Comparative Evaluation and Analysis of Water Sediment Data

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Abstract

With respect to sediment pollution responses of ecotoxicological tests may differ from those of biochemical test systems and moreover both tests are indicating effects instead of simply measuring of chemical concentrations. Because most test results of sediment investigations are commonly given as inhibition values and sediment pollution by chemicals is measured by their concentrations a comparative evaluation of sediments by means of both test results and chemicals at the same time has to consider different scales. Both data transformations on a common scale (standardization) and aggregations lead to loss of information and hamper the interpretation of results. In order to avoid merging of data and to circumvent often-crucial data transformations, partial ordering is used for evaluation of sediment samples from German rivers. The aim here is to compare the evaluation of river sections by different parameter groups, namely biochemical and ecotoxicological tests, as well as concentrations of organic pollutants, heavy metals etc. Fuzzy cluster analysis as a pre-processing step is additionally used to understand the pollution pattern that is given by each test result. It is shown that for most of the river sections, test systems among each other and also compared to chemical concentrations yield different quality pattern and therefore lead to different Hasse diagrams. Sole exception is a bayou where the sediment is undisturbed by shipping traffic and sewage. Moreover, as a consequence of varying pollution pattern during

the sampling period (over several years), only for a few river sections it is possible to derive distinct temporal changes: Except for the nematode sediment contact test, where all parameters are significantly correlated, this holds for both ecotoxicological and biochemical tests, and for chemical concentrations. Furthermore, for one river section it could be observed that chemical concentrations indicate a decline of contamination, whereas ecotoxicological parameters point to an increased toxicity. With respect to the development of a classification system for river sediments it is recommended to take care in the selection of parameters and to base it at least at two parameter groups.

Introduction

In order to ensure shipping traffic in rivers and coastal waters fairways have to be dredged continuously. As a consequence thousands of tons of sediments are to be managed yearly. This dredged material can be contaminated with different pollutants. Depending on the degree of contamination dredged material can be relocated within the water or has to be disposed as hazardous waste. However, exactly the question which sediment can be classified as hazardous or not hazardous is a crucial one and a standardized method about how to classify sediments and dredged material respectively, would be a helpful tool not only for administrative purposes but also regarding economic and environmental aspects. Surveying the way of developing such a system several questions arise, which have to be answered a priori:

- What is the state of sediment pollution of all waterways and what kind of contamination is known, currently and in the past?
- How are 'hazardous' to be defined and what parameter should be taken into account respectively, when sediment/dredged material has to be classified?

The German Federal Institute of Hydrology (BfG) holds an extensive database about sediment investigations of Federal Water Ways considering several parameters (Heininger et al. 1998, Heininger et al. 2003). These data can be divided into three groups, namely chemical, ecotoxicological and biochemical parameters. With respect to the questions above and in order to make optimum use of these data the following question arises.

- Is there a difference between a comparative evaluation of sediments when using different parameter groups or is it sufficient to consider one group or certain parameters as representatives for sediment burden?

The questions put here for sediments could be applied to other environmental evaluation problems just as well, for instance to soil or groundwater pollution. However, a common difficulty with these evaluations is that many of the methods mask and aggregate the data, and therefore both valuable information and transparency are lost. An alternative is partial order ranking that avoids the merging of data and thus preserves important elements of the evaluation. Here we will show that partial order ranking has useful qualities in data analysis and it can be applied for pre-processing in the development of classification systems.

For all calculations and graphical presentations of partial ordered sets the ProRank© Software was used (Pudenz 2004).

Database

For many sections of the main waterways in Germany, namely the rivers Rhein, Elbe and Oder, sediment investigations provide results about

- concentrations of priority pollutants like toxic heavy metals (measured in the fine fraction <20 µm) and hazardous organic compounds (detected in the whole sample <2 mm),
- sediment toxicity as revealed in aquatic ecotoxicological tests with Daphnia, Algae and Bacteria using eluates and pore-water as test medium and in an sediment contact test (whole sediment) with Nematodes; in both tests toxicity is expressed in terms of percent inhibition compared to an unpolluted standard
- biochemical tests measuring enzymatic activities (e.g. aminopeptidase activity, glucosidase activity); the test results are given as percent consumption of a specific indicator substance,
- the basic sediment properties like organic carbon concentration, grain size spectrum, water content, for biochemical tests also DNA content; all basic parameters are measured in the whole sample.

A detailed list about parameters and sample sites can be found in Tables 5 and 6 in the appendix.

Partial order ranking requires complete data sets; alternatively data gaps have to be filled or to be cancelled. In case of time series of river sections the missing parameter could be replaced by e.g. the mean of temporal adjoining measurements. The nearer these measurements are the better is the gap filling. However a detailed review of the data set for this study shows that mainly locations, which were investigated only one time per year, had missing values in certain parameters. Alternatively, cancelling of data gaps means loss of information. In order to minimize loss two different procedures are considered:

- exclusion of the parameter with one or more gaps aiming at data sets with maximum sample number (MAX-SN) and
- exclusion of the sample with one or more gaps aiming at a maximum number of parameter (MAX-PN).

Results

Evaluation of Oder sediments using raw data

Chemical pollutants versus aquatic ecotoxicological tests

For the River Oder there are only a few samples with a fully completed data set. Therefore, the largest sample set consisting of chemical and ecotoxicological parameters is used here. The Hasse diagrams (HD) are based on 33 samples (MAX-SN), which were collected along the whole river between 1997 and 2001. Figure 1 shows the result for inhibition values of ecotoxicological tests in eluate and pore-water. All circles are labelled by identifiers for the sampling site and date, for example WD10/99 means Widuchowa at October 1999. Due to many lines the diagram is rather difficult to interpret.

However, compared to the HD based on chemical parameter (see Fig. 2) it shows a distinct level-structure (five levels). That means, for certain sediments a similar pattern concerning ecotoxicological effects in all tests can be observed. Regarding these lines consisting of samples with increasing values in all tests in more detail, we find one maximal chain with five samples: GG6/99<CB9/98<KR11/98<EH10/95<WD5/98. However, none of these relations is found in the evaluation by chemical concentrations. Moreover, there are only two comparabilities that are common for both Hasse diagrams, namely

- WD10/95 < ZB7/00 and
- WD10/95 < ZB3/00.

More interesting could be an observation about a temporal development of a sample location. However, there are only a few comparabilities indicating a temporal development for a specific site with respect to all tests and inhibition values respectively. For the site Glogau (GG) only the relation GG6/99 < GG5/98 holds, whereas both other samples from there, GG11/97 and GG11/98, are incomparable (see Fig. 1 and Table 1). In addition to Glogau only one more comparability indicates a temporal development with respect to all test results, namely for the site Widuchowa (WD): WD10/95 < WD4/99 (Fig. 1).

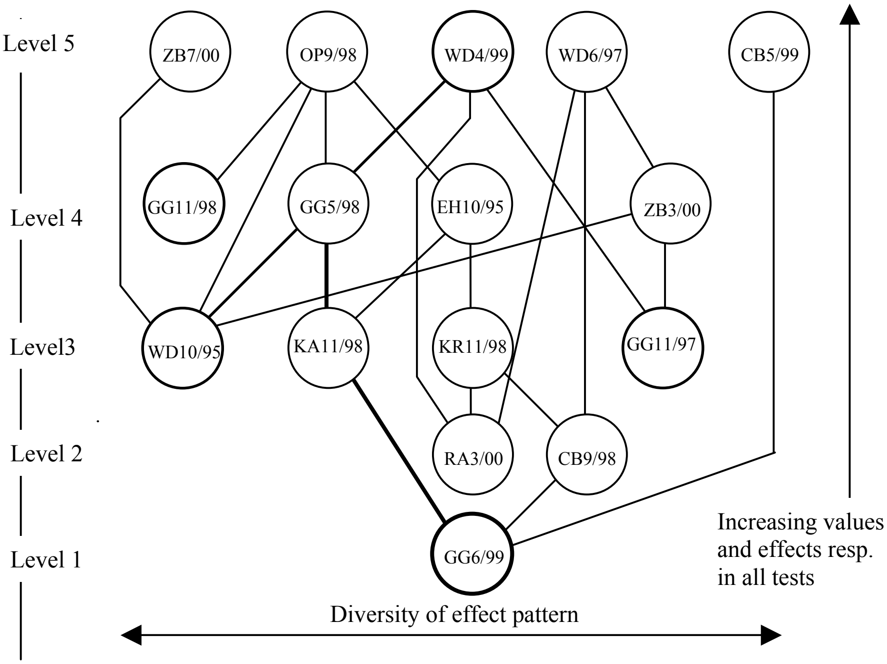


Fig. 1. Hasse diagram of 33 Oder sediment samples concerning six ecotoxicological test results

Table 1. Inhibition (H) of algae (A) and bacteria (B) tests in pore-water (P) and eluate (E); not shown are zero-values for daphnia in all Glogau samples

Sample	HPA	HEA	HPB	HEB
GG11/97	-99,3	-7,4	16,3	3,3
GG5/98	-7,2	-53,1	50,6	19,2
GG11/98	25,7	-7,8	11,4	15,5
GG6/99	-185	-111	15,9	8

In the evaluation by chemical parameters no temporal comparison of a sample location is found. The number of incomparabilities (U=1006) is by far more than the comparabilities (V=25). A high stability value (P(IB)=0,95) c.f. p. 83 indicates that the partial order is very instable against omitting an attribute, where a sensitivity analysis (for details to sensitivity analysis, the reader is referred to e.g. (Brüggemann et al. 2001 and to pp. 91) shows that the evaluation is sensitive against the pollution parameters PCBs, pp'-DDT, PAHs and Sn. However, omitting one of these parameters leads neither to more levels nor to significant more comparabilities as in the diagram based on all parameters.

Summarizing the observations it can be concluded that

- compared to the HD by means of ecotoxicological tests the chemical concentration profile c.f. p. 81 shows by far more diversity (Fig. 2) and yields a different ranking result,
- for both parameter groups temporal developments are hardly to observe.

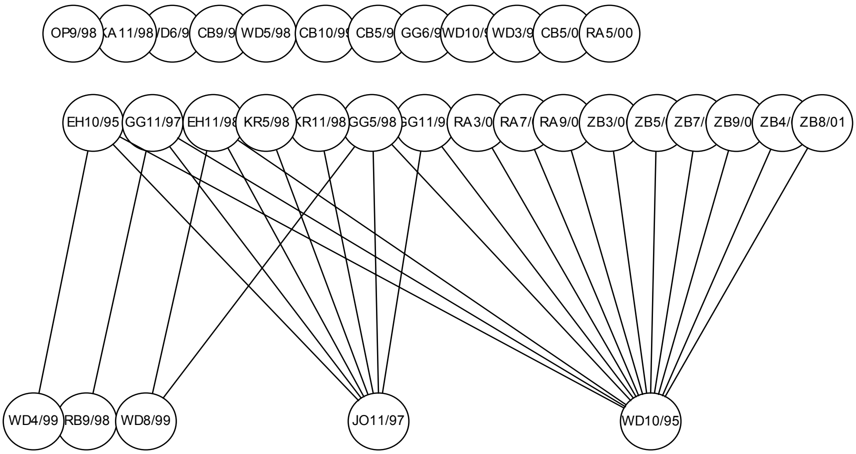


Fig. 2. Hasse diagram of 33 Oder sediment samples concerning concentrations of 22 chemical parameters (except P, B and TBT; see Table 4 in the appendix). Because of shortage of space the upper level consisting of isolated objects is separated

Evaluation of Elbe sediments using raw data

Chemical pollutants vs. aquatic ecotoxicological tests vs. nematode sediment contact test

There are no sediments where all ecotoxicological and biochemical tests and chemical measurements have been carried out together. Therefore we established two sets of samples where the first one contains chemical concentrations and the whole set of ecotoxicological tests (12 samples, see Fig. 3a and 3b) and the other one contains chemical concentrations, biochemical and ecotoxicological tests except nematodes (Fig. 4a and 4b, 28 samples). This data processing procedure leads not only to sets with different samples and size but also to different chemical pollutants that are taken into account. Therefore a comparison between the Hasse diagrams in Fig. 3a-b and Fig. 4a-b is not feasible.

In Fig. 3b it is seen, that the HD for the whole sediment test with nematodes shows most structure compared to the other diagrams in Fig. 3a. It has six levels whereas the diagrams for ecotoxicological tests and chemicals have only three and two levels, respectively. There are several chains with increasing inhibitions in all tests (egg hatch (EH), growth (G), reproduction (R)) simultaneously, for example:

- AE6/00 < FL4/01 < AE10/00 < AK4/01 < FL8/01
- AE6/00 < FL4/01 < FL10/00 < AE4/01 - DE4/01 < FL8/01
- FL6/00 < FL4/01 < FL10/00 < AE4/01 < DE4/01 < FL8/01
- etc.

All four samples of the site FL (Fahlberg List) are comparable (see the bold letters in the sequence shown above), where in year 2000 the toxicity increases from July to October whereas in April 2001 it decreases again and obtains a maximum in August 2001. In contrast to the results of the nematode test the ecotoxicological responses in the other tests indicate a decline of burden from June via October 2000 to August 2001 (as seen in Fig. 3). Moreover, it is noticeable that in the "ecotoxicological HD" the sample FL4/01 (April 2001) is not comparable to all other FL samples. The reason for this antagonism can be easily identified by examining the bar diagram presentation of a HD in Fig. 3: It can be observed that FL4/01 has a relatively high value in the algae test using pore-water (HPA) but a low effect for the eluate (HEA) compared to, for instance FL8/01, which has a lower effect in pore-water and a higher effect in eluate. This may be a hint at different pollution pathways and/or different bioavailability.

Comparing the three HD's in Fig. 3 it is indicated that each of the parameter groups, i.e. ecotoxicological test results with aquatic media, nematodes test results and chemical pollution, lead to different orders and therefore present different effects and responses, respectively.

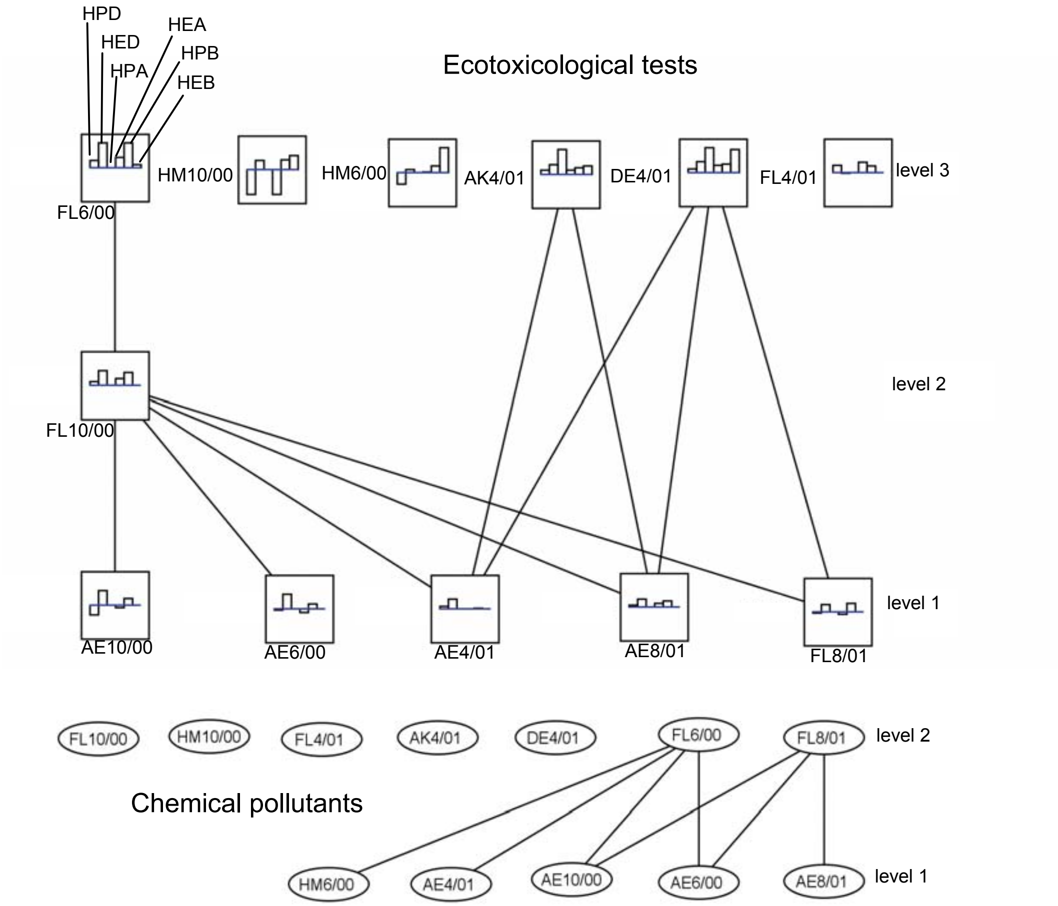


Fig. 3a. Hasse diagrams from evaluation of 12 Elbe sediments for chemical pollutants and ecotoxicological tests. Chemicals without N, S, B, Co, Sn (for abbreviations and speciation of elements, see Table 5 in the appendix). Because of shortage of space evaluation of these samples by nematodes tests is shown in Fig. 3b

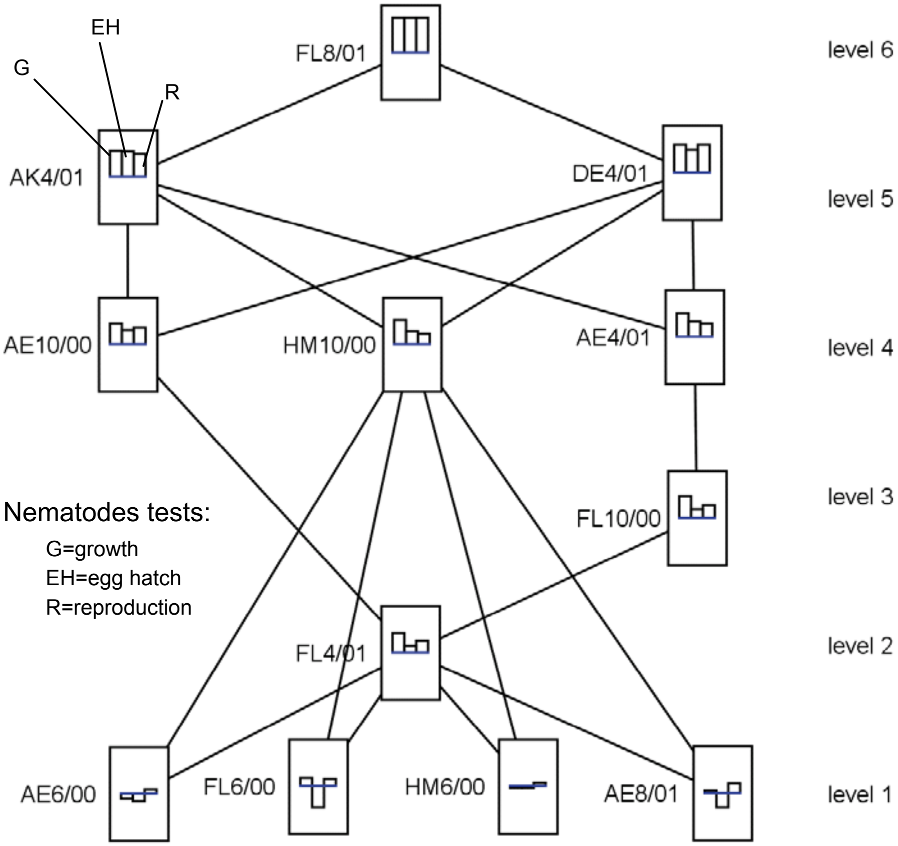


Fig. 3b. Hasse diagram from evaluation of 12 Elbe sediments for nematodes tests corresponding to Fig. 3a

Chemical pollutants versus aquatic ecotoxicological tests versus biochemical tests

Regarding the biochemical tests in comparison to chemical parameters and ecotoxicological tests in Fig. 4 striking differences can be observed too. Instead of a HD consisting of lines and circles, here the so-called level presentation is used. This kind of presentation might be useful when partial ordering results for instance in messy diagrams, as it is the case for ecotoxicological tests indeed. Here, again we want to show that the three parameter groups lead to highly different results, where evaluation by means of chemicals results in solely incomparable samples (a so-called anti-chain) and the biochemical responses are comparable for only three samples. This result may underline the assumption, that the parameter groups yield different responses to sediment quality and therefore to different rankings and classifications respectively. However, it has to be considered that here rough data are used and therefore already small numerical differences may lead to incomparabilities between sediment samples. For example, the HD based on chemical parameters in Fig. 4c consists of only incomparable samples and it is not obvious if data noise is responsible or if it is an effect of different pollution pattern indeed. Therefore, classifying by cluster analysis as pre-processing will be introduced in the following.

HD's after pre-processing by fuzzy clustering

The aggregation of samples is a strategy to get HD's, which is "easier and more robust" to interpret. Here, fuzzy cluster analysis is preferred. In contrast to conventional clustering methods, where each sample will be assigned to a cluster by a "yes/no-decision", fuzzy clustering yields a degree for the assignment of samples to a cluster (membership function with values between 0 and 1). The advantage is that samples, which are located between two clusters because they are outliers or so-called hybrid elements, can be identified (for details, see e.g. Pudenz et al. 2000, Luther et al. 2000). The fuzzy-algorithm used here (k-means fuzzy) requires a default cluster number (FCL) and a threshold value for the membership function (TMF). The TMF determines to which degree a sample belongs to a cluster. Here, preliminary tests have shown that in case of clustering over the whole property space (see below) cluster numbers FCL of six or seven lead to relatively complex diagrams. Therefore a FCL=4 is selected. Correspondingly a high TMF of 0.8 is used, such that hybrid elements and outliers will be identified.

Basically clustering can be distinguished between

- attribute-wise classification, i.e. all samples are clustered for each parameter separately, and
- clustering of all samples by the whole property space, i.e. by means of all parameter at the same time.

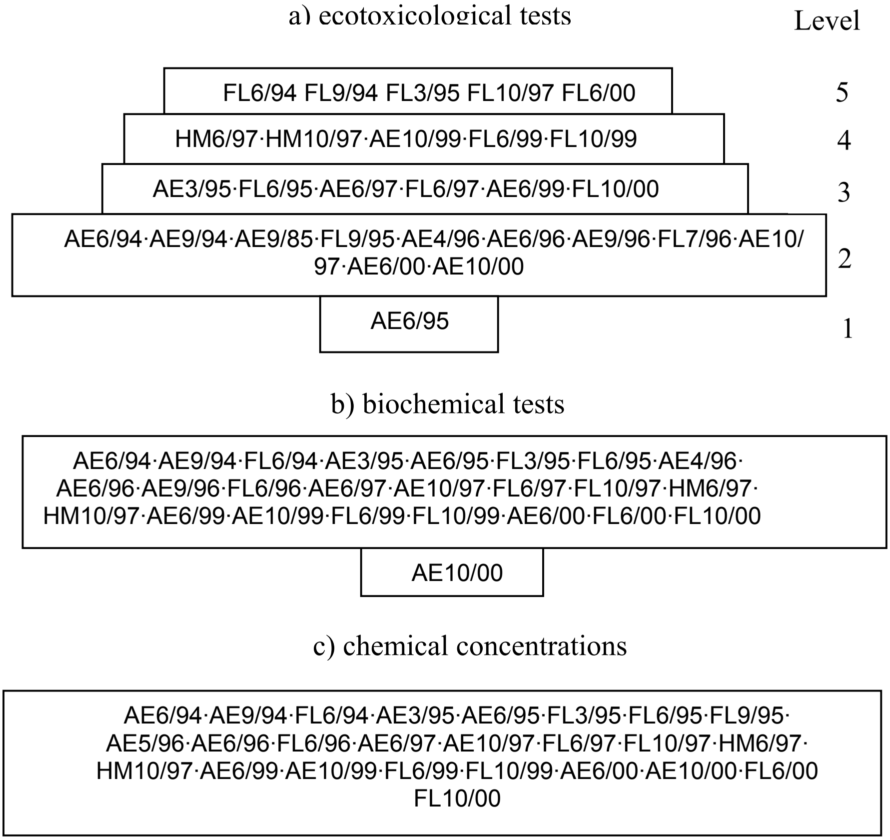


Fig. 4a. HD's as level presentation from evaluation of 28 Elbe samples by means of a) ecotoxicological tests (additionally as Hasse diagram in Fig. 4b), b) biochemical tests and c) chemical concentrations without P, TBT (see Table 5)

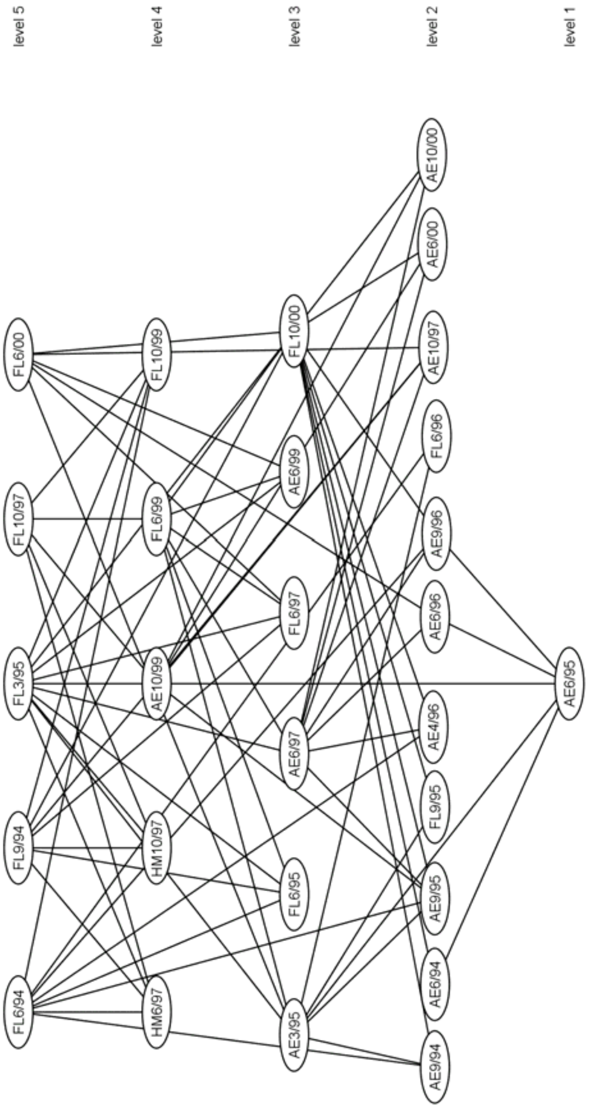


Fig. 4b. Hasse diagram for ecotoxicological tests as shown as level presentation in Fig. 4a

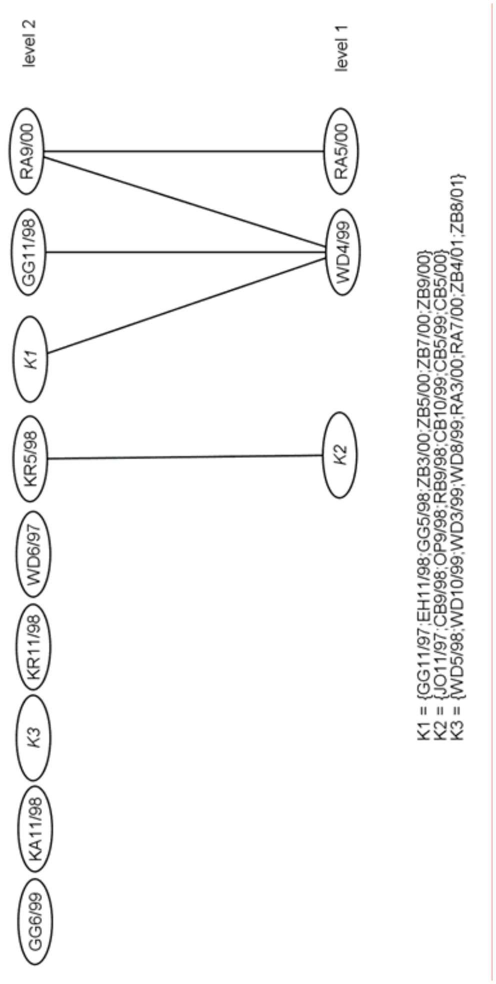
When the whole quality pattern of a location is of interest and samples with similar pattern with regard to all parameter will be identified, then clustering by means of all parameter is convenient. When all samples will be classified by each parameter separately, then efforts are more directed towards neglecting numerical differences between samples. For both methods the aim is, all samples will be ranked by the cluster centre they have been assigned to, instead of their original parameter values. Because of technical software problems, the number of chemical parameter had to be reduced to a maximum number of 20 (only in case of clustering by the whole property space). Here, the following pollutants are seen as the most relevant:

- As, Pb, Cd, Hg, Cu, Cr, Zn
- PAHs, PCBs, pp'-DDT, pp'-DDE, pp'-DDD, AOX, TBT, HCB, α-HCH, γ-HCH

Clustering by the whole property space - River Oder sediments

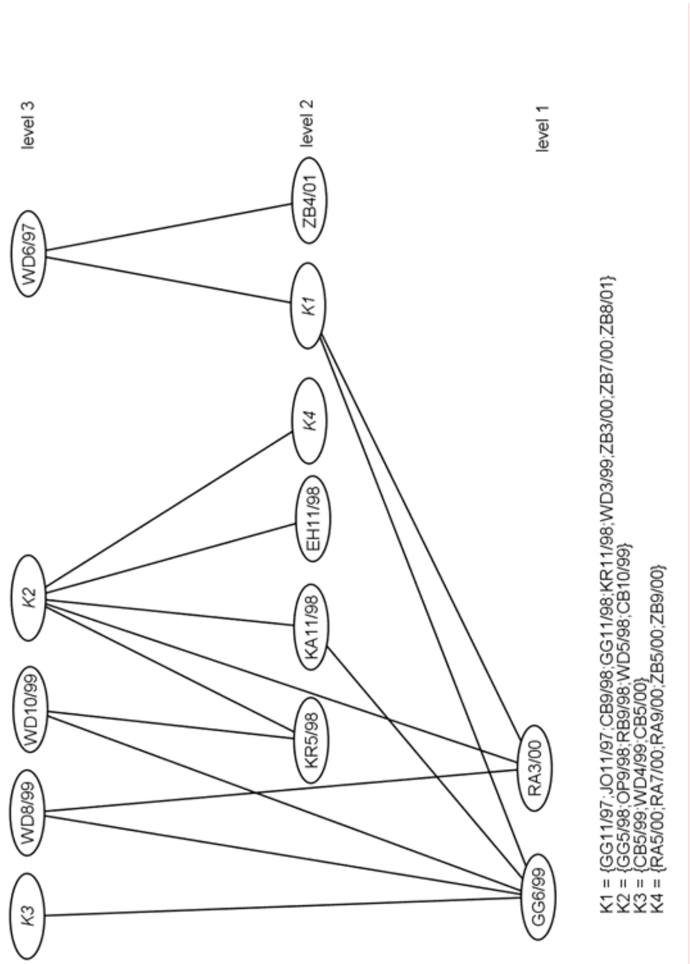
Chemical pollutants versus aquatic ecotoxicological tests

As mentioned above, if samples are assigned to clusters they are ordered by the coordinates of their cluster centre instead of their original parameter values. In Fig.'s 5a and 5b the clustering provided by four clusters (FCL=4) is represented by equivalence classes *K1*, …, *K4*. Samples that are not assigned to a cluster are hybrid elements (due to their characteristic burden pattern) and will be denoted as singletons. Clusters that consist of only one sample are denoted as singletons too, whereas the other clusters are called 'nontrivial' ones. Due to very characteristic values these samples have lead to a single cluster and therefore they can be treated like hybrid elements. In Fig. 5a, clustering of river Oder samples by chemical parameters has apparently lead to only three nontrivial clusters (*K1*, *K2*, *K3*). Here, one cluster consists of only one sample in fact, namely RA9/00: As a single sample RA9/00 (Ratzdorf) represents one cluster because of its comparatively high contamination by heavy metals. Because RA9/00 is greater than (above) RA5/00 it can be concluded that concentrations of all pollutants considered have been increased between May and September 2000. However, RA samples from March and July 2000 (RA3/00, RA7/00) are both incomparable to the May and September samples.



Chemical parameters

Fig. 5a. HD after fuzzy clustering by the whole property space of chemical parameters. River Oder, 31 samples (MAX-PN). Number of hybrid elements = 8 (samples that are not assigned to cluster due to their very characteristic pattern)



Ecotoxicological parameters

Fig. 5b. HD's after fuzzy clustering by the whole property space of ecotoxicological parameters. River Oder, 31 samples (MAX-PN). Number of hybrid elements = 9 (samples that are not assigned to cluster due to their very characteristic pattern)

Examining the clustering results by chemical parameters in detail, the following can be observed:

- Cluster *K3* and equivalence class *K3,* respectively, contains four out of six samples of Widuchowa (WD). That means, except for June 1997 and April 1999 the pollution pattern by the chemicals considered here is quite similar. The patterns of WD4/99 and WD6/97 are incomparable to these four samples of 1999.
- Comparing *K1* and *K3*, it is seen that the pollution pattern of ZB in year 2000 (ZB3/00, ZB5/00, ZB7/00, ZB9/00) is different to 2001 (ZB4/01, ZB5/01).
- All samples of Cerna Budisovka (CB) have the same pollution pattern over the years of investigation.

A comparison between the diagrams in Fig.'s 5a and 5b once again leads to the assumption that chemical concentrations reproduce another pattern than ecotoxicological effects. This is indicated, for instance, by the following findings:

- Whereas in the clustering of ecotoxicological parameters nearly all Ratzdorf samples (except RA3/00) are assigned to one cluster together with ZB5/00 and ZB9/00 (cluster *K4*), clustering of chemical parameter leads to significantly different similarities: RA9/00 as well as RA5/00 show a very characteristic pattern. RA9/00 forms a single cluster (see above) and RA5/00 cannot assigned to any (therefore it is a hybrid element; see section 3.1).
- Instead of four similarities between Widuchowa samples (WD) in case of chemical pollution, ecotoxicological parameters without exception lead to incomparabilities between WD samples, thus indicating significant differences in their ecotoxicity.

Clustering by the whole property space - River Elbe sediments

Chemical pollutants versus aquatic ecotoxicological tests

Fig.'s 6a and 6b shows the clustering results for 62 Elbe sediment samples. Regarding at first the result of chemical parameters and selecting only the comparable samples with respect to a location, the following relations are found:

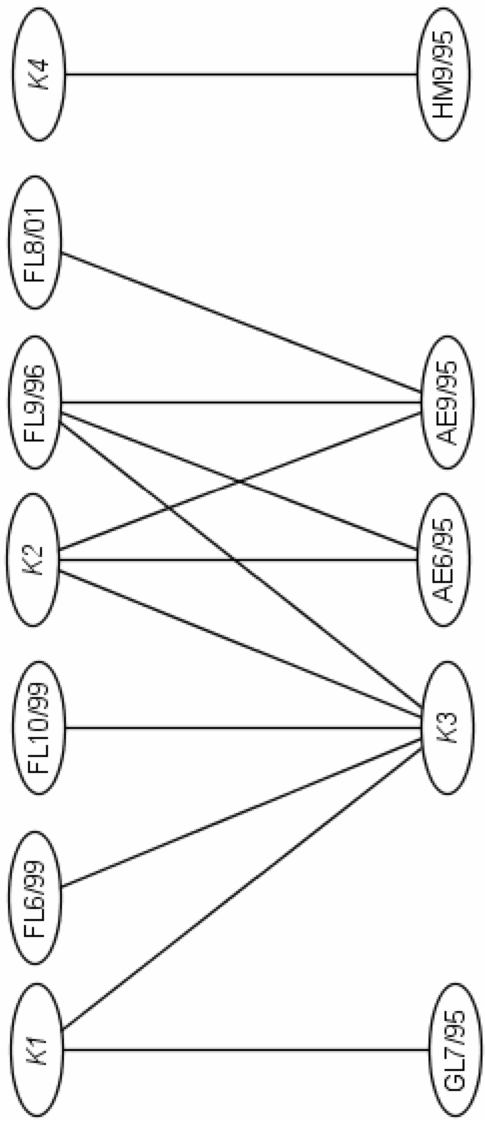
- AE9/94=AE6/97=AE10/97=AE10/99=AE6/99=AE10/00=AE6/00 =AE4/01=AE8/01<AE12/92=AE9/93=AE6/94=AE3/95=AE4/96= AE6/96=AE9/96
- FL6/94=FL6/95=FL6/96=FL6/97
- FL12/92=FL9/95=FL10/00=FL6/00=FL4/01
- FL6/94=FL6/95=FL6/96=FL6/97 < FL10/99

- FL6/94=FL6/95=FL6/96=FL6/97 < FL6/99
- FL6/94=FL6/95=FL6/96=FL6/97 < FL9/96
- HM9/95 < HM9/94=HM11/95=HM6/95=HM6/96=HM10/99
- DA6/97=DA9/97
- WB6/96=WB9/96

Except AE6/95 and AE9/95 all samples of Alte Elbe (AE) are assigned to two clusters (*K3*, *K1*) and moreover both are comparable to each other (*K3*<*K1*). Furthermore, since cluster *K3* only contains samples of recent dates, except AE/94, it is indicated that the concentrations of the chemicals considered here are decreased. Moreover, it is striking too that almost only AE samples of prior date are assigned to cluster *K1*. This could be evidence of a higher pollution of the river section AE in this time period and relatively specific burden pattern too. Indeed, since the Alte Elbe is a bayou with limited exchange to the main waterway river Elbe depending on the discharge conditions a stable pollution pattern can be expected over longer periods of time. A similar result is obtained when using aquatic ecotoxicological tests for evaluation: except AE10/99, AE9/93 and AE6/96, all AE samples are assigned to cluster *K1* and have therefore a similar quality pattern.

Considering the other clusters of Fig. 6a it is evident that also *K2* and *K4* consist of samples from almost one river section, namely FL (Fahlberg List) and HM (Meißen harbour). However, in case of FL cluster *K2* is not comparable to the remaining samples of FL: four of overall ten samples from FL are assigned to *K2*. Moreover, most of the samples of FL are incomparable to all other samples (they are isolated elements). Reasons for this specific pattern could be the discontinuous sewage draining from an old contaminated site there.

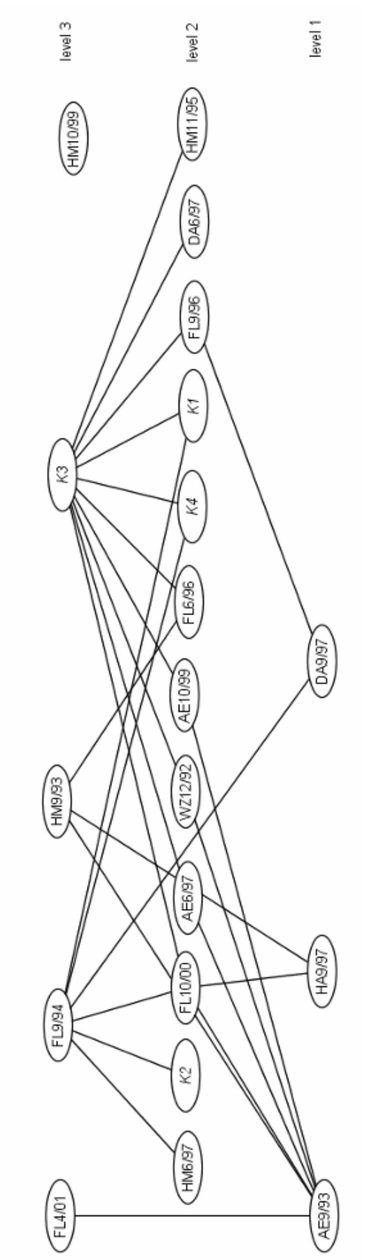
Cluster *K4* consists of five out of 15 samples from HM. HM9/95 is ≤ *K4* and has therefore lower concentrations. HM9/96, HM6/97 and HM6/00 are assigned to cluster K3 together with many samples from AE and other river sections, while *K3* is not comparable to other HM-samples. Moreover, samples HM10/97, HM9/93, HM10/00, HM6/99, HM6/94 and HM11/92 are isolated (incomparable to all other samples).



Isolated objects (not shown in graphic):
FL3/95, FL10/97, HM10/97, HM3/93, HM10/00, HM6/99, HM6/94, HM11/92, FL9/94, WZ12/92, RO12/92, DE12/92

Equivalence classes:
K1 = {AE12/92; DD11/92; AE9/93; AE6/94; AE3/95; AE4/96; AE9/96
K2 = {FL12/92; FL9/95; FL10/00; FL6/00; FL4/01}
K3 = {AE9/94; FL6/94; FL6/95; GL9/95; FL6/96; HM9/96; WB6/96; AE6/97; AE10/97; DA6/97; DA9/97; FL6/97; HA9/97; Hitz; HM6/96; AE10/99, AE6/99; CU1/99; AE10/00; AE6/00; HM6/00; AE6/00; HM6/00, AE4/01; AE8/01}
K4 = {HM9/94; HM11/95; HM6/95; HM6/96; HM10/99}

Fig. 6a. HD's after fuzzy clustering by the whole property space of chemical parameters. River Elbe, 62 samples (MAX-PN)



K1 = {AE12/92; DD11/92; HM11/92; RO12/92; AE6/94;AE9/94; AE9/94; AE3/95; AE6/95; AE9/95; FL6/95; FL9/95; GL7/95; GL9/95; HM9/95; AE4/96; AE6/96; AE9/96; HM6/96; WB6/96; WB9/96; AE10(97; FL6/97; Hitz; AE6/99; CU1/99; AE10/00; AE6/00; AE4/01; AE8/01; FL8/01}
K2 = {DE12/92; FL12/92; FL6/94; HM6/94; HM9/94; HM6/95; HM9/956; FL10/99; HM6/00}
K3 = {FL3/95; FL10/95; FL6/00; FL6/00}
K4 = {HM10/97; HM6/99; HM10/00}

Fig. 6b. HD's after fuzzy clustering by the whole property space of ecotoxicological parameters. River Elbe, 62 samples (MAX-PN)

Obviously, within the sampling period the pollution pattern of Meißen harbour varies more than that of other river sections. This may be due to irregular discharges via a creek flowing into the harbour. Using the results of the aquatic ecotoxicological tests only one HM sediment is isolated, i.e. not comparable to any other sediment. Moreover, whereas HM10/00, HM6/99 and HM10/97 have been singletons (isolated) in the chemical approach here they form one cluster (*K4*). However, many of the HM samples are not comparable among each other even though several of them are assigned to one cluster. For example five HM samples belong to cluster *K2*, three to *K4* and three to *K1,* but neither of them is comparable to each other.

Regarding the results of Oder and Elbe sediments it is noticeable that clustering by ecotoxicological parameters

1. leads to more comparabilities in the Hasse diagram and
2. yields other cluster compositions,

compared to chemical parameters.

Ad(1) More comparabilities have been already observed in the evaluation by rough data, i.e. without pre-processing. Therefore it can be expected that also after pre-processing by clustering this proportion holds.

Ad(2) Not many samples can be found in both clusters of chemical and ecotoxicological parameter. For example, in Fig. 6a cluster *K4* consists exclusively of five HM samples. From these five samples, three (HM9/94, HM6/95), HM10/99) are recovered in cluster *K2* (Fig. 6b), one sample (HM11/95) is a hybrid element (not assigned to any cluster) and moreover not comparable to any other HM sample and another sample (HM6/96) is assigned to cluster *K1* in the ecotoxicological evaluation. More examples of different compositions with respect to a certain river section can be found in both clustering of Oder and Elbe sediments. Therefore cluster analysis over the whole property space (by means of all parameters at the same time) strengthens the assumption of different responses between ecotoxicological tests and chemical parameters describing sediment pollution.

Chemical pollutants vs. aquatic ecotoxicological tests vs. nematode sediment contact test

According to the evaluations of Elbe sediments by raw data of a) aquatic ecotoxicological tests, b) chemical measurements, and c) nematode sediment contact tests in Fig. 3, clustering results by means of all parameters simultaneously (i.e. over the whole property space) for each of the groups and additional partial ordering is shown in Fig. 7. A common characteristic for both chemical and ecotoxicological tests is, that

- all AE samples are assigned to one cluster,
- AK4/01 and DE4/01 form a cluster and
- HM10/00 is a singleton and isolated.

The location of AE samples in the lower level of the Hasse diagram is common for all parameter groups. Again, this may result from the special characteristics of undisturbed sediments in this bayou. Another common characteristic is the similarity of samples AK4/01 and DE4/01 (due to cluster analysis) indicating a typical pattern that leads to analogous responses of chemical parameters and test results. However, except the sediments AK4/01, DE4/01 and all AE sediment samples, for FL and HM sediments the parameter groups lead to different compositions of clusters and therefore indicating different responses between the parameter groups.

In contrast to the partial orders from chemical concentrations and aquatic ecotoxicological tests, the results of the sediment contact tests with nematodes lead to a total order. This corresponds to a correlation analysis that shows a significant correlation between growth, reproduction and egg hatch (r=0,7).

Chemical pollutants, biochemical tests and ecotoxicological tests simultaneously

To complete fuzzy clustering over the whole property space and identifying differences in responses between the parameter groups, respectively, clustering results of each biochemical tests, chemical parameters and ecotoxicological tests are combined in a matrix as basis for partial ordering. In addition to the comparisons shown above this presentation may facilitate the identification of similar responses of tests. Fig. 8 shows that partial ordering leads to two equivalence classes[1] containing all AE samples. Once again this fact strengthens the assumption that the bayou Alte Elbe has specific sediment features leading to similar responses of all test systems.

1 In contrast to the evaluations above where equivalence classes are a consequence of clustering results (instead of original parameter values samples obtain the values of cluster centres), here equivalence classes are a result of equivalent pattern concerning the three parameter groups (chemicals, ecotox. and biochemical tests).

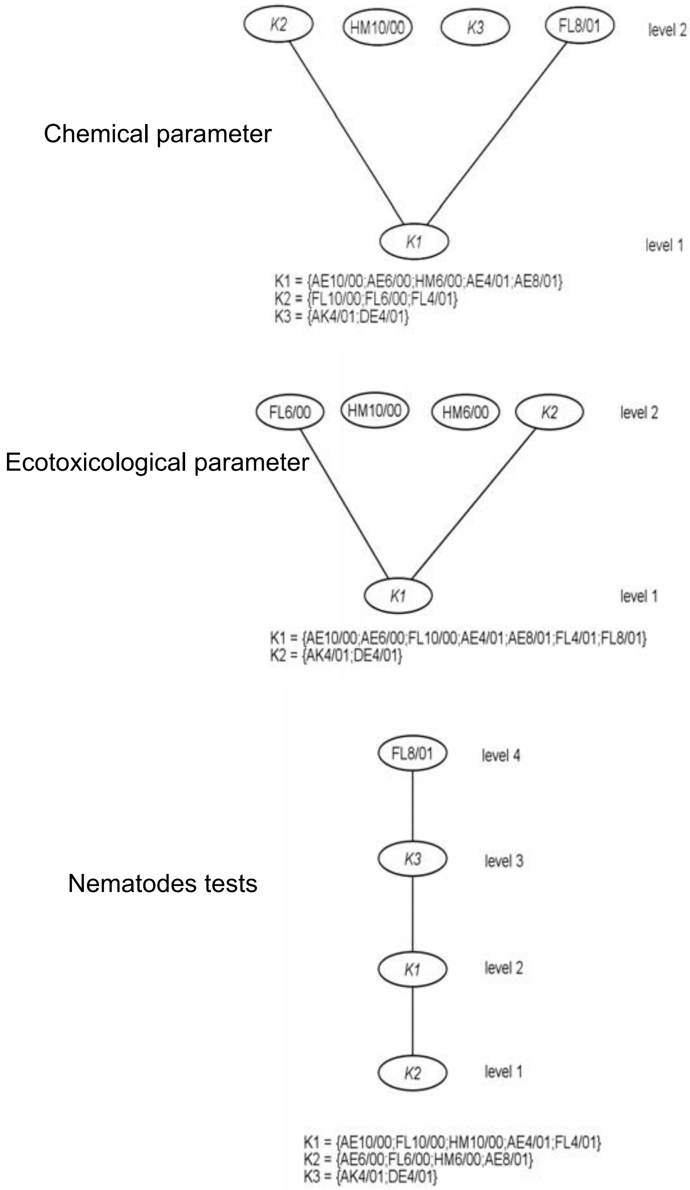


Fig. 7. Clustering results and Hasse diagrams for Elbe sediments

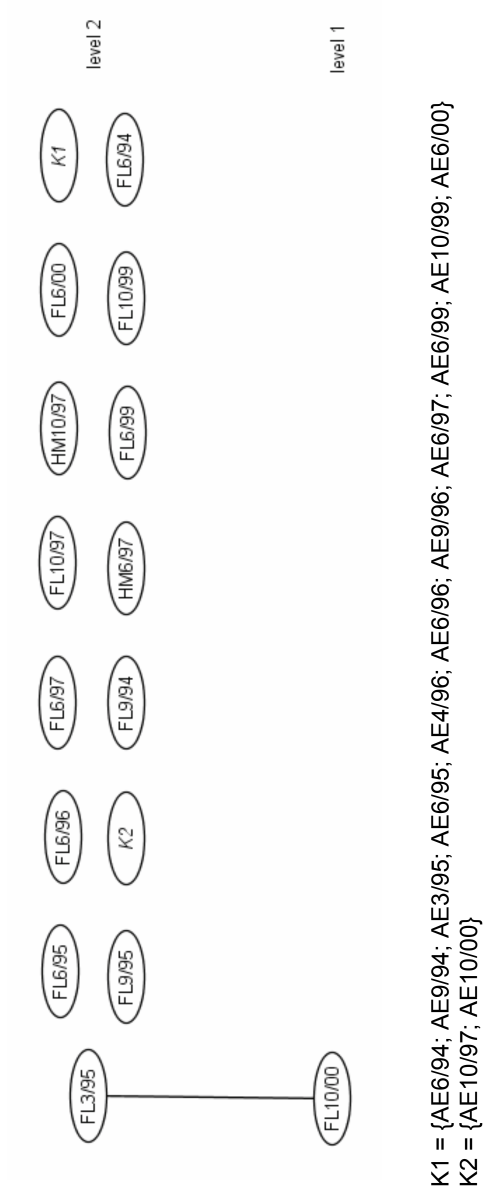


Fig. 8. Hasse diagram of clustering results from three parameter groups: biochemical tests, chemical parameters and ecotoxicological tests (28 Elbe sediments and 36 parameters overall)

The Hasse diagram shows only one comparability, namely between FL10/00 and FL3/95, indicating a decline of concentrations in all chemicals, metals and toxic qualities at the same time. However, all FL samples taken before and in between are not comparable to any other sediment sample, and are therefore expressing different responses of test systems and chemicals.

Attribute-wise clustering - Oder sediments

Aquatic ecotoxicological tests versus chemical pollutants

Fig. 9a and 9b show the evaluations after fuzzy-clustering by means of each parameter separately (attribute-wise clustering). As in the clustering by the whole property space, here for each parameter a cluster number of FCL=4 and a TMF of 0.8 is used. The investigation particularly aims at the discovery of temporal changes in the sediment quality and therefore on the identification of so-called chains[2] with links consisting of samples from a certain river section.

The evaluation by means of chemical concentrations only yields one comparability between samples of a river section, namely ZB4/01 < ZB3/00, whereas the Hasse diagram based on ecotoxicological tests generates several relations as shown in Table 2.

Table 2. Comparabilities of a river section after evaluation by ecotoxicological test

Comparabilities of a river section	Total number of samples of each river section	Incomparable river sections
ZB4/01 < ZB3/00 < ZB7/00 ZB4/01 < ZB8/01	ZB=6	ZB9/00
GG11/97 < GG11/98 GG6/99 < GG11/98 GG6/99 < GG5/98	GG=4	
CB9/98 < CB10/99	CB=4	CB9/96, CB5/00
WD8/99 < WD5/98	WD=6	WD10/99,WD4/99, WD3/99,WD6/97

2 Chains are a sequence of lines in the Hasse diagram indicating that the elements are comparable with each other.

With respect to ecotoxicological responses partial ordering of river section GG (Glogau) indicates an improvement of its pollution status because sample 6/99 is less than 11/98 and 5/98. The incomparability between GG6/99 and GG11/97 is only based on a difference in the bacteria test in eluate (HEB), see Table 2. For river section ZB a conclusion about an improvement is difficult to derive. Though sample ZB4/01 is less than ZB3/00 and ZB7/00, it is not comparable with ZB5/00 and ZB9/00 (Tab. 2).

Both Hasse diagrams in Fig. 9a and 9b indicate neither an increasing nor a decline of sediment burden for a river section, except for GG with respect to ecotoxicological responses.

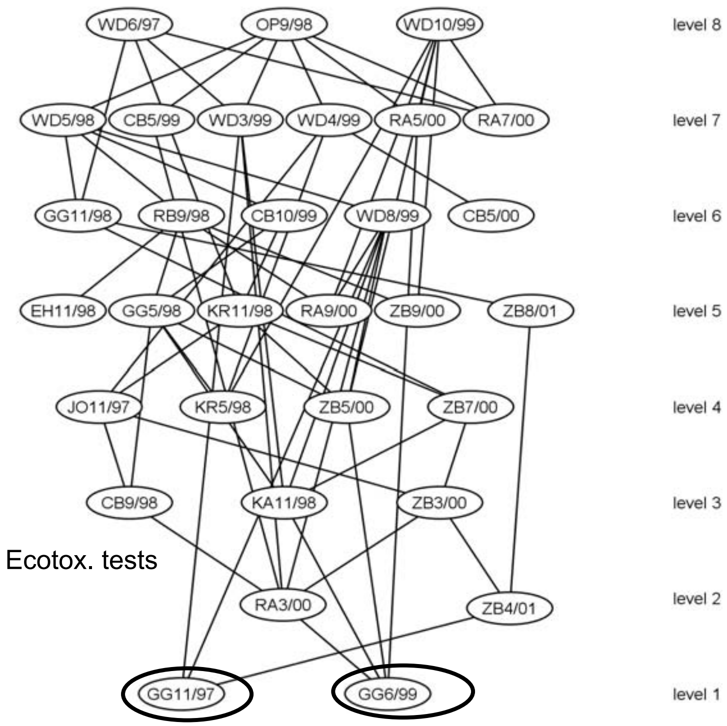


Fig. 9a. Hasse diagram for Oder sediments after attribute-wise clustering of ecotoxicological parameters (FCL=4, TMF=0.8)

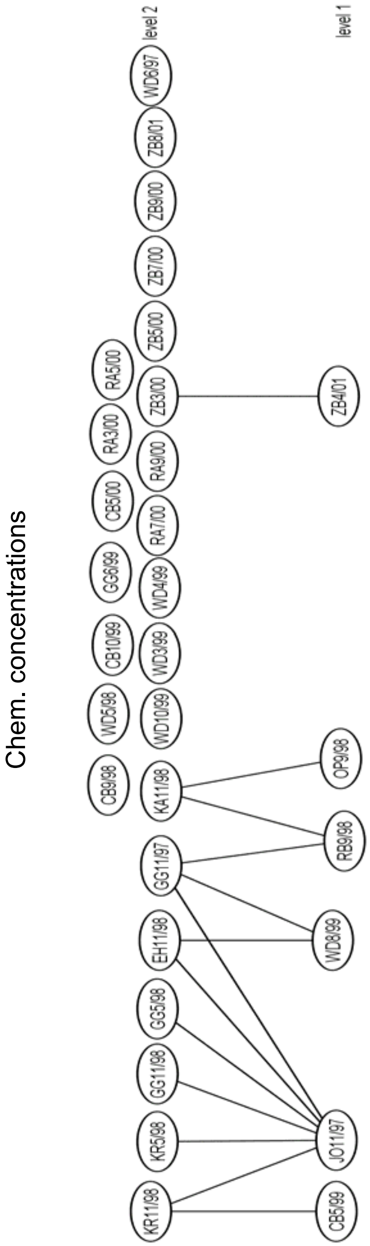


Fig. 9b. Hasse diagrams for Oder sediments after attribute-wise clustering of chem. concentrations (FCL=4, TMF=0.8)

Table 3. Inhibition values of ecotoxicological tests from a selection of samples in Fig. 9. Negative values mean stimulation of test cultures

Sample	HEA	HEB	HED	HPA	HPB	HPD
GG11/97	3,33	1,28	0	-77,33	14,16	0
GG5/98	-44,32	15,87	0	-20,52	47,78	0
GG11/98	3,33	15,87	0	38,63	14,16	0
GG6/99	-96,39	10,11	0	-159,3	14,16	0
ZB3/00	3,33	10,11	0	-20,52	14,16	0
ZB5/00	-96,39	15,87	0	-121,2	32,23	0
ZB7/00	3,33	15,87	0	-20,52	14,16	0
ZB9/00	-198,23	20,4	0	-159,3	47,78	0
ZB4/01	3,33	1,28	0	-20,52	14,16	0
ZB8/01	3,33	5,8	0	7,7	14,16	0

Attribute-wise clustering - Elbe sediments

Aquatic ecotoxicological tests versus chemical pollutants

In contrast to the above made comparisons of quality patterns by chemical concentrations and aquatic ecotoxicological test results for 62 sections (sites) of the River Elbe (see Fig. 6), here we will use attribute-wise clustering to look at temporal changes of only one river section. Afterwards the results of evaluation by a) the nematode test and b) biochemical tests will be compared with the chemical and aquatic ecotoxicological approaches.

Fig.'s 10a and 10b shows the Hasse diagrams after single clustering of each attribute (parameter) for AE sediments using a cluster number of FCL=4 and a TMF=0.8. The equivalence classes *K1* and *K2* in the ecotoxicological evaluation are the only minimal elements, i.e. compared to all samples above their members have the lowest values in all tests. Except *K2* all samples are comparable with *K1*. The fact that except AE9/94, AE6/94 and AE3/95 all samples above *K1* (AE12/92, AE9/93, AE6/95) have been taken at a later date indicates an increasing pollution for AE. Using chemical concentrations for evaluation the temporal trend seems to be contrary. However, both recent samples AE4/01 and AE8/01 are isolated, i.e. not comparable to all other samples. A sensitivity analysis (see e.g. Heininger et al. 2003) shows that the evaluation is most sensitive to the nitrogen content, where omitting this nutrient compensates the isolation of AE4/01 and AE8/01 (see Fig. 11). Moreover, sample AE4/01 is now a minimal element and therefore emphasizes the indication of a decline of the cline of the pollution status with respect to (most of) chemical concentrations.

Fig. 10a. Hasse diagrams for AE sediments after clustering of each parameter (FCL=4, TMF=0.8): ecotoxicological tests

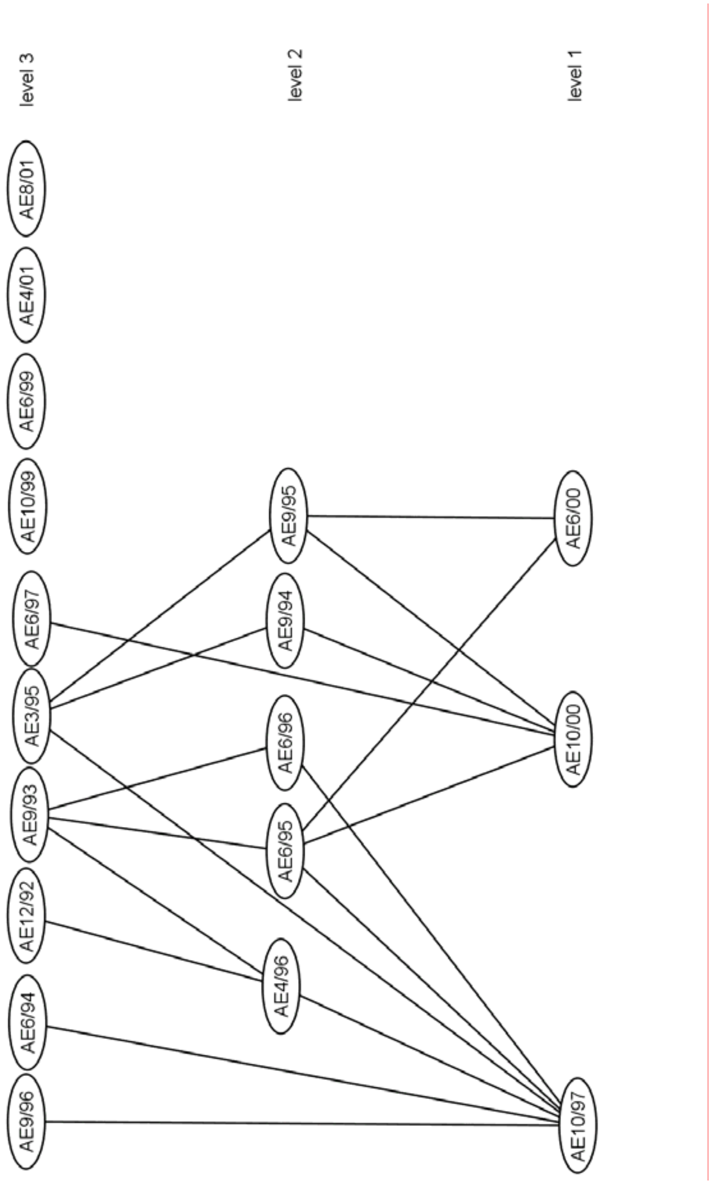


Fig. 10b. Hasse diagrams for AE sediments after clustering of each parameter (FCL=4, TMF=0.8): chemical concentrations

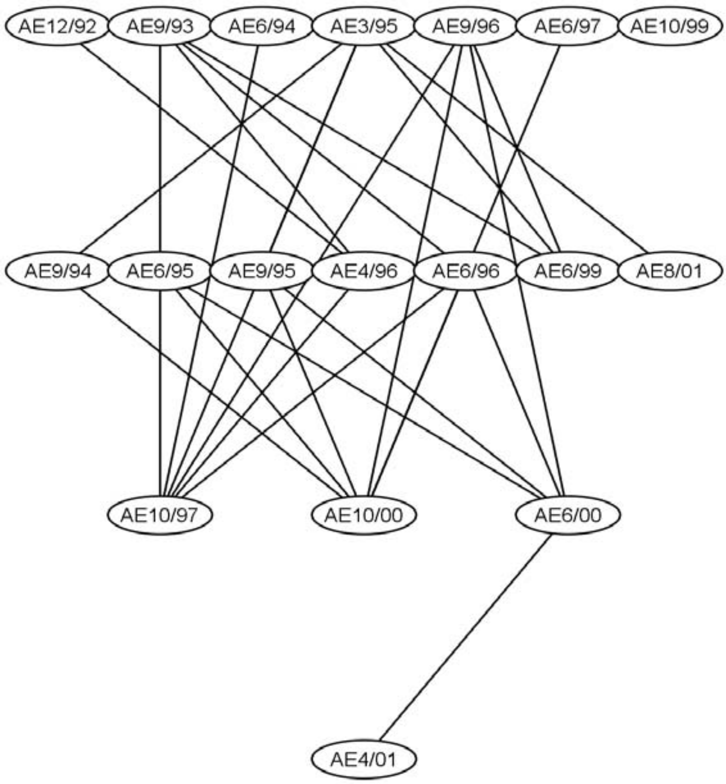


Fig. 11. Hasse diagram for AE sediments after omitting nitrogen (in HD of chem. conc.; Fig. 10)

Seasonal effects may lead to incomparabilities between samples and therefore hamper the analysis of long-term temporal changes. For this reason only annual mean values of each parameter will be clustered as basis for partial ordering. In addition to the evaluation above, here the biochemical test results will also be considered (parameters are shown in Table 5 in the appendix).

Fig. 12 shows that averaging does not facilitate the interpretation of the Hasse diagrams. Different quality patterns between younger and older samples are the reason for incomparabilities. Again, sensitivity analysis may be a method to identify sensitive parameters whose significance may be subject of expert discussion. In case of minor relevance of such a parameter simply omitting may lead to a result that is at least easier to interpret (as shown in Fig. 11). Whereas for biochemical and ecotoxicological tests sensitivity analysis does not yield any striking sensitivity values, the evaluation by chemical parameters is again sensitive to the nitrogen content (c.f. Fig. 12). Now, the results can be discussed as follows:

- Evaluation by means of biochemical tests reveals a positive quality trend of section AE. The pollution patterns of both AE00 and AE99 are less than AE95 and AE97, but incomparable with those of 1996 and 1994. Reasons for that incomparability are higher values (after clustering) in both parameters DHGS and PRV whereas all remaining parameters of AE00 and AE99 have lower values than AE95 and AE97.
- Similar to the trend of biochemical test results the position of AE00 in the Hasse diagram indicates a decline in ecotoxicity. Here, the incomparability of AE00 to the years 1995 and 1994 is due to the bacteria test (eluate) that yields higher values for year 2000 whereas algae (in pore water and eluate) and bacteria in pore water have identical or lower values in 2000 (daphnia tests yield only zero values for all years).
- From the analysis of all AE samples a high sensitivity to nutrient pollution (nitrogen) has been expected (c.f. Fig. 10 and 11). From the water ecological point of view nitrogen is a limiting factor for algae growth and therefore important for evaluation. Considering the management of dredged material (e.g. from AE) this may be important for the relocation in waters, which are sensitive to eutrofication.

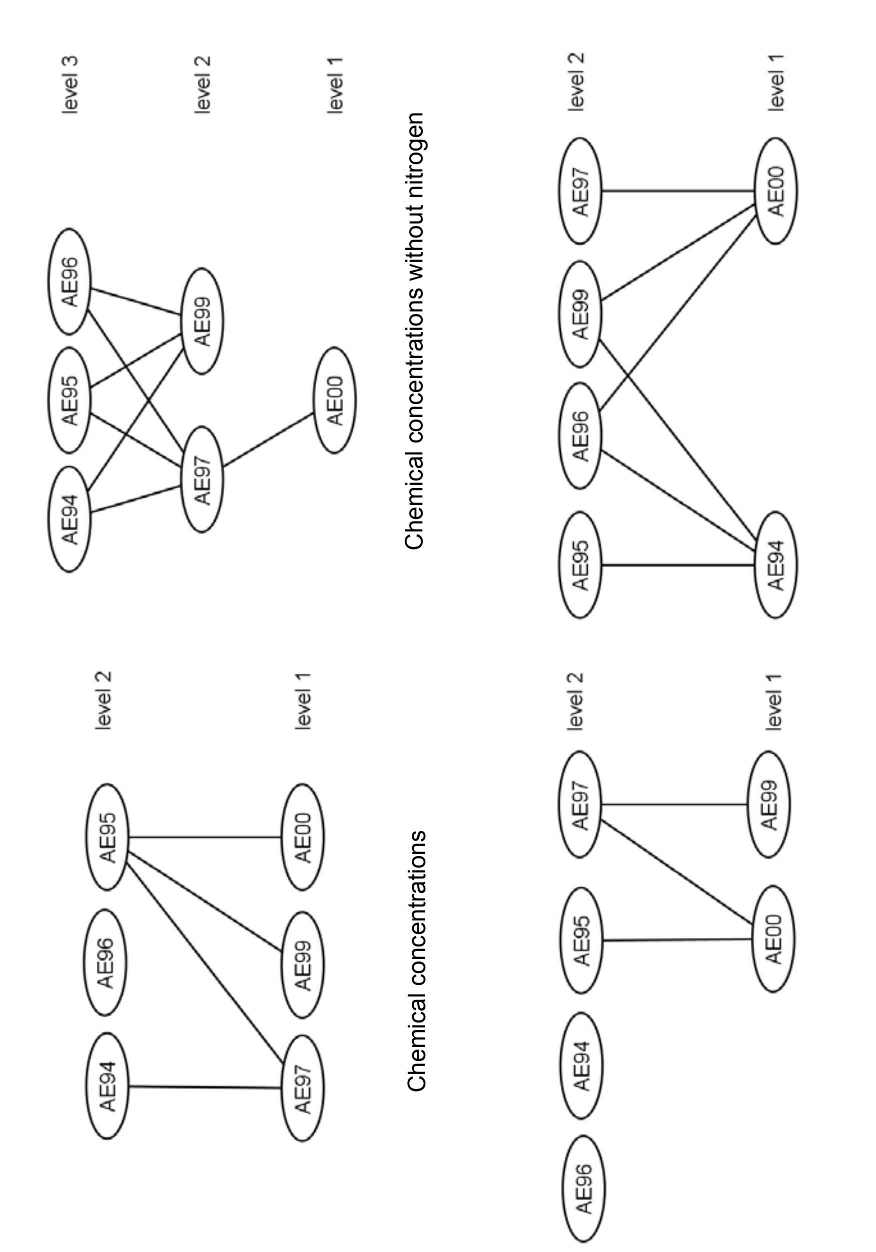


Fig. 12. Clustering and evaluation of annual mean values of river section AE

Attribute-wise clustering – Elbe and Oder sediments

Chemical pollutants vs. aquatic ecotoxicological tests vs. nematode sediment contact test

According to the clustering over the whole property space the evaluation by nematode tests after single clustering will be compared with those of chemicals and aquatic ecotoxicological tests too. However, here the sample set includes additional samples from River Oder due to relatively few samples from River Elbe (nematodes tests started in 2000 only).

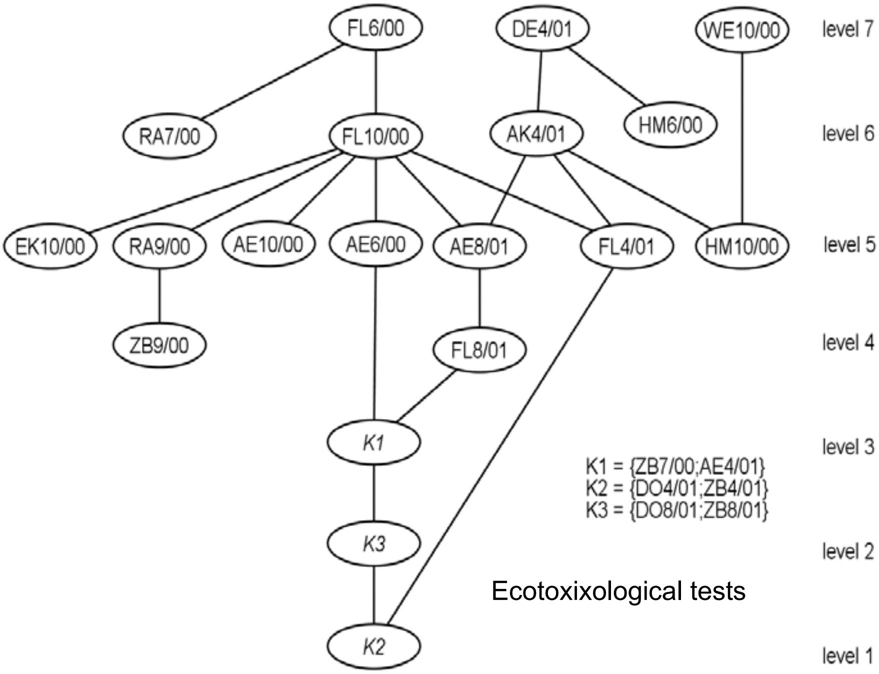
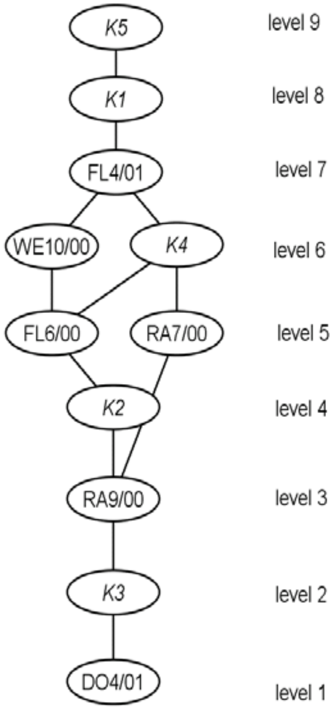


Fig. 13a. Hasse diagram for evaluation of river Elbe and Oder sediment samples after single clustering of parameters (22 samples): ecotoxicological tests



K1 = {AE10/00;FL10/00;HM10/00;AE4/01}
K2 = {AE6/00;HM6/00;AE8/01}
K3 = {EK10/00;ZB4/01}
K4 = {ZB7/00;ZB9/00;DO8/01;ZB8/01}
K5 = {AK4/01;DE4/01;FL8/01}

Nematodes tests

Fig. 13b. Hasse diagram for evaluation of river Elbe and Oder sediment samples after single clustering of parameters (22 samples): nematodes tests

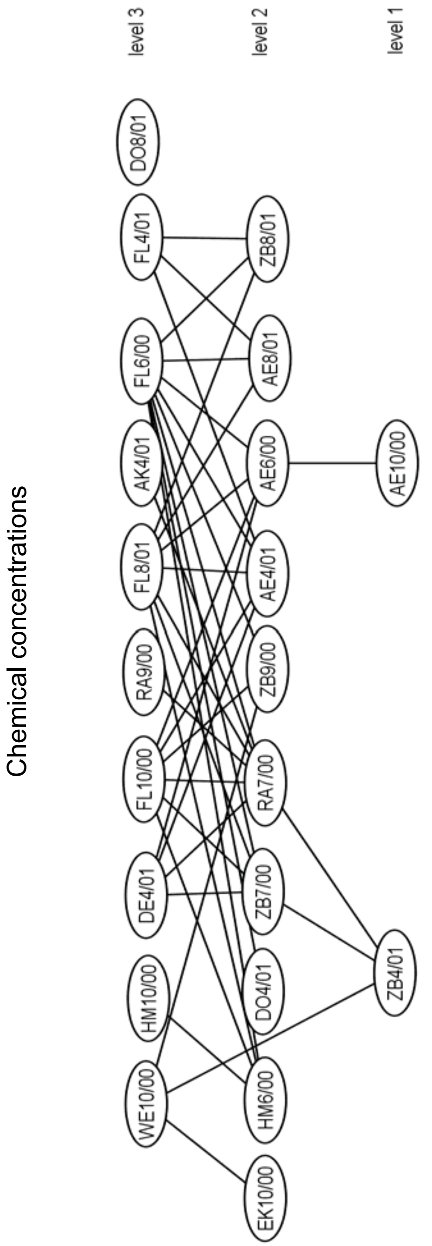


Fig. 13c. Hasse diagram for evaluation of river Elbe and Oder sediment samples after single clustering of parameters (22 samples): chemical concentrations

Compared to the results of nematodes tests, evaluation by chemical concentrations and ecotoxicological tests present a familiar picture (c.f. Fig. 7 and 13a,b,c), which is dominated by incomparabilities (and no equivalence classes) and therefore a higher diversity of pollution pattern. Again, due to high correlation between the three parameters egg hatch, growth and reproduction, evaluation of samples by nematodes tests results in nearly total order.

In contrast to the comparison between biochemical tests, aquatic ecotoxicological tests and chemical concentrations, here averaging is not convenient since nematodes have been investigated only for two years. Moreover, instead of considering only one river section and visual examining of differences between the Hasse diagrams, the Tanimoto index and the W-matrix will be used for similarity investigations between evaluation results. For the Tanimoto index T holds the higher the index the more similarity, where a value of one means total similarity: Two approaches of the Tanimoto index are used here:

1. $T_1 = \frac{A \cap B}{A \cup B} = \frac{\sum_{sr}}{\sum \leq_A + \sum \leq_B - \sum_{sr}}$, where $\sum \leq_A$ and $\sum \leq_B$ are the numbers of comparabilities in set A and B respectively, and $\sum_{sr}$ counts the comparabilities which are common in both sets A and B (for details see Pudenz et al. 1998).
2. T_2 quantifies similarity by a rank correlation analysis and in comparison to T_1 it takes more information into account: $T_2 = \frac{\sum_{sr}}{\sum_{sr} + \sum_{rr} + \sum_{irA} + \sum_{irB}}$, where $\sum_{rr}$ is the sum of pairs for which a reverse ranking is observed (i.e. $x < y$ in set A and $y < x$ in set B), $\sum_{irA}$ counts the number of pairs that are comparable in set A but incomparable in set B and $\sum_{irB}$ is the sum of pairs that are comparable in set B but incomparable in set A (for details see Sørensen et al. 2003).

Table 4. Similarities between Hasse diagrams in Fig. 13 (Elbe and Oder sediments) calculated by two similarity indices

Similarity between A and B:	T_1	T_2
Chemicals – Ecotoxicological tests	0,22	0,22
Chemicals – Nematodes tests	0,15	0,19
Ecotoxicological tests – Nematodes tests	0,26	0,27

For both Tanimoto indices T_1 and T_2 similar results can be observed where the highest value results from the comparison between ranking by nematodes and ecotoxicological tests (Table 4). However, all values show a relative low similarity between the Hasse diagrams in Fig. 13 and therefore the different property pattern of sediments indicated by chemical concentrations, ecotoxicological and nematodes tests should be taken into account for sediment evaluation.

Summary and Conclusions

Partial ordering of sediment data from German rivers Elbe and Oder has shown that Hasse diagram technique is a powerful tool to analyse the sediment status. The diversity of pollution pattern of river sections can be identified and the effects of pollutants on different test systems can be compared without merging of data. However, as shown here a relatively high diversity of the quality pattern may also increase the degree of incomparability between sediment samples and therefore hampers the identification of e.g. temporal changes. But also incomparabilities between samples may give reasons for expert discussion, for instance the consideration of secondary information of river sections (discharge of pollutants) that could be responsible for a specific quality pattern and for incomparabilities, respectively.

In order to reduce incomparabilities and to facilitate the interpretation of Hasse diagrams, pre-processing by two strategies of fuzzy cluster analysis has been applied to sediment data:

- classification of sediments over the whole property space (by means of all parameter at the same time) aiming at the identification of similar quality pattern and
- classification of sediment samples by each parameter separately focusing on disregard of small numerical differences between parameter values on the one hand and in conclusion on ranking with respect to their quality on the other hand.

Cluster analysis over the whole property space often leads to clusters containing time series of samples from one river section. The sediments in particular from the River Elbe section Alte Elbe are characterised by relatively constant pattern over the years of investigation. This is underlined by the fact that for each parameter group similar clustering results can be observed with respect to the site Alte Elbe. An instructive example is the

Hasse diagram in Fig. 8 that considers clustering results of biochemical and aquatic ecotoxicological tests and chemical measurements at the same time, where exclusively all AE samples are assigned to two equivalence classes. It is assumed in this case the specific conditions of a bayou lead to similar responses of different test systems. However, for most of the samples from rivers Oder and Elbe the parameter groups lead to different clustering results and therefore indicate different responses in the sediment contact test with nematodes, in biochemical and aquatic ecotoxicological tests among each other and also compared to chemical concentrations.

This result is also confirmed by partial ordering of sediment samples after an attribute-wise clustering. Here, additional similarity calculations with Tanimoto indices indicate relatively high differences between ranking results.

Whereas the clustering over the whole property space indicates a similar pattern during the sampling period with respect to chemical concentrations and aquatic ecotoxicological tests for river section Alte Elbe (c.f. Fig. 8), attribute-wise clustering enables a more differentiated comparison. Here, the Hasse diagrams indicate contrasting temporal changes for AE. Following the chemical concentrations and additionally omitting nitrogen concentration from the parameter group a decline can be observed whereas the ecotoxicological tests suggest an opposite trend. However, by averaging and therefore eliminating seasonal effects, the opposite trend indicated by ecotoxicological tests is slightly weakened.

In summary, by each parameter group different responses to sediment quality can be expected. Comparing the responses of the different parameter groups, the diversity obtains a maximum when using chemical concentrations for partial ordering, thus hampering a comparative evaluation of sediments.

Regarding the evaluation of dredged material further expert discussions aiming at a detailed selection of parameters should be initiated. Here, sensitivity analysis has shown that for instance omitting nitrogen leads to significant changes in the ranking result.

Furthermore, a basic problem for the evaluation of dredged material seems to be the high diversity of sediment quality as represented by all parameter groups. Though partial ordering is helpful to analyse differences in responses of test systems, due to many incomparabilities it is crucial to derive a decision. Therefore, it has to be investigated whether a linear mapping of the partial order by e.g. linear extensions and an average rank probability (Brüggemann et al. 2004) or other approaches like fuzzy-logic (Ahlf, Heise 2005) are useful for decision purposes.

Appendix

Table 5. Parameter groups and their composition for evaluation of river sediments

Parameter group	Parameters
25 chemical pollutants and basic parameters (concentrations in mg/kg, µg/kg; g/kg)	AOX, pp'-DDT, pp'-DDD, pp'-DDE, HCB, α-HCH, γ-HCH, PAHs (sum of 16 according to EPA 610), PCBs (sum of congeners 28, 52, 101, 138, 153, 180), TBT; N, S, TOC, As*, B, Cd, Cr, Cu, Co, Hg, Ni, P, Pb, Sn, Zn
6 ecotoxicological test results with pore water and eluates (inhibition, %)	Daphnia (HED), algae (HEA), bacteria (HEB) each in sediment eluate and pore-water (HPD, HPA, HPB)
3 nematode test results with the whole sediment (inhibition, %; details in Traunspurger et al. 1997)	egg hatch, reproduction, growth
11 biochemical test results (reduced on the maximum number of tests used here; for details see Heininger, Tippmann 1995).	DHP=Dehydrogenase activity in pore-water DHgS= Dehydrogenase activity in sediment AP=Alanin- Aminopeptidase activity in pore-water AV=Alanin- Aminopeptidase, D1 value of dilution series AS=Alanin- Aminopeptidase activity in sediment βGP=β-Glucosidase activity in pore-water βGV=β-Glucosidase activity, D1 value of dilution series βGS=β-Glucosidase activity in sediment PR=Protease activity PRV=Protease activity, D1 value of dilution series DNAP=DNA- content in pore-water

* Heavy metals, boron (B(V)), arsenic and total phosphorus were determined in the fraction < 20 µm to improve the comparability of the results. This fraction was separated from the freeze-dried and non-milled samples by ultrasonic sieving (Ackermann 1980). Metals were analysed after microwave-assisted digestion with aqua regia at 180 °C in closed vessels by inductively coupled plasma optical emission spectroscopy, atomic fluorescence spectroscopy (mercury) and hydride atomic absorption spectroscopy (arsenic).

Table 6. Sample sites/river sections

Abbr.	Site	Abbr.	Site	Abbr.	Site
AE	Altarm Alte Elbe	HK	Havelkanal	SA	Saale, Buhnenfelder
AK	Hornhafen Aken, Elbe	HL	Hirschsteiner Lache, Elbe	SS	Seddinsee vor Insel
CB	Cermna Budisovka, Oder	HM	Hafen Meißen	TS	Tiefer See
CU	Cumlosen, Elbe	JO	Jocinkou, Odergebiet	UW	Unterwarnow, R6
DA	Damnatz, Elbe	KA	Kaczawa, Oder	VS	Veltener Stichkanal
DD	Dresden, Hafen Pieschen	LA	Lauffen	WA	Warthe, Swierkocin
DE	Dessau, Leopoldhafen	ME	Mescherin	WB	Wittenberge
DÖ	Dömitz, MEW	OD	Oder	WD	Widuchowa
EH	Eisenhüttenstadt, Oder	OK	Oder-Havelkanal	WE	Weiße Elster
EK	Eldenburger Kanal, MEW	OP	Mnichov, Opava, Oder	WO	Westoder
FL	Fahlberg List, Elbe	RA	Ratzdorf	WT	Wettin, Saale
FS	Finowschleuse, Oder	RB	Ramzovskybach, Oder	WU	Wusterwitz, EHK
GG	Glogau, Oder	RG	Rothenburg, Saale	WZ	Wittenberge, Zellwollehafen
HF	Hohensaathe-Friedrichsthaler Wasserstraße	RO	Rodleben, Elbe	ZB	Hohenwutzen, Zollbrücke
				ZD	Zehdenick, OHW

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