

# Salt pollution of the middle and lower sections of the river Werra (Germany) and its impact on benthic macroinvertebrates 

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#### Abstract

In two survey phases (2003 and 2008) organic, nutrient and salt contamination parameters have been investigated in the lower Werra in order to estimate the importance of these different kinds of pollution for the quality component of macroinvertebrates according to the European Water Framework Directive. The chemical and biological investigations have been carried out comparing a "reference" section without salt contamination with the salt contaminated section due to the potash mining industry from Vacha to Hannoversch Münden close to the mouth of the Werra. The results show that the drastic differences between the macroinvertebrate assemblages of the Werra upstream and downstream the salt contaminated sections are clearly caused by the salt load. The other kinds of chemical impacts are not responsible for the observed fundamental change within the composition of the benthic invertebrate assemblage. General degradation of stream morphology, indicated by macroinvertebrates, shows a good ecological status for the non-salt-contaminated part of the river and a bad status for the salt contaminated sites of the lower Werra.


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## Introduction

The River Werra has been polluted by waste waters with extremely high salt concentrations from the potash mining industry between the Thuringean sampling sites Vacha and Gerstungen for more than 100 years. This salt contamination has continued up to now downstream not only to the Hessian section of the Lower Werra but also to the river Weser until its mouth.

At the beginning of the 20th century the potash mining industry emitted salt waste water for the first time in 1901 into the Werra (Hübner 2007). Just 10 years later salt pollution caused the first problems for the drinking water supply of the city of Bremen. In 1913 a potash commission stated first threshold values for important salt water components. For the Werra at the sampling site Gerstungen the thresholds for chloride amounted to $842.5 \mathrm{mg} / \mathrm{l}$, for total hardness to $48.4^{\circ}$ German hardness (Gh), for the Weser at Bremen to $250 \mathrm{mg} / \mathrm{l}$ for chloride and to $20^{\circ} \mathrm{Gh}$ for total hardness. A first adjustment of these limits to rising amounts of salt effluents took place in 1924 with values of $1781 \mathrm{mg} / \mathrm{l}$ chloride and $63.1^{\circ}$ Gh at Gerstungen. For the river Weser at Bremen the limits were raised to $350 \mathrm{mg} / \mathrm{l}$ for chloride and $23^{\circ} \mathrm{Gh}$ for total hardness. A second adjustment fixed a threshold of $2500 \mathrm{mg} / \mathrm{l}$ for chloride

[^0]and $50^{\circ} \mathrm{Gh}$ for the total water hardness. For the third time the limit was adjusted for total hardness to $65^{\circ} \mathrm{Gh}$ in 1996. A fourth time in 1998/1999 the limits were fixed again to a higher level of $90^{\circ} \mathrm{Gh}$ which is permitted up to now.

Both the extremely high salt load as permitted and the specific salt composition, differing significantly from natural ionic composition of riverine or estuary waters, form a specific situation among the rivers not only in Germany but also in central Europe. The saline pollution leads to a permanent chemical impact on the aquatic coenoses.

The European Water Framework Directive (EU WFD 2000) classifies the ecological status of running waters into 5 quality classes: 1 = high, 2 = good, 3 = moderate, 4 = poor, 5 = bad (EU WFD 2000). It demands that natural bodies of water attain a good ecological status by 2015 and heavily modified water bodies a good ecological potential. The ecological status or potential is defined by multimetric index systems for the biotic quality components: fish, macrozoobenthos, macrophytes and phytobenthos (EU WFD 2000).

The main objective of this study is to analyse the specific pollution of the Werra and to work out the importance of salt contamination compared to other anthropogenic impacts. This will be done using the example of the benthic macroinvertebrate communities in the salt polluted section of the Werra, compared to non salt polluted reference sections of the River Werra and to a naturally salty stream, the Salzbach near Witzenhausen.


Fig. 1. Sampling sites at the River Werra.

In a first step, the macrozoobenthos will be evaluated using ecological metrics according to the German WFD methodology and the results will be related to the saline pollution. Further the benthos data as well as environmental parameters will be analysed applying a multivariate approach in order to estimate the relative importance of saline pollution, physical habitat, and nutrients for the community structure.

## Study sites

The study sites cover the natural geographic regions of the middle and lower section of the River Werra. Based on a German system of stream types (Pottgiesser and Sommerhäuser 2004, 2008) both
sections of the Werra have been classified as type 9.2, a large highland river with a large floodplain (over 300 m wide). All river sections under study belong to this type. The Salzbach is a small tributary of the River Werra near Witzenhausen which may be classified morphologically as a type 7 , a small coarse substrate dominated calcareous highland stream according to Pottgiesser and Sommerhäuser (2004). Its high natural salt concentration results from geological layers of zechstein in its catchment area. Because of its extremely high salinity the Salzbach stream chemically and biologically represents a special type which is not comparable to other "regular" streams of type 7.

Fig. 1 shows the position of the actual potash mines and the sampling sites of the sampling periods in 2003 and 2008.

Table 1
Sampling site parameters: site code, mean discharge, distance from source, mean slope of river bed, exposition to saline pollution, sampling frequency in 2003 and 2008 . W: River Werra; S: creek Salzbach.

| Site code | Sampling site | Distance from source [km] | Slope of river bed [\%] | Mean discharge [ $\mathrm{m}^{3} / \mathrm{s}$ ] | Exposition to salt pollution | Sampling frequency 2003 |  | Sampling frequency 2008 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | Chemistry | Biology | Chemistry | Biology |
| W01 | Breitungen | 101 | 0.85 | 21.1 | No |  |  | 2 | 1 |
| W02 | Barchfeld | 106 | 0.80 | 21.2 | No | 4 | 3 | 2 | 1 |
| W03 | Bad Salzungen | 113 | 0.20 | 21.5 | No |  |  | 1 |  |
| W04 | Vacha | 129 | 0.35 | 22.1 | Yes |  |  | 1 |  |
| W05 | Harnrode | 137 | 1.49 | 28.3 | Yes |  |  | 1 |  |
| W06 | Widdershausen | 145 | 0.35 | 29.1 | Yes |  |  | 1 |  |
| W07 | Gerstungen | 158 | 0.45 | 31.0 | Yes | 4 | 3 | 2 | 1 |
| W08 | Hörschel | 174 | 0.36 | 35.0 | Yes |  |  | 1 |  |
| W09 | Frieda | 232 | 0.69 | 41.4 | Yes | 6 | 3 | 1 |  |
| W10 | Niederhone | 243 | 0.65 | 43.2 | Yes | 6 | 3 | 1 |  |
| W11 | Albungen | 245 | 0.70 | 47.4 | Yes | 6 | 3 | 1 |  |
| W12 | Witzenhausen | 275 | 0.81 | 49.0 | Yes | 6 | 3 | 1 |  |
| W13 | Blickershausen | 282 | 0.37 | 50.4 | Yes | 6 | 3 | 2 | 1 |
| W14 | Hann. Münden | 297 | 0.34 | 51.0 | Yes |  |  | 1 |  |
| S01 | Wendershausen | 0,2 | 79.89 | 0.01 | No | 6 | 3 |  |  |

## Methods

## Sampling design

## Survey phase 1, 2003

In order to evaluate changes in the zoocoenosis of macroinvertebrates by the impact of salt effluents, the Werra was investigated in 2003 upstream from the first-known salt contamination area at Barchfeld (Middle Werra). This sampling site is located upstream from the waste water treatment plant (WWTP) at Bad Salzungen to avoid influences of domestic sewage.

The sampling site near Gerstungen (Middle Werra) is located in the section of the highest salt contamination in this river. The salt immissions originate not only from waste pipes but also from diffuse intrusions of salt waste water from the underground, caused by the rising salt enriched groundwater. This salty waste water has been anthropogenically pressed into the geological formation of the so called "Plattendolomit", a special form of zechstein, formerly believed to be a dense salt-retaining layer several hundred meters below the surface. Due to numerous tectonic fracture zones this layer became locally permeable for rising salt waste waters.

The following 4 sampling sites are located downstream in the section of the Lower Werra at Frieda, Niederhone, Albungen, Witzenhausen and Blickershausen.

In 2003 chemical surveys took place 4 times in the Werra at Barchfeld and Gerstungen, 6 times from Frieda to Blickershausen and in the Salzbach at Wendershausen. Chemical sampling data cover all seasonal aspects from spring to winter. At the same sites morphological and biological surveys were carried out three times in spring, summer and autumn to estimate the ecological effects on benthic invertebrates of the Lower and Middle Werra. All sections of the river Werra were investigated upstream from the confluence of tributaries in order to avoid their diluting influences on the Werra invertebrate coenoses. Additionally, a small stream naturally rich
in salt, the Salzbach, was investigated in order to compare a natural salt water stream with an anthropogenically salinised stream and the structure of their benthic invertebrate coenoses.

## Survey phase 2, 2008

In February and August 2008 a second phase of investigations was established in order to rate the actual impact of different pollutants of the lower Werra downstream. In this phase the impact of different pollutants (organic oxygen consuming waste water from domestic sources, plant nutrients and salt components) on the Werra downstream was studied. In February 11 sites were investigated by water chemistry analyses regarding the prevailing point sources of salt contamination as well as the areas of diffuse intrusions of salt into the Werra due to salt disposal into the underground into the "Plattendolomit". Two sites were established in the non-salt-polluted segment of the Werra between Breitungen and Barchfeld. The 9 other sites reveal the increasing salt-contamination and the following dilution by the tributaries of the Werra. In August chemical and biological studies were carried out at 4 sites, two in the non-salt-polluted (Breitungen and Barchfeld) and two in the salt contaminated section (Gerstungen and Bickershausen, see Fig. 1). Table 1 is a compilation of some general data characterising the investigated sampling sites and the sampling design of this study which were used for statistical analyses.

Chemical analyses covered water temperature, oxygen content and saturation, electrical conductivity, pH , orthophosphate-phosphorus, nitrate-, and ammonium-nitrogen, total nitrogen, hydrogen carbonate, total hardness, carbonate hardness, chloride, sulphate, sodium, potassium, calcium and magnesium. In 2008 biochemical oxygen demand in 5 days $\left(\mathrm{BOD}_{5}\right)$ and dissolved organic carbon (DOC) were analysed additionally. Temperature, oxygen, pH and electrical conductivity were measured in the field using measuring equipment by WTW "MultiLine P4".

Table 2
Mean percentage of substrate types at sampling sites in 2003 (according to Hübner 2007). phytal: plants; pelal: mud, silt; psammal: sand; akal: gravel; lithal: larger stones.

| Site | Litho-phytal | Xylal | Macropelal | Micropelal | Psammal | Akal | Mesolithal | Macrolithal |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Barchfeld | 5 | 5 | 10 | 2 | 28 | 8 | 22 | 20 |
| Gerstungen | 3 |  | 2 |  | 17 | 18 | 37 | 17 |
| Frieda |  |  | 2 | 13 | 63 |  | 18 | 3 |
| Niederhone |  |  | 2 | 12 | 13 |  | 20 | 50 |
| Albungen |  |  | 3 | 13 | 2 | 3 | 28 | 43 |
| Witzenhausen |  |  |  | 5 | 25 |  | 15 | 52 |
| Blickershausen |  |  |  |  | 10 | 5 | 43 | 42 |
| Salzbach Wendersh | 3 |  | 8 |  | 22 | 28 | 33 | 5 |



Fig. 2. Chemical data of the River Werra and the creek Salzbach in 2003.


Fig. 3. Biological data of the Werra and the creek Salzbach in 2003: (a) number of benthic invertebrate taxa, (b) macroinvertebrate diversity, (c) dominance values of 6 dominant taxa in the salinised Werra, (d) biological similarity of all sites, cluster analysis of site-pooled macrozoobenthos data. W: Werra; W02: Barchfeld; W07: Gerstungen; W09: Frieda; W010: Niederhone; W11: Albungen; W12: Witzenhausen; W13: Blickershausen; S01: Salzbach at Wendershausen.

All other chemical parameters were analysed according to German Standard Methods (DIN).

## Invertebrate sampling

For biological sampling of macroinvertebrates a handnet according to Braukmann (2000) was used, details see Hübner (2007). The collection was performed as multihabitat sampling of 20 m length. It covered $1 \mathrm{~m}^{2}$ in total and consisted of 10 subsamples of $0.1 \mathrm{~m}^{2}$ each. All substrate types were collected corresponding to their relative abundance in the section in question.

Organisms found were analysed alive and counted in the field. Unidentifiable taxa were sorted from the sample, preserved in $70 \%$ ethanol and identified in the laboratory, if possible to species level. Abundance was expressed in individual numbers per $\mathrm{m}^{2}$.

## Statistical data analysis

## Descriptive statistics

## Box and whisker plots of original abiotic variables

According to the German evaluation system "Perlodes" (Hering et al. 2004), 4 metrics were calculated from site-pooled macrozoobenthos data (German Fauna Index (Lorenz et al. 2004), \% metarhithral taxa (Moog 1995; Schmedtje and Colling 1996), \% EPT (Richardson 1928), Diversity (Shannon-Wiener, Margalef, Simpson)).

These metrics are aggregated to an index of "Overall degradation". This index is a compulsory part of the "Perlodes" system and is
mainly interpreted as an indicator of physical habitat deficit. However, it is sensitive to most other anthropogenic impacts too (Lorenz et al. 2004). This fact is crucial for identification of key stressors, followed by decisions on priority strategies in river restoration. Further analyses in this paper will focus on the benthos community structure.

Hierarchical Cluster analysis (UPGMA, Sneath and Sokal 1973) was used in Q-mode to visualise the faunistic similarity structure of the macrozoobenthos communities. For this analysis the seasonal samples were pooled by sampling sites to give an overall view of the community composition. Further the impact of seasonality on the community structure was assessed by ANOSIM (Clarke 1993) using unpooled data. Finally, partial Mantel tests (Mantel 1967; Legendre and Legendre 1998) on multiple environmental variable groups were carried out to rank the importance of longitudinal zonation, saline pollution, nutrient pollution/eutrophication and physical habitat structure for the benthic zoocoenoses. The selection and assignment of abiotic variables into these four groups is documented in the lower part of Table 6.

As the raw benthos data matrices contain few dominant taxa but many zeros and singleton records, the Steinhaus index was calculated from raw abundance data after $\log (x+1)$ transformation as recommended by Legendre and Legendre (1998). This index is asymmetric (double absences are not counted as indicators of proximity) and gives more weight to common presence of species. Similarity matrices based in the Steinhaus index were used in all the above described analyses. The environmental data matrices (independent variables and covariables) were normalised, followed by calculation of Euclidean distances.

Table 3
Biological assessment of the River Werra in 2003 by macroinvertebrates with the programme "Asterics/Perlodes (2008)" (according to Hering et al. 2004). E: Ephemeroptera, P: Plecoptera, T: Trichoptera; quality classes: 1: high, 2: good, 3: moderate, 5: bad; -: no adequate stream type existing (unpolluted zechstein creek).

| Sampling sites | German Fauna Index | \% Metarhithral taxa | EPT | Diversity |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Barchfeld | 2 | 3 | 3 | 1 |  |
| Gerstungen | 5 | 5 | 5 | 5 |  |
| Frieda | 5 | 5 | 5 | 5 | 5 |
| Niederhone | 5 | 5 | 5 | 5 | 4 |
| Albungen | 5 | 5 | 5 | 5 | 5 |
| Witzenhausen | 5 | 5 | 5 | 5 | 5 |
| Blickershausen | 5 | 5 | - | - | 5 |
| Salzbach Wendershausen | - | - |  | - | 5 |

The Mantel analysis is based on the assumption that correlation between (dis)similarity structure of samples in biotic space and of sampling sites in environmental space may be used as an indicator for causal relationship between the biota and the environmental parameters under study. If a strong statistical relation is detected, causality may be discussed using additional ecological and physiological knowledge. The partial Mantel test may be seen as the multivariate equivalent to the partial correlation coefficient. The degree of relationship between two distance matrices is calculated after the effect of a third matrix has been removed, i.e. the effect of one single subsets of variables can be separated by partialling out the effect of the others.

Statistical analyses were conducted using Statistica, version 6.0 (descriptive statistics), MVSP 3.1 (clustering) and Brodgar 2.5.1 (ANOSIM, partial Mantel tests).

## Results

## Survey phase 2003

In 2003 besides morphological parameters like substrate distribution of the river bed chemical parameters showing nutrient and salinisation characteristics of the Werra and the Salzbach were studied.

## Substrates

All sites of the Werra were sampled close to river edge. They showed rather similar substrate conditions with prevailing coarse substrates (macro-, mesolithal, akal) which are compiled in Table 2.

## Chemistry

Fig. 2 is a compilation of several chemical parameters which were regarded important for ecological characterisation and assessment of the River Werra and, for comparison, a small naturally salty stream, the Salzbach.

## Nutrients

The investigated nutrient parameters total nitrogen and ortho phosphate phosphorous showed similar ranges at all Werra sites (Fig. 2a and b). Median values of total $N$ lay between 3.8 an $4.8 \mathrm{mg} / \mathrm{l}$. In the Thuringean section at Barchfeld and Gerstungen. Phosphorous values were higher in range and median (median between 0.17 and $0.19 \mathrm{mg} / \mathrm{l}$ ) than in the downstream Hessian sections (median between 0.1 and $0.12 \mathrm{mg} / \mathrm{l} \mathrm{P}$ ).

## Salinisation parameters

For the characterisation of salt load the most important components of the marine salt deposits of the geological zechstein formations like sodium, potassium, calcium, magnesium, chloride and sulphate were analysed. Magnesium and potassium are extracted by the potassium industries and processed further as components of agricultural fertiliser. The other salts are dumped as waste water, either directly into the Werra, or recharged into the
underground (dolomite-layer), or as solid waste on salt piles. The salt from the piles are washed out into the Werra by precipitation.

In contrast to nutrients except from carbonate hardness all salinisation parameters (electrical conductivity, carbonate hardness, chloride, sodium, calcium, magnesium and sulphate) showed clear differences between the two uppermost sites in the non salinised sections at Barchfeld and the salinised site at Gerstungen and all other downstream salinised Werra sites.

In sharp contrast to the Werra sites especially magnesium and potassium values are much lower in the naturally salty Salzbach. At this site with the highest electrical conductivity and sodium concentration and with the second highest chloride concentration of all sites, very low magnesium (mean $31.2 \mathrm{mg} / \mathrm{l}$ ) and potassium (mean $11.9 \mathrm{mg} / \mathrm{l}$ ) concentrations were measured which were much more comparable to the non salinised Werra section (Mg mean $13.8 \mathrm{mg} / \mathrm{l}$, $K$ mean $4.2 \mathrm{mg} / \mathrm{l}$ at Barchfeld) but to the salinised sections of the Werra (Fig. 2 f and g).

The median magnesium concentration at Barchfeld in 2003 was 15 times lower, the median potassium concentration even 35 times lower than at the site at Gerstungen.

## Benthic invertebrates

Benthic macroinvertebrate assemblies changed drastically between the non salinised Werra section and the salinised one. This is illustrated by the number of invertebrate taxa (Fig. 3a), different diversity indices (Fig. 3b) and the most dominant taxa (Fig. 3b).

Some results of the assessment of benthic invertebrate assemblies carried out using the programme "Asterics/Perlodes" developed for bioindication by (benthic invertebrates in Germany according to WFD (Hering et al. 2004) are compiled in Table 3. This table shows typical aspects of the metric "general degradation" which is designed as a biological feature indicating mainly biocenotically relevant morphological degradations.

The metric "general degradation" is derived from parameters like "German Fauna Index", "\% Metarhithral taxa", "EPT" (proportion of ephemeroptera, plecoptera and trichoptera as important parts of the total invertebrate fauna) and diversity aspects.

In the over-all aspect "general degradation" the sampling site at Gerstungen appears in a good quality status (class 2), the other two sites, clearly due to the salt impact, are classified bad (class 5). In detail also the metrices "German Fauna Index" and "diversity" show class 2 (good) for the non-salt-contaminated sites, and 5 (bad) for the contaminated ones. The metrices "percentage of metarhithral taxa" and "proportion of EPT" (ephemeroptera, plecoptera, trichoptera) indicate also class 1 (high status) for Breitungen, class 3 (good) for Gerstungen and class 5 for the salt polluted sections Gerstungen and also Blickershausen near the mouth of the Werra.

## Survey phase 2008

## Chemistry

Additional to nutrient and salinisation parameters in 2008 BOD and DOC were measured in order to obtain an impression of the


Fig. 4. Chemical data of the river Werra in 2008, (a-f): February, (g and h): August.
actual organic impacts from domestic waste water regarding the question if the fact that less than $50 \%$ of Thuringian inhabitants in the Werra catchment area are connected to WWTP leads to an impact on benthic invertebrates comparable to salinisation parameters. In Fig. 4 essential chemical parameters are compiled.

## Organic pollution

The degree of organic pollution is indicated by $\mathrm{BOD}_{5}$ as well as by DOC (Fig. 4a). Also ammonium-nitrogen (Fig. 4b) indicates organic pollution. In order to characterise organic pollution, four sites (Breitungen, Barchfeld, Gerstung and Blickershausen) were sampled in August 2008 during the period of pessimal water quality conditions regarding the oxygen conditions in rivers in order to find out the maximal impact of organic pollution on benthic invertebrates. Except Blickershausen at all other sites BOD values clearly lay below the orientation value of LAWA (2007) of $6 \mathrm{mg} / \mathrm{l}$ as a threshold value
for the transition from good to moderate quality for large mountain rivers (type 9.2) (Fig. 4a). Despite the lower degree of connection to domestic waste water treatment plants of townships in Thuringia ( $50 \%$ ), compared to Hessia (above $90 \%$ ), $\mathrm{BOD}_{5}$ as well as DOC values were lower in Thuringian river sections than in Hessian ones.

Ammonium concentrations as an indicator for insufficiently treated waste water were well below the orientation threshold value of $0.3 \mathrm{mg} / \mathrm{l} \mathrm{NH}_{4}{ }^{+}-\mathrm{N}$ for the transition from good to moderate quality according to LAWA (2007) (Fig. 4b).

## Nutrients

As in 2003 nitrate-N and orthophosphate-P were also measured in 2008. In February, during a slight flood period, nitrate-N values were similar at all stations (Fig. 4c). The maximal value reached $4.2 \mathrm{mg} / \mathrm{l}$ at Blickershausen. In August Nitrate-N values lay between 3.0 and $3.3 \mathrm{mg} / \mathrm{l}$.


Fig. 5. Biological data of the river Werra in 2008: (a) number of benthic invertebrate taxa, (b) macroinvertebrate diversity, (c) dominance values of 6 most dominant taxa in the salinised Werra, (d) Saprobic index of 6 sites.

Downstream from Gerstungen orthophosphate values from February samples lay above the orientation value of $0.07 \mathrm{mg} / \mathrm{l}$ according to LAWA (2007) (Fig. 4d). The values in Thuringia were lower than in Hessen despite the low degree of waste water treatment. In August 2008 phosphate-P lay between $0.15 \mathrm{mg} / \mathrm{l}$ (Blickershausen, Hessen) and $0.26 \mathrm{mg} / \mathrm{l}$ (Barchfeld, Thuringia). As in the case of organic load also in the nutrient load no evident differences between the sampling sites could be observed either.

## Salinisation parameters

In 2008 the same salinisation parameters were analysed as in 2003.

## Electrical conductivity

In the middle Werra between Barchfeld and Gerstungen the electrical conductivity (Fig. 4c) increases drastically due to the direct discharge of salt waste water from the mining industry in the area of Hattorf. Additionally the diffuse impact of upwelling saltwater being pressed out of the dolomite layer by the waste salt brine which had been sunk into this geological layer affects the water quality of the river.

Contrary to the organic and nutrient parameters the investigation of the salt components in 2008 along the sampling sites displayed a continuous increase of the electrical conductivity from Breitungen with about $460 \mu \mathrm{~S} / \mathrm{cm}$ rising at Vacha with the first salt impacts up to the maximum of $7240 \mu \mathrm{~S} / \mathrm{cm}$ at Gerstungen. Tributaries dilute the electrical conductivity down to $2400 \mu \mathrm{~S} / \mathrm{cm}$ at the end of the Werra in Hannoversch Münden.

## Chloride, total hardness, magnesium, potassium

At Barchfeld the Werra is a typical carbonate river with naturally rather high values of magnesium and total hardness caused by geological conditions of the catchment area containing dolomite
formations. Here the chloride concentration was $25 \mathrm{mg} / \mathrm{l}$. At Gerstungen $2037 \mathrm{mg} / \mathrm{l}$ were measured, a value which was 81 times higher than at Barchfeld. The official "legal" threshold of $2.500 \mathrm{mg} / \mathrm{l}$ chloride in the Werra which exists since 1942 is about 12.5 times higher than the orientation value of $200 \mathrm{mg} / \mathrm{l}$ between a good a moderate ecological status for running waters according to LAWA (2007). Similarly drastic differences were also found in total hardness (mainly due to wasted magnesium), magnesium and potassium concentrations (Fig. 4 f and h ).

Carbonate hardness (mainly determined by calcium bicarbonate) stays nearly stable along the river, total hardness (dominated by magnesium discharged into the river) increases abruptly downstream from the first salt influent at Vacha reaching a maximum at Gerstungen.

It is obvious that in contrast to the organic and nutrient load change in chemism of the Werra is clearly caused by all named salt components. The natural relation between concentrations of several ions especially between calcium, magnesium and potassium typical for natural rivers, e.g. at Breitungen and Barchfeld above the first salt influence, is dramatically inverted in the salty section of the river beginning at Vacha.

## Benthic invertebrates

Fig. 5 gives an overview of some aspects of benthic macroinvertebrates found in August 2008 in non salinised and salinised sections of the river Werra.

Like in 2003 a considerable breakdown in taxa number and diversity was observed from the non salinised sections at Breitungen and Barchfeld downstream to the salinised section at Gerstungen. At Gerstungen just two taxa (Gammarus tigrinus and Potamopyrgus antipodarum reached $99.8 \%$ of the total number of all specimen over all taxa (Fig. 5c, Table 8 in Appendix).

Table 4
Biological assessment of the River Werra in 2008 by macroinvertebrates with the programme "Asterics/Perlodes (2008)" (according to Hering et al. 2004). E: Ephemeroptera, P: Plecoptera, T: Trichoptera; quality classes: 1: high, 2: good, 3: moderate, 5: bad.

| Sampling sites | German Fauna Index | \% Metarhithral taxa | EPT | Diversity |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Breitungen | 2 | 1 | 1 | 2 | General degradation |
| Barchfeld | 2 | 3 | 3 | 2 |  |
| Gerstungen | 5 | 5 | 5 | 5 | 2 |
| Blickershausen | 5 | 5 | 5 | 5 | 5 |

Table 5
Results of ANOSIM analysis.

| ANOSIM 1-way permutation test: |  | 9999 of 66512137 total permutations, global statistic $=0.179, p=0.012^{*}$, nMDS stress $=0.0099$ |  |
| :--- | :--- | :--- | :--- |
| Group 1 | Group 2 | Max. permutations | Statistic |
| Spring | Summer | 1716 | 0.310 |
| Spring | Autumn | 1716 | 0.235 |
| Summer | Autumn | 1716 | 0.071 |

Levels of significance: ${ }^{*} 0.05 \geq p>0.01,{ }^{* *} 0.01 \geq p>0.001,{ }^{* * *} p \leq 0.001$.

Regarding organic pollution by means of saprobic indicators of macroinvertebrates, Breitungen reveals the lowest degree of pollution with a good quality status. The other sites are in a moderate state. The differences between all sites are rather small which corresponds well to the chemical data of organic and nutrient loads.

The assessment of biologically indicated general (mainly morphologically induced) degradation by "Asterics/Perlodes" according to WFD (Table 4) results for 2008 are very similar to those for the year 2003 (see Table 3).

Again benthic invertebrates show a good ecological quality for the metric "general degradation" for the non salinised Werra section and, in all aspects, a bad quality for all sites within the salinised Werra section. For the naturally salty creek Salzbach no natural reference type exists, because this stream type is very rare in Germany. Therefore using "Asterics/Perlodes" no result could be obtained. In this small stream neither morphological nor chemical pollutants could be observed. So this stream might be regarded as a reference stream for this very special stream type and give an idea of natural concentrations of magnesium or potassium at a high level of chloride.

## Statistical analysis

Cluster analysis of site-pooled macrozoobenthos data from 2003 (Fig. 3d) reveal a group formed by the salt polluted sites W07 to W13. This group is well separated from the unpolluted site W01 and from the natural saline site S 01 , although the latter has a magnitude of chloride concentration and conductivity similar to the polluted Werra sites. Within the group of polluted sites, W09, W10, W12 and W13 form a compact sub-cluster indicating a vast loss of species diversity in the most polluted river section.

Macrozoobenthos data were sampled in 2003 during three seasons (spring, summer and autumn). ANOSIM of non-pooled data indicate that at least the spring samples differ considerably from the other two seasons (Table 5). Thus it seems reasonable to use the sampling season as stratifying nominal variable within permu-
tational procedures in the Mantel tests. The nMDS coupled to the ANOSIM procedure gives a good two-dimensional representation of the original similarity relationships within the resemblance matrix (stress $=0.0099$ ).

Design and results of partial Mantel tests are presented in Table 6. As the river section between W02 and W13 covers a distance of about 176 km , first the importance of longitudinal zonation was tested. Here only a slight relevance was found. However, longitudinal variables were used as covariables within all further tests to fix the results for effects due to longitudinal zonation of the river.

The four variable groups used as explanatory variables in the partial Mantel tests No. 1-4 are relevant for the community structure in the following order: salinity $>$ habitat structure $>$ longitudinal zonation $>$ nutrients and eutrophication. The last-mentioned impact seems to have nearly no relevance under the paramount anthropogenic salinisation.

## Discussion

In this chapter the ecological effects of the chemical load of the river Werra caused by the potash mining industry mentioned above on the quality component macrozoobenthos of the EU-WFD will be discussed. Caused by the far reaching changes of the hydrochemical conditions as a consequence from the impact of salt wastes, a distinct change in the aquatic zoocoenosis takes place between the non-salt-influenced upper section of the Werra and the salt contaminated lower Werra below Hattorf.

Reasons for this change may generally be: salt, plant nutrient from agriculture and domestic waste water, organic pollution and hydromorphological deficits.

From the chemical results presented in the former chapter it could be concluded that salt pollution is the most important factor responsible for the biological changes. This hypothesis is clearly supported by the outcome of the partial Mantel tests.

Table 6
Design and results of partial Mantel tests.

| Partial Mantel test No. | Matrix of explanatory variables | Matrix of covariables | $p$ | Test statistic, $r_{\mathrm{M}}$ |
| :--- | :--- | :--- | ---: | ---: |
| 1 | Longitudinal zonation | Habitat structure, nutrients and eutrophication, salinity | 0.0770 | 0.1497 |
| 2 | Habitat structure | Longitudinal zonation, nutrients and eutrophication, salinity | 0.4436 | $0.0050^{* *}$ |
| 3 | Nutrients and eutrophication | Longitudinal zonation, habitat structure, salinity | 0.7264 |  |
| 4 | Salinity | Longitudinal zonation, habitat structure, nutrients and eutrophication | 0.0379 | 0.7759 |

Levels of significance: ${ }^{*} 0.05 \geq p>0.01,{ }^{* *} 0.01 \geq p>0.001$, ${ }^{* * *} p \leq 0.001$.
Season was used as blocking variable for permutation in all tests.
Longitudinal zonation variables: distance to source $[\mathrm{km}]$, mean discharge [ $\left.\mathrm{m}^{3} / \mathrm{s}\right]$, channel slope $[\mathrm{m} / \mathrm{m}]$, water temperature $\left[{ }^{\circ} \mathrm{C}\right]$.
Habitat structure variables: phytal-m, phytal-e, lithophytal, xylal, macropelal, micropelal, argillal, psammal, akal, mesolithal, macrolithal [\% coverage of channel bottom] Nutrients and eutrophication variables: N tot, o- $\mathrm{PO}_{4}-\mathrm{P}[\mathrm{mg} / \mathrm{l}], \mathrm{pH}$, oxygen saturation $\left[\mathrm{abs}\left(\mathrm{O}_{2} \%-100 \%\right)\right]$.
Salinity variables: $\mathrm{Cl}^{-}, \mathrm{SO}_{4}{ }^{2-}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}, \mathrm{Mg}^{2+}[\mathrm{mg} / \mathrm{l}]$, carbonate hardness $[\mathrm{mmol} / \mathrm{l}]$.

Despite a comparable organic pollution and similar nutrient contents the zoocoenosis of the section at Breitungen and Barchfeld is totally different from the one at Gerstungen. The Werra at the sites at Breitungen and Barchfeld for instance may be characterised as a moderately polluted larger carbonate river of the central low mountain range being inhabited by a species-rich fauna consisting of characteristic benthic groups like mollusca, gammaridae, ephemeroptera, plecoptera, trichoptera, coleoptera und diptera in relatively balanced proportions.

The investigations of the invertebrate fauna of the Werra and its main tributearies carried out by Hübner (2002, 2005, 2007), Braukmann and Hübner (2003), Hübner and Braukmann (2005a,b, 2006) and in 2008 by Braukmann and collaborators (published here) reveal the fundamental faunistic change between Barchfeld and Gerstungen.

At the site at Barchfeld 14 mostly river-specific, partly very rare red-list-species, were found, e.g. Brachyptera braueri, numerous larval specimen of the caddisfly Brachycentrus subnubilus and abundant specimen of the groundbug Aphelocheirus aestivalis. At Barchfeld altogether 74 different macroinvertebrate taxa were found.

In a sharp contrast to this finding the benthic invertebrate coenosis of the salt contaminated lower Werra at Gerstungen with the highest salt concentration is extremely poor in species and nearly completely inhabited by alien species. It is mainly dominated by two neozoic salt-tolerant species Gammarus tigrinus which was introduced into the Werra by Schmitz in 1957 (Schmitz 1960) and Potamopyrgus antipodarum, an invasive neozoon from New Zealand. All other species or taxa were found just in single specimens usually downstream from the mouth of freshwater tributaries. This observation is strongly related to the seasonality of the benthos data, in detail to the deviant community pattern in spring. During snow melt the Werra as well as the tributaries enhance flow rates and-at least temporarily-intensified transport of particulate matter. The salt load in the Werra is more diluted than in later seasons. Specimens of native species, drifting from unpolluted upstream river sections and tributaries into the salt polluted Werra section, have the chance to outlast there for days or weeks. However, one may assume that the ostensibly successful colonisers are not able yet to complete here their reproductive cycle. They seem to establish no persistent populations and disappear throughout the following months.

In the area with the highest salt concentration nearly all typical benthic groups named above disappeared.

At Gerstungen just 13 Taxa were observed ( $18 \%$ of the site at Barchfeld). Only 9 out of 78 taxa in total match at both sampling sites (Barchfeld and Gerstungen). In terms of the quantitative Steinhaus index, the similarity between these two sites is only $8.9 \%$.

The sampling of macroinvertebrates carried out during pessimal quality conditions in August 2008 (low water level, high temperatures, high fluctuation in oxygen concentration etc.) resulted in 34 taxa at Breitungen and 42 at Barchfeld.

The total list of taxa (see Table 8, Appendix) gives an overview of the invertebrate assemblages of all sites of survey phase 2 in 2008. At Barchfeld there have been very little changes in the species stock between 2003 and 2008. The same species were dominant in both years. Again a large individual number of Aphelocheirus aestivalis and Brachycentrus subnubilus was found. Also both characteristic river gammarids Gammarus pulex and Gammarus roeselii occurred in high numbers.

A considerable drop in taxa number from 42 to just 4 took place at Gerstungen, the site with the highest salt concentration. The saltwater gammarid Gammarus tigrinus was absolutely dominant (98.4\% dominance). Other taxa were: Potamopyrgus antipodarum (1.4\%), Dendrocoelum lacteum ( $0.1 \%$ ) and Oulimnius rivularis ( 1 specimen, 0.03\%).

Table 7
Reference conditions of the lower section of the River Werra regarding physicochemical aspects of water quality (presumed potential natural conditions) (from Hübner 2007, modified).

| Parameter | Reference condition |
| :--- | :--- |
| Chloride | $<100 \mathrm{mg} / \mathrm{l}$ |
| Sulphate | Clearly below $100 \mathrm{mg} / \mathrm{l}$ |
| Potassium | $\leq 5 \mathrm{mg} / \mathrm{l}$ |
| Calcium | $60-80 \mathrm{mg} / \mathrm{l}$ |
| Magnesium | $10-15 \mathrm{mg} / \mathrm{l}$ |
| Total hardness | $2.0-2.5 \mathrm{mmol} / \mathrm{l}\left(11-14^{\circ} \mathrm{Gh}\right)$ |
| Water temperature (summer) | $<19$ to $<20^{\circ} \mathrm{C}$ |
| Saprobic index | 1.65 |
| Turbidity | Low |

Our comparative ecological investigations of the non-saltcontaminated Werra and the heavily polluted section as well as its tributaries (Hübner 2002, 2005, 2007; Braukmann and Hübner 2003; Hübner and Braukmann 2005a,b, 2006) prove the fundamental change in the benthic community of macroinvertebrates. The findings of the statistical analyses of the data collected in 2003 can be assumed to be valid until now. A comparison of multimetric evaluation results for the sampling sites near Barchfeld, Gerstungen and Blickershausen from 2003 (Table 3) and 2008 (Table 4) reveals that the degradation of the benthic community within the salt polluted Werra section is as severe as some years ago, even though the metric "diversity" of the unpolluted site at Barchfeld has slightly improved.

## Importance of the creek Salzbach with its natural salt composition

The Salzbach stream is a typical example of low magnesium and potassium concentrations) in naturally salty running waters where parts of indigenous species like Gammarus pulex can survive even under extreme sodium chloride conditions comparable to the heavily salinised Werra section at Gerstungen.

## Leitbild (reference conditions) for the River Werra

Based on his investigations, Hübner (2007) has reconstructed reference conditions (the "leitbild") for the river Werra in its potentially non-salt-polluted lower sections, based on studies of historical data as well as recent research programmes carried out at the Department of Water Ecology and Management of the University of Kassel. These reference conditions represent the preindustrial status of the river's chemistry and biology without salt pollution by the potash mining industry. Hence they provide a set of target values for the future restoration of the water body. These reference conditions are summarised in Table 7.

According to this "leitbild" the River Werra should be naturally a normal freshwater river of a carbonate type with an electrical conductivity of about $600 \mu \mathrm{~S} / \mathrm{cm}$, chloride concentration of clearly less than $100 \mathrm{mg} / 1$ and natural potassium values less than $5 \mathrm{mg} / \mathrm{l}$. These conditions differ drastically from the actual chemical situation and lead to severe damages of aquatic life in this salt polluted river.

As a result of the discharge of salt waste water the natural chemical character of the Werra changes from a typical freshwater river having a salinity of $0.4 \%$ to a miohaline (Remane 1971) river with brackish water of $4.6 \%$ salinity, containing unnatural salt composition and an extremely high chemically unbalanced total hardness of $70^{\circ} \mathrm{Gh}(12.5 \mathrm{mmol} / \mathrm{l})$. The salt concentration increases, and this is caused by direct discharge and indirect diffuse salt ingress in the area of the grouting (Verpressung) between Hattorf and Gerstungen by 11.5 -fold. Potassium and magnesium concentrations are extremely overrated due to the insufficient separation from the waste salt components compared to the natural situation in the Werra.

The continuing high salt load prevents a permanent recolonisation by typical sensitive freshwater species. Above all the toxical impact of potassium on freshwater invertebrates like gammarids has been proved sufficiently in literature for a long time (Albrecht 1954; Schmitz et al. 1967; Koop 1994). Regarding water management aspects, it is necessary to reduce not only the chloride concentration of the Werra from $2500 \mathrm{mg} / \mathrm{l}$ to less than $1000 \mathrm{mg} / \mathrm{l}$ but especially the concentrations of potassium from currently more than $150 \mathrm{mg} / \mathrm{l}$ by a factor of 10 and magnesium from about $220 \mathrm{mg} / \mathrm{l}$ by a factor of 15 to at least $15 \mathrm{mg} / \mathrm{l}$ each. Further utilisation of the actual legal limits by the potash mining industry obviously impedes a considerable improvement of the ecological status of the Werra. This obligatory objective is demanded by the European WFD. It can be achieved only by a decrease of the overall salt load in combination with a significant reduction of the physiologically harmful
potassium and magnesium concentrations. Thus the actual legal limits for chloride and total hardness have to be revised.

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## Appendix A.

Table 8

Table 8
Taxa list of four sampling sites of the River Werra, August 2008, Ind $/ \mathrm{m}^{2}$.

| Taxaname | Breitungen | Barchfeld | Gerstungen | Blickershausen |
| :---: | :---: | :---: | :---: | :---: |
| Baetis fuscatus | 700 | 7 |  |  |
| Simulium sp. | 200 | 10 |  |  |
| Baetis vardarensis | 200 | 3 |  |  |
| Serratella ignita | 55 | 58 |  |  |
| Elmis maugetii | 35 | 45 |  |  |
| Leuctra fusca-Gr. | 30 | 25 |  |  |
| Hydropsyche incognita | 21 | 6 |  | 49 |
| Aphelocheirus aestivalis | 10 | 210 |  |  |
| Dugesia gonocephala | 10 | 15 |  | 7 |
| Hydroptila sp. | 10 | 5 |  | 15 |
| Lasiocephala basalis | 10 | 5 |  |  |
| Sphaerium corneum | 9 | 20 |  |  |
| Rhyacophila nubila-Gr. | 9 | 9 |  |  |
| Orthocladiinae | 8 |  |  |  |
| Atherix ibis | 6 | 5 |  | 5 |
| Brachycentrus subnubilus | 5 | 125 |  |  |
| Stylodrilus heringianus | 5 | 2 |  |  |
| Gammarus roeselii | 4 | 60 |  |  |
| Simulium argenteostriatum | 4 | 4 |  |  |
| Ancylus fluviatilis | 4 | 1 |  |  |
| Gammarus pulex | 3 | 120 |  |  |
| Heptagenia sulphurea | 3 | 10 |  |  |
| Piscicola geometra | 3 | 2 |  |  |
| Perlodes sp. | 3 |  |  |  |
| Wilhelmia-Gr. | 2 | 2 |  |  |
| Lumbriculidae | 2 | 1 |  | 10 |
| Radix balthica | 1 | 2 |  | 3 |
| Erpobdella octoculata | 1 | 2 |  |  |
| Brillia cf. longifurca | 1 | 1 |  |  |
| Eiseniella tetraedra | 1 | 1 |  |  |
| Helobdella stagnalis | 1 | 1 |  |  |
| Tanypodinae | 1 | 1 |  |  |
| Brychius elevatus | 1 |  |  |  |
| Goeridae | 1 |  |  |  |
| Barbatula barbatula | 1 |  |  |  |
| Asellus aquaticus |  | 20 |  |  |
| Bithynia tentaculata |  | 10 |  |  |
| Potamophylax rotundipennis |  | 7 |  |  |
| Dendrocoelum lacteum |  | 3 | 5 | 3 |
| Prodiamesa olivacea |  | 1 |  | 24 |
| Ceraclea albimacula-alboguttata-Gr. |  | 1 |  |  |
| Chironomus sp. |  | 1 |  |  |
| Colymbetes fuscus |  | 1 |  |  |
| Ecdyonurus torrentis |  | 1 |  |  |
| Ephemera danica |  | 1 |  |  |
| Halesus tesselatus |  | 1 |  |  |
| Plectrocnemia sp. |  | 1 |  |  |
| Gasteroceus aculeatus |  | 1 |  |  |
| Gammarus tigrinus |  |  | 3500 | 2000 |
| Potamopyrgus antipodarum |  |  | 50 | 1000 |
| Dicrotendipes sp. |  |  |  | 95 |
| Proasellus coxalis |  |  |  | 65 |
| Hydropsyche contubernalis |  |  |  | 14 |

Table 8(Continued)

| Taxaname | Breitungen | Barchfeld |
| :--- | :--- | :--- |
| Tubificidae |  |  |
| Limnius volckmari |  |  |
| Anacaena bipustulata |  |  |
| Chironomus plumosus-Gr. |  |  |
| Dicrotendipes notatus |  |  |
| Nepa cinerea |  |  |
| Oulimnius cf. rivularis |  | 1 |

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