

APPLICATION OF STATISTICAL METHODS IN NATURAL ATTENUATION ASSESSMENT

T. Wachter¹, B. Schlenz¹, D. Schäfer¹, A. Dahmke¹

¹Institute for Geosciences, Department for Applied Geology
Ludewig-Meyn-Str. 10, 24098, Kiel, Germany
phone: +49 431 880-2853 fax: +49 431 880-7606
email: twachter@gpi.uni-kiel.de

Abstract

For reliable results in Natural Attenuation (NA) assessment, field data have to be sampled with a certain density depending on site and parameter. For increased effectiveness, sampling is also to be concentrated on key-parameters that provide e.g. the necessary information if and to which extent Natural Attenuation (NA) is occurring at a contaminated site. Goal of this study was to find out the individual correlation lengths of the investigated parameters and to define the sampling density by interpretation of variograms and plots of kriging standard deviation. The study investigated data of a BTEX contaminated site in Saxony-Anhalt, Germany. The data contained analyses of 180 sediment samples from 12 sediment cores and groundwater analyses from about 90 observation wells, 30 allowing multilevel sampling. With the employed geostatistical methods, correlation lengths of the investigated parameters were determined and the hypotheses could be confirmed that sulfate, BTEX, methane and alkalinity are the key parameters. For other parameters like dissolved Fe_{tot} correlation length was less than sampling distance and no information on its spatial distribution was gained. Heterogeneities of the sediment caused the applied geostatistical methods to fail even with the large data set of sediment analysis.

Introduction

In many cases active treatment approaches like pump-and-treat have failed the cleanup goals. For example, (1), report that none of the superfund-sites of the US EPA was to be considered as successfully remediated after 10 years of remediation. Therefore in the 1990s the idea arose to use the intrinsic remediation capacity of the site, referred to as natural attenuation (NA) which already is accepted as cleanup strategy by US EPA (2, 3). For NA to be an acceptable approach the preconditions lined out in the lines-of-evidence-concept (3, 4) have to be met. Unless there is sufficient proof in historical data, a field investigation program has to be set up for proving and quantifying NA processes and NA capacity of a contaminated site. In any of these investigations the number of sampling points, both in time and space, will be limited by financial resources. Thus, goal of this study is to find out the key parameters and their individual correlation lengths to define the required sample density using geostatistical methods. These methods have a long history in earth sciences (5); correlation lengths have been determined previously in hydrogeology (6, 7) and in soil microbial environments (8). To our knowledge, however, correlation lengths have not been investigated at contaminated sites in context with NA. The objective of this study is to find out the required sample density and identify the key parameters that are necessary for geochemical characterization of the site and quantification of mass fluxes and degradation rates.

Material and Methods

Data for the study originate from a BTEX-contaminated test site in Zeitz, Saxony-Anhalt, Germany. The aquifer is equipped with more than 90 monitoring wells for survey of the contaminant plume. 30 of these monitoring wells have multilevel sampling devices. Groundwater samples were analysed for electrical conductivity, pH, dissolved oxygen, redox potential, alkalinity, methane, BTEX compounds, sulfide, nitrate, nitrite, ammonia, phosphate, and total contents of sodium, potassium, calcium, silica,

aluminium, iron and manganese. Additionally, 180 samples of the solid phase have been taken from 12 boreholes and were analysed for Fe(II) and Fe(III) content using 1M and 5M HCl extractions (9); (10) as well as acid volatile sulfides (11) and Cr(III)-reducible sulfides (12) in order to quantify the Oxidation Capacity (OXC) of the field. Sulfate reduction was identified as the most important BTEX-degrading process whereas Fe(III) reduction and methanogenesis were of only secondary importance (13, 14).

To determine the required sampling density an interpolation tool is required that provides a reliable estimation for the region between the sampling points. Different interpolation tools are compared in a virtual aquifer study (15, 16). A contaminant plume was generated in a heterogeneous flow field using the model TBC (17) which was then sampled at virtual sampling wells. Fig. 1(a) shows kriging interpolation results of the virtual plume for the parameter Alkalinity in a setup containing 24 monitoring points which is dense compared to most field studies. Despite the dense grid of sampling points major deviations between simulated and interpolated geometry can be seen, especially at the fringe of the plume. The corresponding kriging standard deviations (fig 1(b)) illustrate that regions with higher deviations between estimated and simulated values coincide with regions of elevated kriging standard deviation. Compared to other interpolation tools like 'triangulation with linear interpolation' or 'inverse distances' kriging provided good results in approximating the simulated plume and is therefore applied on the field data. The great advantage of kriging towards other tools is that kriging standard deviation provides important information on the quality of the interpolation. In this study variogram analysis and subsequently kriging is applied to identify key parameters and their correlation lengths while the quality of the interpolation is monitored by mapping the kriging standard deviation.

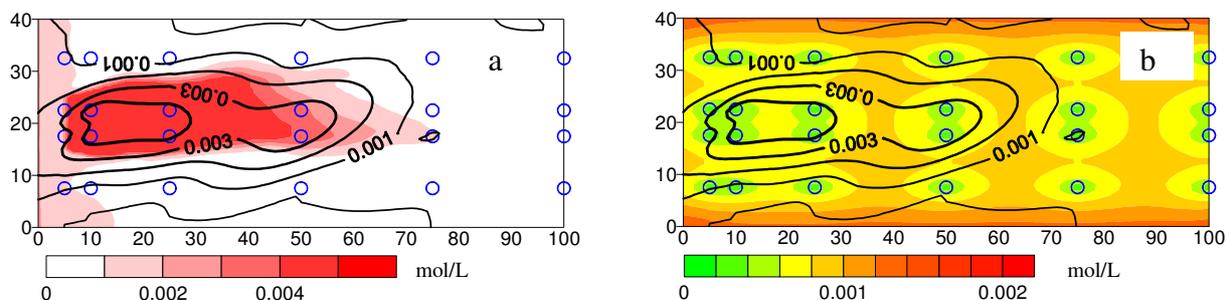


Fig. 1: Virtual aquifer study: (a) interpolation results for the parameter alkalinity in a setup containing 24 monitoring points. Contour lines give the interpolated concentration whereas the simulation results are indicated by colour shades. (b) interpolated values of Alkalinity (contour lines) and kriging standard deviation (colour shades)

Application of kriging requires, (I), that the discussed parameter has the same statistical data distribution within the field under consideration (assumption of homogeneity), (II), that there are no trends and (III) that there are no drift phenomena (detailed information e.g. in (18, 19)). Drift, trends, and anisotropies can be corrected using adequate software algorithms and therefore represent no problem. To facilitate variogram analysis, outliers were manually removed when deviating more than two standard deviations from the mean. Variogram analysis was started assuming homogeneity; the assumption was rejected when the scattering of the variogram was too high. Distribution of benzene concentration was log-normal, data were logarithmized. In the case of dissolved Fe_{tot} which also showed log-normal distribution, logarithmizing did not improve the variogram and results were discussed with the original data. The extent of the autocorrelation of each parameter and a variogram model were the results of the subsequent variogram analysis. For regionalization of the data contour-plots were created based on the variogram-models using the Surfer 7.0[®] software (20). As variogram model a spherical function (21) was fitted using a least-square-algorithm, that was superposed by a constant function (nugget effect) where considerable zero-displacement was observed in the experimental variogram. The extent of the anisotropies of the aquifer was respected in the variogram model.

Results and Discussion

Calculation of variograms for the December 2002 sampling campaign provided graphs as displayed in fig. 2, (a)-(d). Parameters of the variogram modelling can be found in table 1. They are sorted with descending range of autocorrelation and can be divided into two major groups: spatial variables with a range higher than the sampling distance (from electrical conductivity to alkalinity), and random

variables where no spatial dependence can be found and, as a consequence, data regionalisation gives no additional information.

No range value could be assigned to the parameters electrical conductivity and calcium because the variogram had not reached its supposed plateau value within the surveyed field. High ranges indicate that the values of these parameters are changing over a distance that is larger than the test site. As a consequence, the parameters could serve as indicators for regions where NA processes already have ceased but secondary reactions are still in progress. Benzene, methane, sulfate (fig. 2(c)) and alkalinity showed ranges between 300 and 60 m and are all strong indicators for NA processes. Because electron acceptor processes like sulfate-reduction and methanogenesis do occur only at parts of the contaminant plume, the range of the variogram model for sulfate and methane is shorter than that of the contaminant. The range for benzene approximately equals the plume extension and so can be an indicator for the plume length. The short range of alkalinity was attributed to reactions of carbonate equilibrium. So, even in an environment like the test site where BTEX is the only relevant carbon source, the range of alkalinity differs widely from that of BTEX and therefore the easily measurable parameter alkalinity cannot be used as estimator for the BTEX degradation. The random variables (grouped at the bottom of tab. 1) can be divided into two subgroups, where the group containing the parameters pH, silicon, sodium, and magnesium have low standard deviations in comparison to the mean values and thus are well characterized by the mean value as estimator for the complete investigation area. The lack of spatial dependence in the case pH evidently is due to buffering reactions, the other parameters were expected not to be influenced by NA processes. These conservative parameters can be determined in a wider grid. The parameters redox potential, manganese, and dissolved Fe_{tot} have high standard deviations compared to their mean values. Interpolation of these values is not helpful and the statistical standard parameters provide only little information. Therefore they were of no help for the NA assessment even if they take part in the NA reactions and were expected to show spatial dependence but evidently it is overlaid by the scattering.

Interpolation is discussed for the parameters sulfate and dissolved Fe_{tot} because both sulfate and dissolved Fe_{tot} (under the given conditions mainly Fe(II)) are species with high relevance in electron accepting processes. Sulfate concentrations show a spatial distribution with a range of 140m while dissolved Fe_{tot} shows a random distribution with a range below the average sampling distance.

Tab. 1: Results of variogram modelling for the groundwater analyses. Note that range and anisotropy are not defined in the nugget model and the scale equals the variance (square of standard deviation), the respective cells are therefore greyed out.

	Model	Scale	Range [m]	Anisotropy [-]	Standard Deviation	Arithmetic Mean
Electrical Conductivity	spherical	412000 ($\mu\text{S}/\text{cm}$) ²	>300	1.98	1280 $\mu\text{S}/\text{cm}$	1520 $\mu\text{S}/\text{cm}$
Calcium	spherical	9980 (mg/L) ²	>300	3	200 mg/L	260 mg/L
log (Benzene in mg/L)	spherical	645	300	3	1.4	0.9
Methane	spherical	5,8 (mg/l) ²	150	2	2170 $\mu\text{g}/\text{l}$	1300 $\mu\text{g}/\text{L}$
Sulfate	spherical	132 000 (mg/l) ²	140	2,4	350 mg/L	431 mg/L
	nugget	20 000 (mg/l) ²				
Alkalinity	spherical	66 000 (mg/l) ²	62	1,8	309 mg/L	570 mg/L
	nugget	28 000 (mg/l) ²				
dissolved Fe_{tot}	spherical	241 (mg/l) ²	(30)	(2)	52 mg/L	16 mg/L
Manganese	nugget				4.0 mg/L	2.3 mg/L
Redox potential	nugget				140 mV	100 mV
Silicon	nugget				1.7 mg/L	7.1 mg/L
PH	nugget				0.4	7
Sodium	nugget				18 mg/L	50 mg/L
Magnesium	nugget				20 mg/L	60 mg/L

Interpolation of dissolved Fe_{tot} concentrations does not make sense for the data set under discussion because of the predominant random distribution of the data. This is illustrated by a plot of kriging standard deviation for both dissolved Fe_{tot} , and sulfate displayed in fig. 3. With the exception of the densely sampled center of the plume the kriging standard deviation equals the overall standard deviation, i.e. the kriging estimation has the same statistical significance as the overall mean value.

Compared to dissolved Fe_{tot} , kriging standard deviation is small compared to overall standard deviation in the case of sulfate because of its higher range of autocorrelation (140 m).

The ranges found in the analyses are still very short in comparison to data found in hydrogeological literature. (6) for instance found a range of about 9 km for alkalinity which they identified as a parameter changing very slowly, as a function of the aquifer geology. At the contaminated RETZINA test site the NA-reactions lead to a range of 60 m for alkalinity. Variograms for the solid phase investigation did not allow reasonable variogram modelling. This is illustrated in fig. 2(d) at the example of 1M HCl-extractable Fe(III) (which can be referred to as 'bioavailable' Fe(III)). As a consequence no spatial estimation was possible for the solid phase parameters. So, the amount of 180 sediment analyses provides only the advantage of elevated statistical foundation if compared to e.g. the mean value of just a few samples.

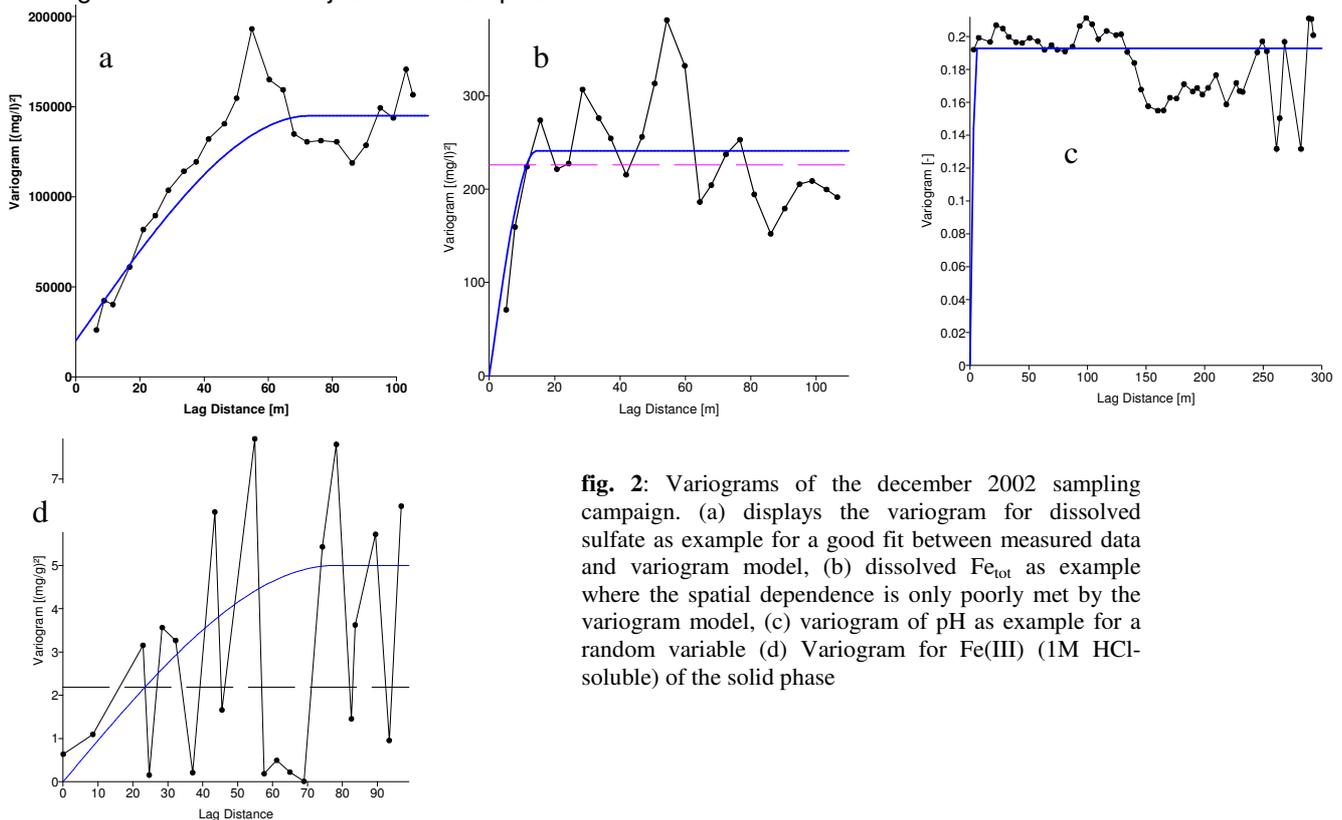


fig. 2: Variograms of the december 2002 sampling campaign. (a) displays the variogram for dissolved sulfate as example for a good fit between measured data and variogram model, (b) dissolved Fe_{tot} as example where the spatial dependence is only poorly met by the variogram model, (c) variogram of pH as example for a random variable (d) Variogram for Fe(III) (1M HCl-soluble) of the solid phase

Conclusions

By variogram analysis it could be identified whether the sampling distance was sufficient for the parameters under investigation or the sampling grid has to be refined. The possibility of the kriging method to obtain predictions of the estimation error proved to be a helpful tool. Based on the results important information for NA assessment such as mass fluxes and degradation rates can be derived. The application of geostatistical methods with interpretation of variograms and plots of kriging standard deviation were a helpful tool to describe the properties of the parameters under investigation and their correlation lengths. The results obtained in this study should be transferable to other BTEX contaminated fluvial aquifers in principle and should allow development of a site investigation strategy in similar cases.

Variogram analysis further allowed to distinguish between parameters that showed spatial dependence in the area under observation and predominantly random parameters. The importance of parameters like sulfate, methane and alkalinity as key parameters was confirmed because the spatial correlation was similar to that of the pollutant. Part of the random parameters were conservative in the scale of the test site like pH showing little variance, others, like dissolved Fe_{tot} , had high variances due to heterogeneities or fast reactions and could not be further interpreted. Regionalisation failed for parameters measured in the sediment due to sediment heterogeneities. When data processing shows that kriging will not lead to reliable results alternatives have to be found. As a first measure the sampling grid could be refined. In the example of dissolved Fe_{tot} an appropriate sampling distances could be 10-20 m resulting in 150-600 drillings for the RETZINA site. Site investigation in

consequence would become extremely costly. Relying on other interpolation algorithms like triangulation or inverse distances will not result in better results than kriging and do not offer the possibility to control interpolation errors. Promising methods investigating greater volumes of soil with integrating techniques like integrative pumping tests (22) or reactive tracers (23) have recently been developed and are already being applied.

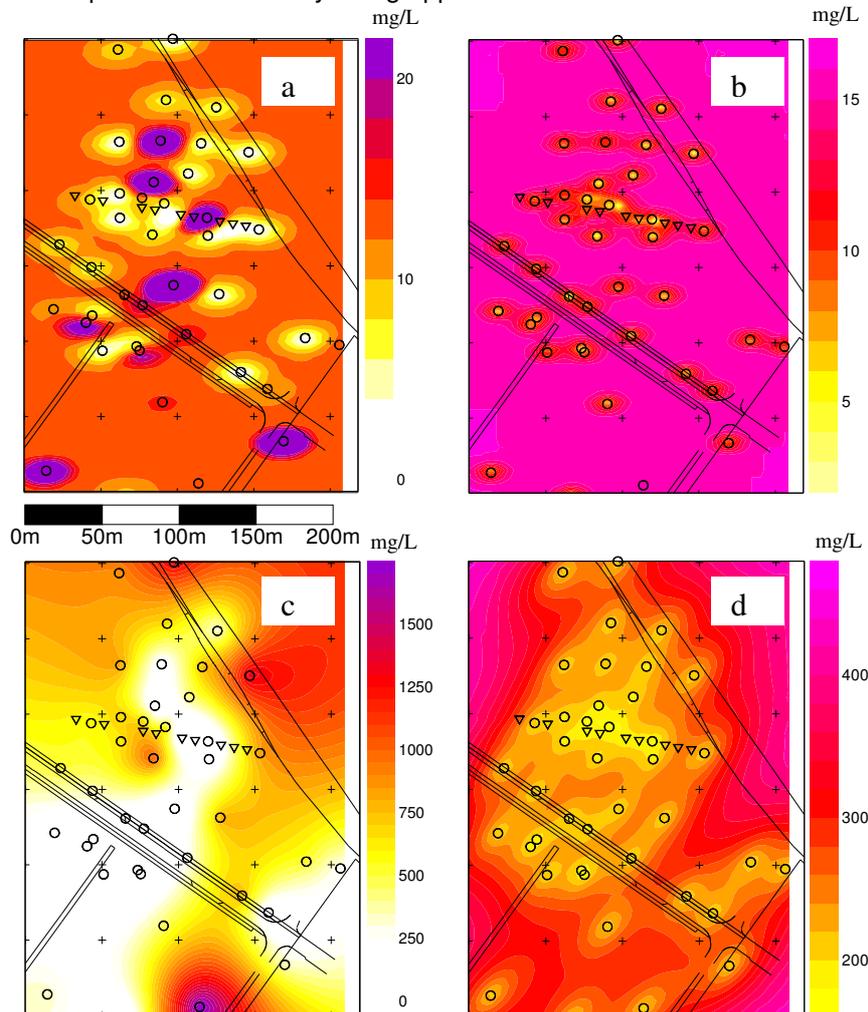


fig. 3: Plots of 'dissolved Fe_{tot}' (a) and 'sulfate' (c) in groundwater of the RETZINA test site in december, 2002. The regionalization is based upon the variogram model displayed in fig. 2. Kriging standard deviation is displayed in (b) and (d). The figures illustrate the extent of autocorrelation of the parameters.

Literature

- (1) C.C. Travis, and C.B. Doty. Can contaminated aquifers at Superfund sites be remediated. *Environmental Science and Technology*, **24**(10): 1646-1466 (1990).
- (2) US EPA. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. Directive Number 9200.4-17, United States Environmental Protection Agency. Office of Solid Waste and Emergency Response, Washington D.C. (1997)
- (3) US EPA. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. Number: 9200.4-17P, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response (OSWER), Washington D.C. (1999)
- (4) T.H. Wiedemeier, H.S. Rifai, C.J. Newell, and J.T. Wilson. Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. John Wiley & Sons, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto (1999)
- (5) G. Matheron. Principles of geostatistics. *Economic Geology*, **58**: 1246-1266 (1963).
- (6) P.P. Goovaerts, P. Sonnet, and A. Navarre. Factorial kriging analysis of springwater contents in the Dyle River basin, Belgium. *Water Resources Research*, **29**(7): 2115-2125 (1993).
- (7) M.-T. Schafmeister. Geostatistik für die hydrogeologische Praxis. Springer-Verlag, Berlin, Heidelberg, 172 pp. (1999)
- (8) F.J. Brockman and C.J. Murray. Subsurface microbiological Heterogeneity: current knowledge, descriptive approaches and applications. *FEMS Microbiology Reviews*, **20**, 231-247 (1997).
- (9) G. Heron, C. Crouzet, A.C.M. Bourg and T.H. Christensen. Speciation of Fe(II) and Fe(III) in Contaminated Aquifer Sediments Using Chemical Extraction Techniques. *Environmental Science and Technology*, **28**: 1698-1705 (1994).

- (10) K. Wallmann, H. Kristof, I. König, W. Petersen, and H.D. Knauth. New procedure for determining reactive Fe(III) and Fe(II) minerals in Sediments. *Limnology and Oceanography*, **38(8)**: 1803-1812 (1993).
- (11) J.C. Cornwell, J.W. and Morse. The Characterization of Sulfide Minerals In Anoxic Marine Sediments. *Marine Chemistry*, **22**, 193-206 (1987).
- (12) D.E. Canfield, R. Raiswell, J.T. Westrich, C.M. Reaves, and R.A. Berner. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology*, **54**, 149-155 (1986).
- (13) S. Goedeke, H. Weiss, T. Wachter, R. Trabitze, and M. Schirmer. Benzenabbau im Grundwasser unter verschiedenen Redox-Bedingungen - Fallbeispiel Zeitz (Sachsen-Anhalt). *Grundwasser*, submitted.
- (14) S. Klüglein. Modellierung des Selbstreinigungspotentials eines benzolcontaminierten Aquifers, Diploma Thesis, Christian-Albrechts-Universität, Kiel, 94 pp, (2002).
- (15) G. Hornbruch, B. Schlenz, D. Schäfer and A. Dahmke. Virtual aquifer - a concept for evaluating investigation and monitoring approaches in aquifers. *Meyniana*, submitted.
- (16) D. Schäfer, B. Schlenz and A. Dahmke. Evaluation of exploration and monitoring methods for verification of natural attenuation using the virtual aquifer approach. *Biodegradation*, submitted.
- (17) D. Schäfer, W. Schäfer and W. Kinzelbach. Simulation of reactive processes related to biodegradation in aquifers 1. Structure of the three-dimensional reactive transport model. *Journal of Contaminant Hydrology*, **31**: 167-186 (1998).
- (18) A.G. Journel, and C. Huijbregts. Mining Geostatistics. Academic Press, London, 600 pp. (1978)
- (19) H. Akin, H. Siemes, . Praktische Geostatistik - Eine Einführung für den Bergbau und die Geowissenschaften. Springer Verlag, Berlin, Heidelberg, New York, London, Paris, 304 pp, (1988).
- (20) Golden-Software, 2001. Surfer 7.05, Golden, Colorado.
- (21) Y. Pannatier. VarioWin - Software for spatial data analysis in 2D. Springer-Verlag, New York, 91 pp (1996).
- (22) T. Ptak, G. Teutsch and R. Schwarz. Grundwasser-Gefährdungsabschätzung durch Emissions- und Immissionsmessungen an Deponien und Altlasten: Numerische Untersuchungen zur Anwendung und Auswertung, Forschungszentrum Karlsruhe, Karlsruhe (1998).
- (23) F. Dethlefsen, F.Bliss, T. Wachter, and A. Dahmke. Determination of the sediment oxidation capacity with reactive tracers, ConSoil 2003, Gent, Belgium (2003).