# Robust statistics: The solution to the heterogeneity problem?

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## Introduction

Geochemical data almost never show normal or log-normal distribution (Reimann and Filzmoser, 2000). Reasons for this phenomenon are the spatial dependence, bad data quality, geochemical processes, and different, often over-lapping element sources (e.g. seaspray, pollution). This results in inhomogeneous data sets which makes the statistical analysis very difficult. Neither the computation of a uni-variate mean nor the application of multivariate methods are reliable.

## Methods

A way out can be the usage of robust statistical methods. Beginning with univariate analysis, graphical tools like boxplots or cdf-plots and even scattergrams are much more informative than classical histograms. Using the median and the MAD (median absolute deviation) makes much more sense that taking mean and standard deviation, which are both highly sensitive with respect to outliers.

Also for multivariate analyses very efficient tools exist. Multivariate methods based on a robust estimation of center and covariance will not be affected by outlying observations. Detecting hidden processes in data could therefore be done by robust factor analysis (Pison et al., 2003) because factor analysis is a tool for finding structures which cannot directly be observed (Reimann et al., 2002).

A general rule in robust statistics is to fit the model to the bulk of the data. However, if multivariate data are extremely inhomogeneous caused by several different processes, this direct approach might no longer be helpful. In that case one can use cluster analysis, or, if pre-knowledge is existing, robust discriminant analysis. For data sets with a large number of observations, also robust multivariate methods applied to random subsets of the data will be helpful.

In our presentation we will discuss the above ideas in detail and present real data examples.

## Summary

Classical statistical assumptions are most often not fulfilled for geochemical data. Robust statistical methods still work for deviations from assumptions and should therefore be used. Robust multivariate methods can also be used for detecting hidden processes in heterogeneous data sets.

## References

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# Methanogenesis from methylamine and methanol at changing hydrogen concentrations

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Methylotrophic methanogens in pure culture metabolize methylated substrates (e.g. methanol, methylamine, acetate) to $CH_4$ and $CO_2$ in a predictable ratio. Detailed studies revealed, that the proportion of the two products can deviate from the predicted stoichiometry. Phelps et al. (1985) showed that methanogenesis from acetate yielded more $CO_2$, if the methanogen was cocultured with a sulfate reducer oxidizing the hydrogen produced by the methanogen. The continuous leakage of reducing power (as $H_2$) from the methanogen, as a result of sulfate reducing activity, allows the methanogen to oxidize a greater proportion of the carbon to $CO_2$. We hypothesized that natural variations in $H_2$ concentrations in aquatic sediments will affect the degree to which $H_2$ liberation and oxidative metabolism of methylotrophic substrates occur. To test this hypothesis, we performed incubation experiments using methanogenic sediments in which $H_2$ concentrations were caused to vary as a function of temperature or sulfate concentration. The conversion of methanol and methylamine to $CH_4$ and $CO_2$ in these treatments was quantified using radiotracer techniques. Decreasing temperatures and increa-sing sulfate concentrations both resulted in decreasing $H_2$ concentrations. With decreasing $H_2$ concentrations, the methanogens produced more oxidized carbon. At the lowest $H_2$ concentrations, the fraction of electrons lost to $H_2$ leakage significantly exceeded that channeled into methane production. This was true even in the absence of sulfate (e.g., for the lowest temperatures). Thus, dependent on the $H_2$ concentration, protons can represent a more important electron acceptor than the methyl carbon for methylotrophic methanogenesis.

Marine sediments are spatially separated according to the electron acceptor used for terminal oxidation. The control of reducing power in the cells by external $H_2$ concentration can help understand the exclusion of the different electron accepting processes. In the sulfate reducing zone, $H_2$ concentrations are kept low, thus prohibiting $CH_4$ production from either competitive or uncompetitive substrates.

## References

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