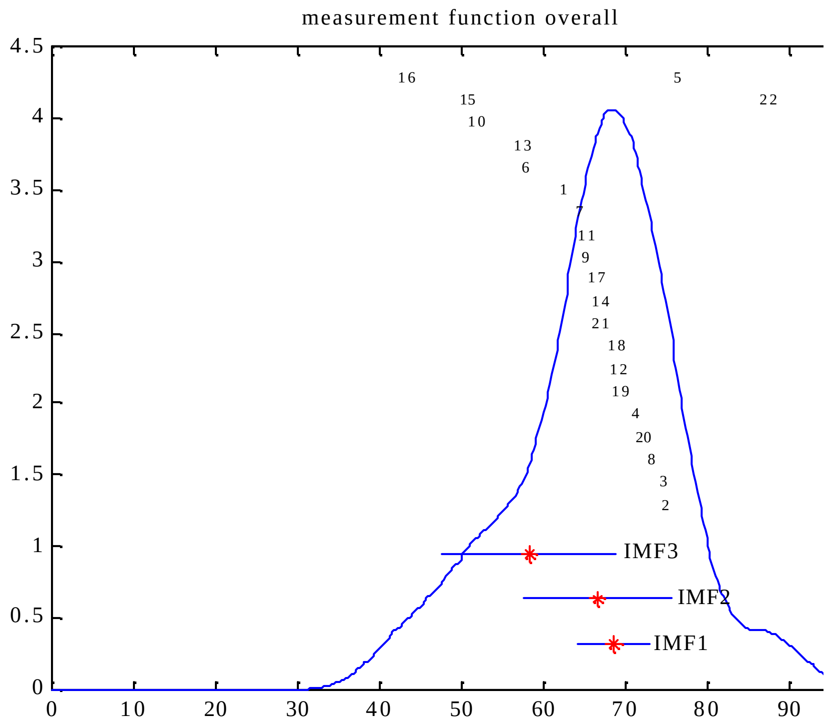
Independently assigned value: 6.1 ug/kg

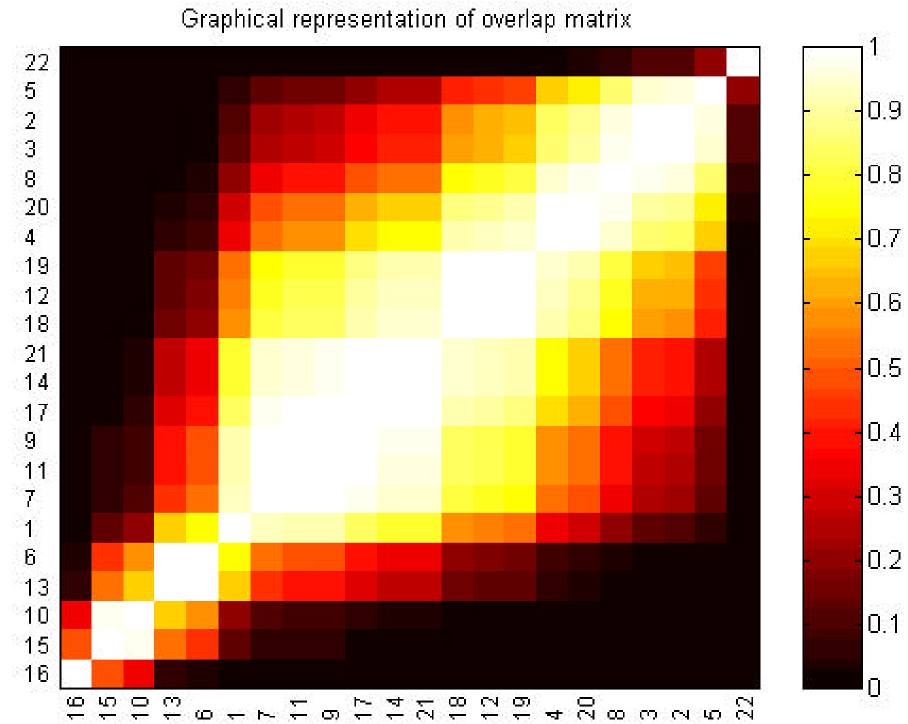
BCR Reference material 349 - Chlorobiphenyls in fish oil

		Certificate	IMF1	IMF2
CB28-	mean	68.0	66.1	73.0
	std	11.7	9.8	16.2
	%		63.2	17.5
CB52-	mean	149.1	164.9	133.2
	std	28.5	25.4	29.4
	%		42.7	20.7
CB101-	mean	371.8	371.6	370.7
	std	29.9	31.5	42.0
	%		67.9	19.7
CB153-	mean	936.3	938.1	908.0
	std	59.3	58.6	83.3
	%		64.8	15.1
CB180-	mean	281.5	277.2	275.3
	std	33.3	26.8	48.8
	%		55.8	18.6

Bimodal character !

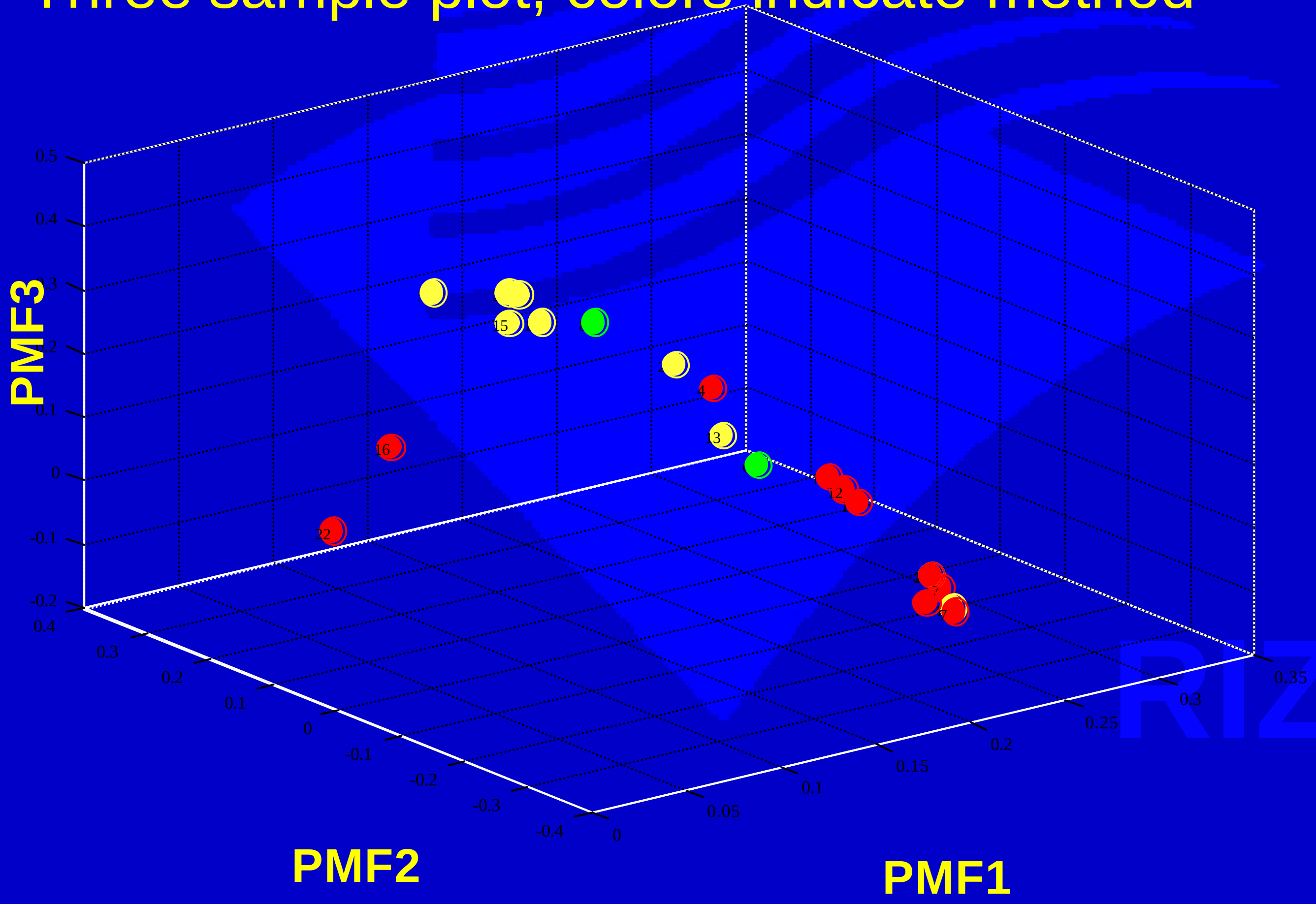
Investigating differences between methods : RIZA interlaboratory study on suspended solids (I)





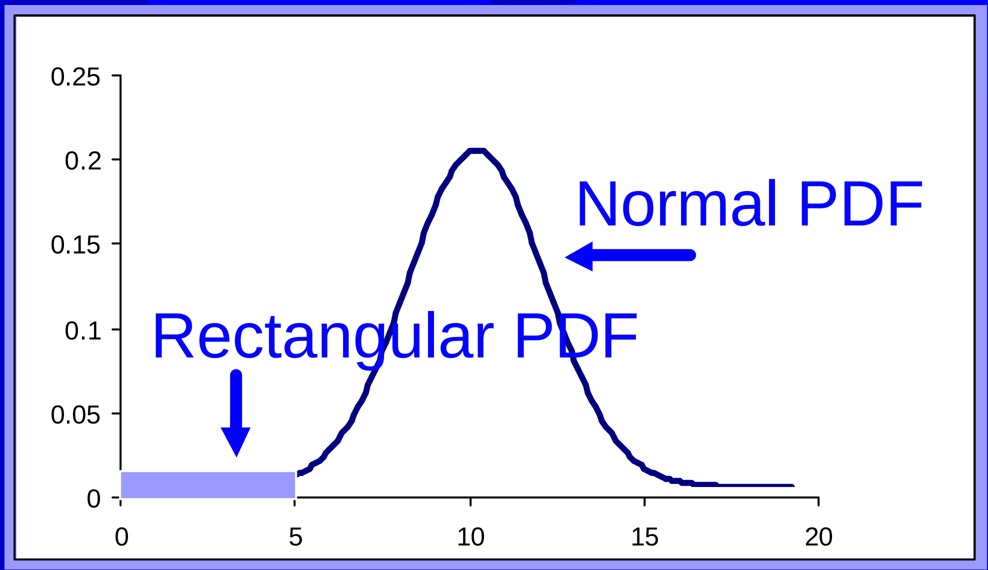
Investigating differences between methods : RIZA interlaboratory study on suspended solids (II)

Three sample plot, colors indicate method



Dealing with less than values

- Approach
  - Basisfunctions based on normal distributions for data above Limit of Determination (LOD)
  - Use of rectangular pdf for less than values



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Example
(note: publication in preparation)

Data from EU-CRM 444, CB138, one value <1 added:

mean: 1.95, 1.12, 1.68, 0.78, <1

std: 0.61, .50, .205, .13

	Less than value included	Less than value deleted
mean	1.333 (60%)	1.438 (65%)
std	0.60	0.55

Summary

- A new model has been developed for the interpretation of experimental data and has been applied to interlaboratory studies
- The model takes the uncertainty into account
- It provides in addition to the commonly obtained population characteristics
  - graphs providing information on structures in the data (e.g. method related)
  - a new measure for the degree of comparability
- It can cope with a large range of distributions

The model is described in Chemometrics and Intelligent Laboratory Systems 53 (2000) 37-55, a paper describing its application to 'less than values'is being prepared. The software, a MATLAB toolbox, is available upon request (without charges)