Water-Quality Data-Assessment of Long-Term Time Trends, Weser River Basin, Germany – A Case Study

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ABSTRACT

The 1979-2008 period of record for the four Weser River basin monitoring sites was used for demonstrating several data-assessment techniques and evaluation of time trends. Statistical and graphical analyses were conducted, and anomalous or possible erroneous data values were highlighted, modified, and/or deleted as a key part of the quality-assurance/quality-control (QA/QC) process. An overview of results is as follows:

- For major salt-ions as a function of specific conductance (SC), bivariate plots were made. Relative good regression functions resulted for magnesium (Mg), sulphate (SO_4), and especially for chloride (Cl). Such functions can be used to fill in missing data values or gaps in the record.
- Time series plots indicated no time trends in streamflows but rather distinct periods of anthropogenic impacts and post-remediation trends for many of the variables. Seasonality was apparent for water temperature, dissolved-oxygen concentrations, and SC (for this variable, especially in the early part of the period of record (POR)).
- Nitrate-N exhibited a slight downward time trend, especially during the recent period.
- During the data assessment, several anomalous data values and other errors in data entry were apparent. These were changed or otherwise noted in the modified dataset file for further consideration.

The long-term time trends and bivariate relationships provide useful information regarding this monitoring program as well as benefits attained through mining-related remedial actions, especially in the upper part of the basin, changes in agricultural-fertilizer application, and wastewater-treatment plant improvements. Decreased concentrations (hence, loads) of major ions are primarily a result of control of salt point sources and of nitrate as well as a result of controls of application of fertilizers to agricultural lands.

It is recommended that similar data-assessment methods be applied for other monitoring sites having long-term water-quality data. Additional information will be discussed in the presentation, extracted from the river-basin management plan prepared for the Weser River Basin Commission, in accordance with the EU Water Framework Directive (WFD).

INTRODUCTION AND BACKGROUND

As part of ongoing applied research at the Friedrich-Schiller-Universität Jena’s (FSU-Jena’s) Department of Geoinformatics, Hydrology, and Modelling, this water-quality data assessment for the Weser River basin was conducted in order to evaluate the information content of selected available long-term monitoring data.

The Weser River basin has a total catchment area of 49,000 km^2 (Figure 1). The primary land uses include agricultural lands and grasslands. The catchment's total population is 9.34 million inhabitants (FGG-Weser, 2008; 2009). The principal water-quality issue ('pressure') involves diffuse pollution from agriculture. In addition, historically, salt discharges were made into this catchment from adjacent areas, contributing to major ionic loads and higher concentrations historically. In conducting a data search on the Flussgebietsgemeinschaft Weser *(undated)* (www.fgg-weser.de) website, it was found that long-term water-quality data were tabulated in a series of annual data files for the period-of-record (POR) 1979-through-2008. For this case study, selected data for four of the 15 long-term monitoring sites were used to demonstrate various data-assessment methods as well as to evaluate both natural and anthropogenic effects over this 30-year period.

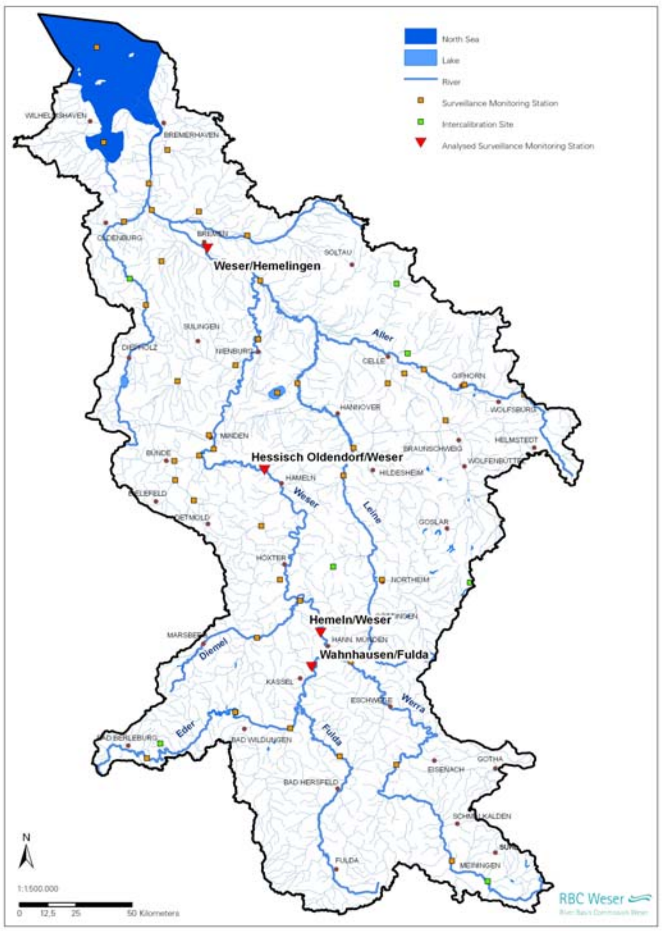


Figure 1 – Weser River Basin, Showing Locations of Water-Quality Monitoring Sites

Approaches

Key water-quality monitoring sites throughout the Weser River basin are indicated on Figure 1. For this case study, four monitoring sites were selected to demonstrate several data-analysis procedures and QA/QC protocols. The period of record at each site was used for this purpose. During the course of this assessment, statistical and graphical analyses were conducted, and anomalous or possible erroneous data values were highlighted, modified, and/or deleted as a key part of the QA/QC process.

An important role of any data assessment is to derive information from the basic data (Ward, 2002). Data without analysis and evaluation have minimum value; only when data are subject to graphical and statistical analyses and/or inputs into empirical or process models or summarized in other forms for interpretative-report documents, is value added for specific uses of the data.

Relatively simplistic but useful data-assessments tools applied to this case study consist of graphical analyses (bivariate-regression or time-series plots), and period-of-record or sub-period statistics. These methods are patterned after previously-developed methods (Steele, 1972; 1973) and applications (Steele and others, 1974; Steele, 1980; Bongartz and others, 2007). The overall objective in this application of these tools is to derive information from the basic data, in terms of long-term time variability and changes in streamflows and several water-quality variables and in assessing conditions responding to various impacts occurring in this river basin, either through natural processes or various anthropological impacts (human-related economic activities). For the statistical summary, nondetects were set to ½ the detection limit. This data assessment demonstrates preliminary analyses and findings and is not intended to be all-inclusive. Additional, more-detailed and really-extensive, analyses are recommended.

RESULTS

A variety of river-basin conditions and human-related activities affect the water-quality conditions at the monitoring sites selected for this case study. Examples include the extensive agricultural areas throughout the basin and industrial and mining impacts. These latter effects were in particular noted for pre-unification times when effluents from such activities adversely impacted water quality of this stream. Descriptions of causal effects are aided upon the cited literature (Cherlet, 2007) as well as understanding of the basin's conditions provided by this paper's second author.

Graphical analyses (Weser-Hemelingen as an example)

Figure 2a exhibits the commonly observed inverse relationship between specific conductance (SC) and streamflow. SC variability is significantly greater at the low end of the range of streamflows. As will be noted later, most of the higher SC values occurred prior to 1991, when high-salinity effluents were curtained in the river basin.

Figure 2a -- Weser-Hemelingen, Specific Conductance vs Streamflow

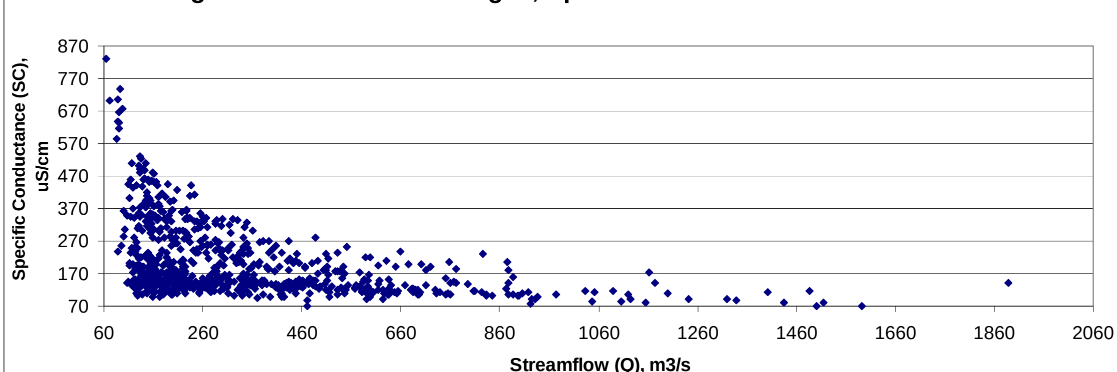


Figure 2b gives the stream time-series, using values associated with biweekly sampling surveys over the period of record. Seasonal and year-to-year variations are apparent; however, and this and other monitoring sites in this case study, no streamflow time trend was apparent from the various data series.

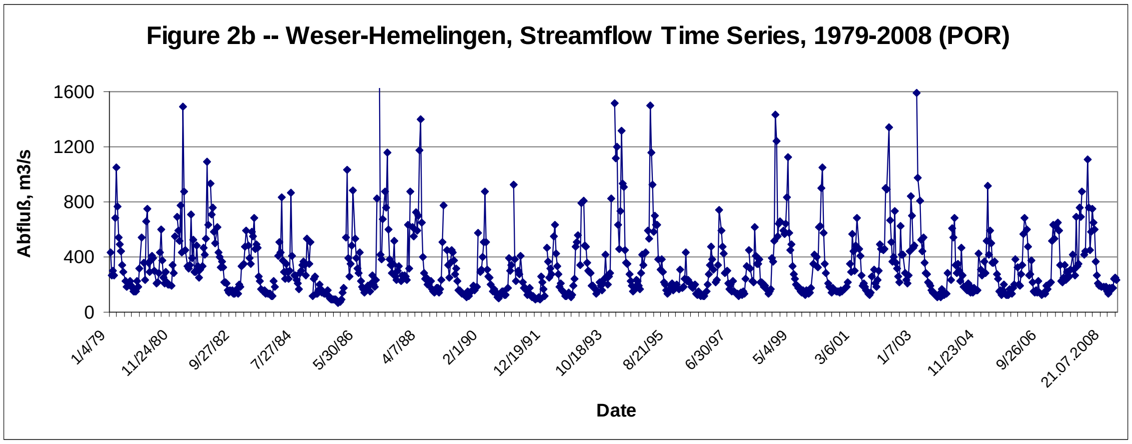


Figure 2b -- Weser-Hemelingen, Streamflow Time Series, 1979-2008 (POR)

The possibility for bivariate regression functions with SC as the independent variable were analyzed for calcium (Ca), magnesium (Mg), sulphate (SO4) and chloride (Cl) (Steele and Houshang, 2009). The Cl-SC plot (Figure 3) gives the best correlation ($r^2 = 0.93$), indicating the quite good bivariate regression function for these variables. This type of plots indicates the inherent interdependence of major ions with SC; this often can be used as an independent variable to estimate ion concentrations as a function of SC when fewer or no data are available (Steele, 1972).

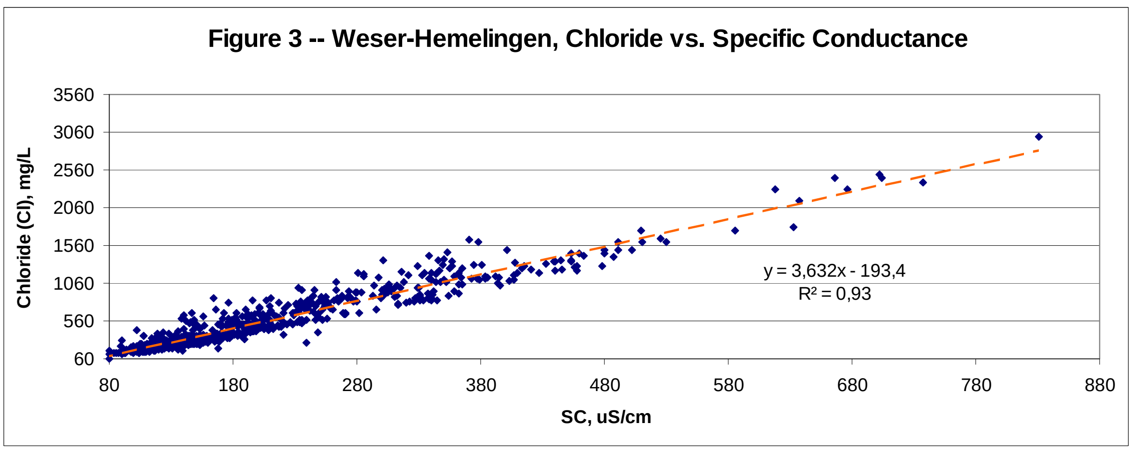
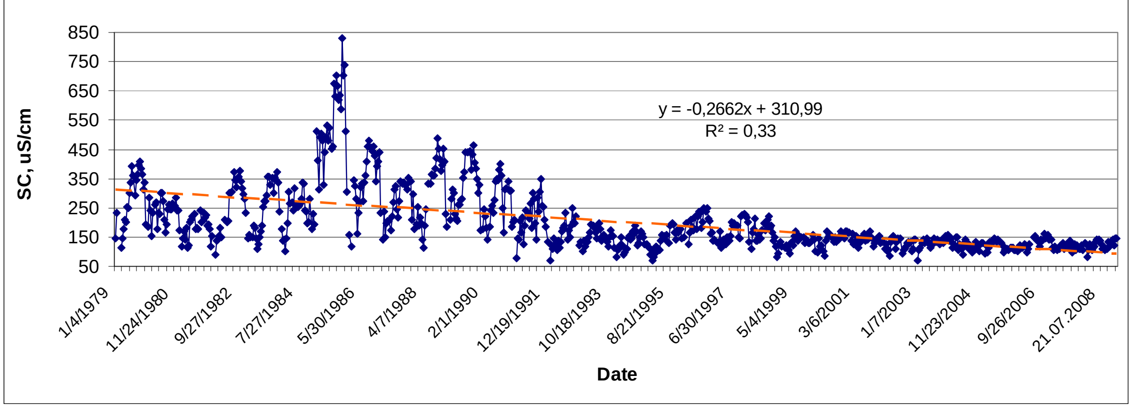


Figure 3 -- Weser-Hemelingen, Chloride vs. Specific Conductance

The time-series plot for streamflows (Figure 2b) exhibits naturally occurring seasonal variations but no distinctive time trend. This condition confirms that water-quality time trends for the major ions most likely are caused by anthropogenic effects rather than multiyear variations or trends in flows at this Weser River monitoring site downstream in the basin.

Figure 4 provides a time-series plots for SC for the entire (30-year) period of available record. This time-series plot exhibits seasonality (high flows/low SCs vs. low flows/high SCs) and the relative greater SCs occurring in the late 1980s and early 1990s. This pattern confirms similar time trends apparent for the major ions (Steele and Houshang, 2009). Beginning in 1992, SCs were consistently lower and exhibited a slight decreasing time trend. Shorter-term time-series SC plots exhibited decreasing trends, possibly indicating continuing improvements in curtailing salinity sources to this mainstem river.

Figure 4 -- Weser-Hemelingen, Specific Conductance Time Series, 1979-2008 (POR)



The nitrate (NO3-N) time series exhibited seasonality over time and only a slight time trend over the entire 1979-2008 POR (Figure 5a). However, this downward trend was more apparent when considering only the more recent (1991-2008) period, as given in Figure 5b.

Figure 5a -- Weser-Hemelingen, Nitrate Time Series, 1979-2008 (POR)

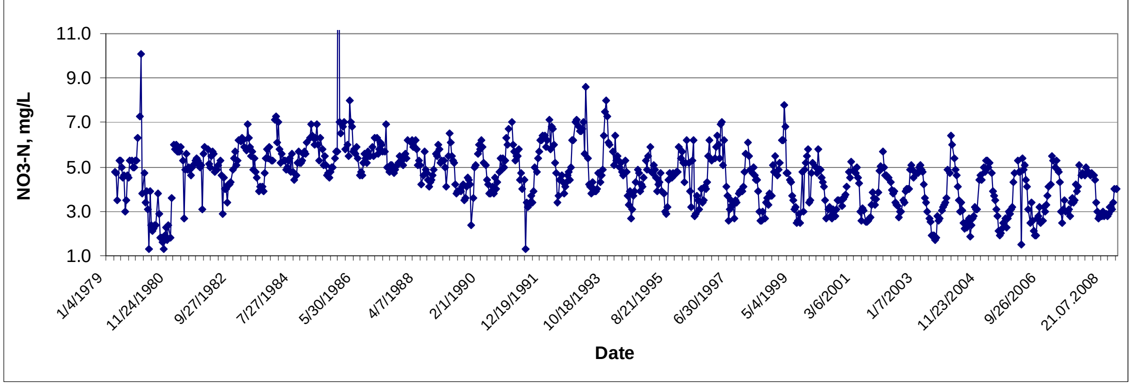
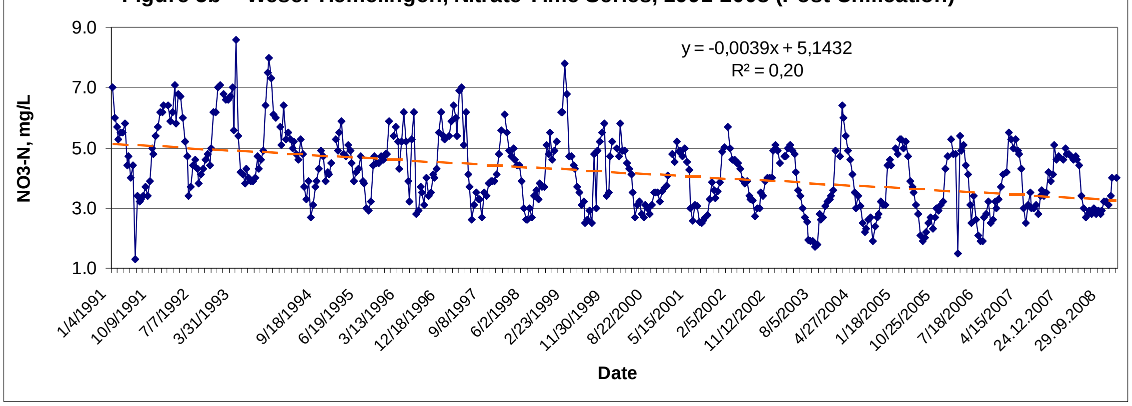
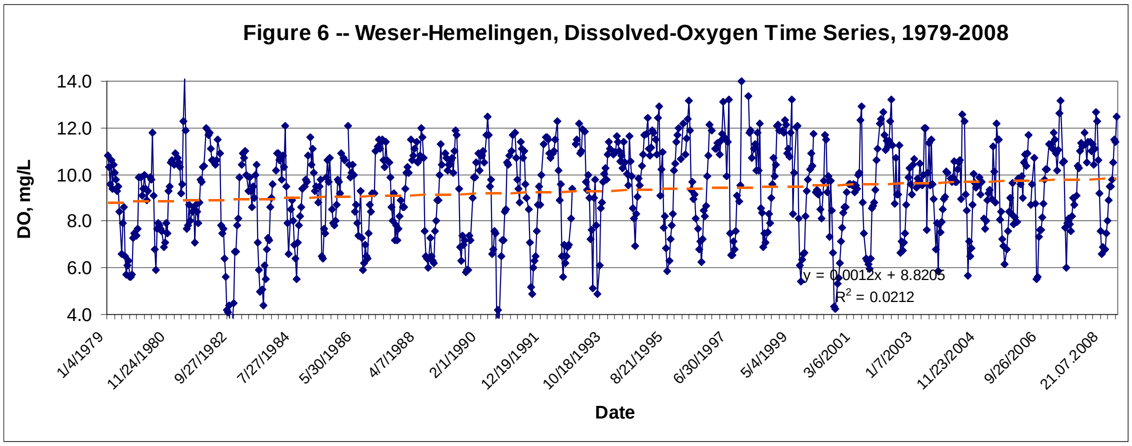


Figure 5b -- Weser-Hemelingen, Nitrate Time Series, 1991-2008 (Post-Unification)



Water temperature time-series plots exhibit a typically consistent seasonal pattern with no time trend. This seasonal pattern can be accurately characterized by a simple-harmonic function (Steele, 1974). Although function coefficients often can be regionalized (as a function of elevation and/or latitude), this aspects is left as a recommended future study effort for a more extensive data assessment for all monitoring sites.

Dissolved-oxygen concentrations indicate some seasonality (Figure 6), although this pattern is not as consistent as for water temperature (Steele and Houshang, 2009). However, on a seasonal basis, the inverse relationship between water temperature and dissolved-oxygen concentrations is apparent (high T/low DO during summer vs. low T/high DO during winter), a pattern consistent in many streams in the northern hemisphere.



The pH time-series plots (Steele and Houshang, 2009) also indicate some seasonality. During 2004, unexplained increases in pH values (highest for the POR) were noted.

For assessing trace-metals (TMs) data, three species were selected for this assessment (Steele and Houshang, 2009). TMs were analyzed in water only through 2000, 6-to-8 times per year from 1979 through 1985 and then biweekly from 1986 through 2000. Beginning in 2001, these metals were analyzed in sediments approximately monthly at this downstream monitoring site. Relevant details are provided in the companion data-assessment report (Steele and Houshang, 2009). Only a few anomalously high concentrations occurred randomly in each time-series. In the case of TMs analyzed on sediments, some variability was exhibited; however, no time trend or seasonal variability was apparent.

Statistical summary and time trends (Weser River at Hemlingen monitoring site)

Both POR (Table 1a) and recent-period (Table 1b) basic statistics were calculated for the variables discussed above through the graphical analyses. These results are useful to confirm findings from the graphical analyses as well as some quantification of noteworthy time trends. It is useful (and recommended) and the sample sizes (that is, numbers of values for each variable) be noted in the summaries. These statistical-summary results are tabulated below:

Table 1a – Statistical Summary, Selected Variables over Entire Period of Record

Variable	*Units*	**Average**	*# Values*	Maximum	Minimum
1979-2008 POR					
Streamflow	*M^3/s*	**340**	*782*	1888.7	65.1
Specific Conductance	*mS/m*	**202**	*765*	831	70
Calcium	*mg/L*	**81**	*735*	110	53
Magnesium	*mg/L*	**56**	*710*	190	13
Sulfate	*mg/L*	**155**	*774*	380	53
Chloride	*mg/L*	**544**	*766*	3000	65
Nitrate (as Nitrogen)	*mg/L*	**4.6**	*775*	25	1.3
pH	*S.U.*	**7.8**	*760*	9.0	6.7
Water Temperature	*deg C*	**12.1**	*775*	25.5	0.4
Dissolved Oxygen	*mg/L*	**9.3**	*777*	15.5	2.9
1979-2000 POR					
Chromium in Water	*ug/L*	**2.9**	*430*	25.4	1
Zinc in Water	*ug/L*	**31.2**	*430*	460	3
Manganese in Water	*ug/L*	**146**	*427*	1500	25

Source: Excel file WeserRWQPlotsStatsR2.xls

Table 1b – Statistical Summary, Selected Variables over Recent Period of Record

Variable	*Units*	**Average**	*# Values*	Maximum	Minimum
1990-2008 Years					
Streamflow	*^{m}/s*	**336**	*469*	1591.21	88.6
Specific Conductance	*mS/m*	**145**	*463*	350	70
Calcium	*mg/L*	**78**	*431*	110	53
Magnesium	*mg/L*	**39**	*404*	100	13
Sulfate	*mg/L*	**132**	*469*	240	61
Chloride	*mg/L*	**306**	*461*	1100	65
Nitrate (as Nitrogen)	*mg/L*	**4.4**	*469*	8.6	1.3
pH	*S.U.*	**7.8**	*453*	9.0	6.7
Water Temperature	*deg C*	**12.5**	*465*	25.5	0.4
Dissolved Oxygen	*mg/L*	**9.6**	*465*	15.5	4.3
1990-2000 Years					
Chromium in Water	*ug/L*	**1.7**	*261*	8.4	1
Zinc in Water	*ug/L*	**23.8**	*261*	83	9
Manganese in Water	*ug/L*	**115**	*261*	890	41
2001-2008 Years					
Chromium in Sediments	*ug/kg*	**53.7**	*99*	80	27
Zinc in Sediments	*ug/kg*	**749**	*99*	1200	310
Manganese in Sediments	*ug/kg*	**3170**	*99*	6200	1500

Source: Excel file WeserRWQPlotsStatsR2.xls

These statistical results further support the time trends exhibited in the various time-series plots and discussed in the previous section. Specifically, although streamflows between the POR and recent period were nearly the same (within 2 percent), SC values for the recent period were nearly 30 percent lower, and the major-ion concentrations lower in the range of four to 55 percent (Ca and Cl, respectively).

Selected data-assessment highlights for three more monitoring sites (see Figure 1)

Fulda-Wahnhausen.— For this upstream site in the Fulda River basin on a major tributary, water-quality conditions are quite good relative to characteristics indicated further downstream (described previously). SC vs. streamflow indicates a typical hyperbolic relationship, with lower SCs at higher flows. Although considerable scatter is shown, bivariate plots of major ions versus SC indicate general trends of the interrelationships between these variables. Time-series plots of flow and water quality indicate mixed patterns and vary, in part, with the time period considered. For the 30-year available period, Ca, Mg, and Cl indicate no time trend (for example, Figures 7 for Cl), SC gives a slightly increasing trend over time, and SO4 and NO3-N (Figure 8) show a decreasing time trend. For the shorter time period since unification of Germany, SC indicates a slight upward trend over time at this upstream tributary site (Figure 9a). Information was not sufficient for this part of the Weser River basin to evaluate possible causes of the SC time-series nor the decreasing time trends in SO4 and NO3-N at this upstream location.

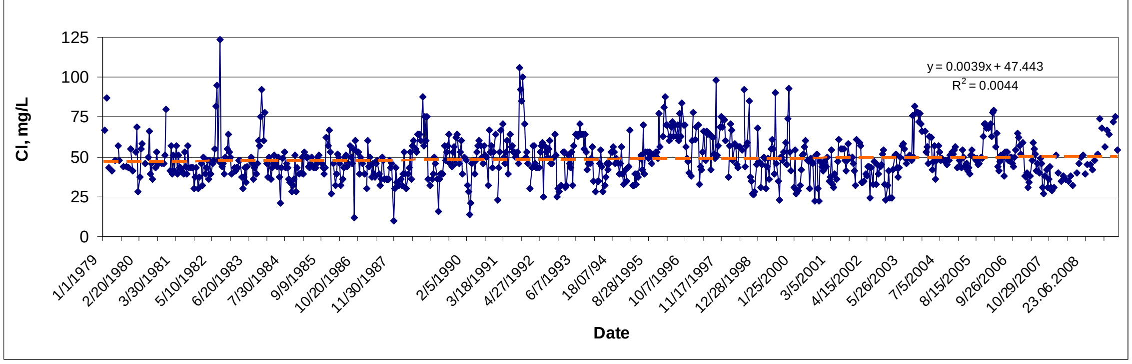


Figure 7 -- Fulda-Wahnhausen, Chloride Time Series, 1979-2008

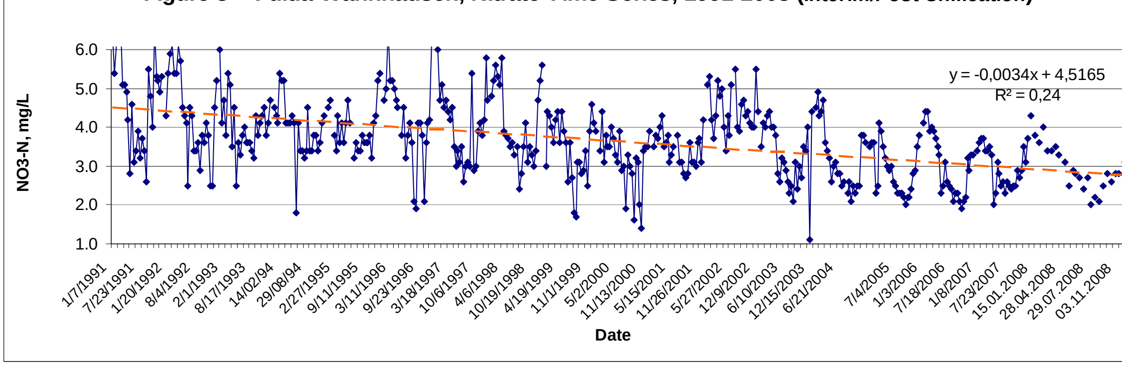


Figure 8 -- Fulda-Wahnhausen, Nitrate Time Series, 1991-2008 (Interim/Post-Unification)

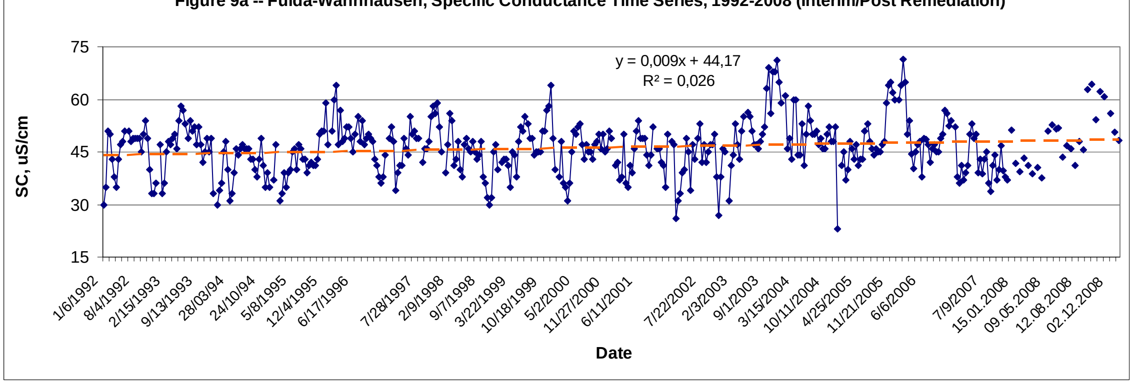
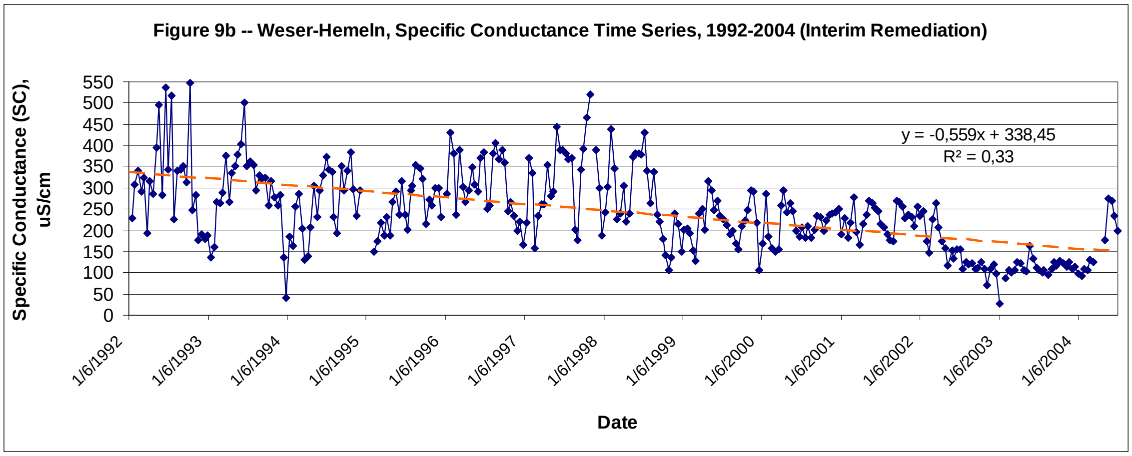
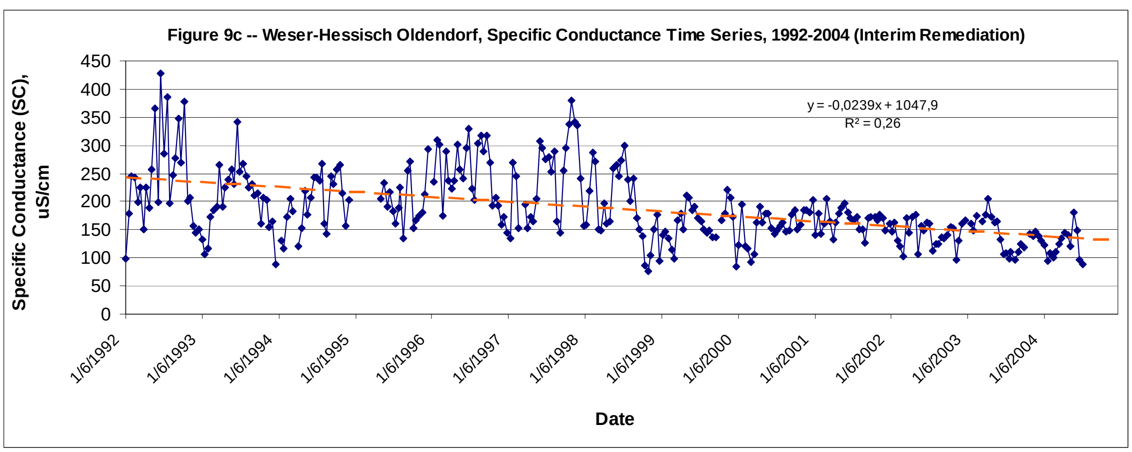


Figure 9a -- Fulda-Wahnhausen, Specific Conductance Time Series, 1992-2008 (Interim/Post Remediation)

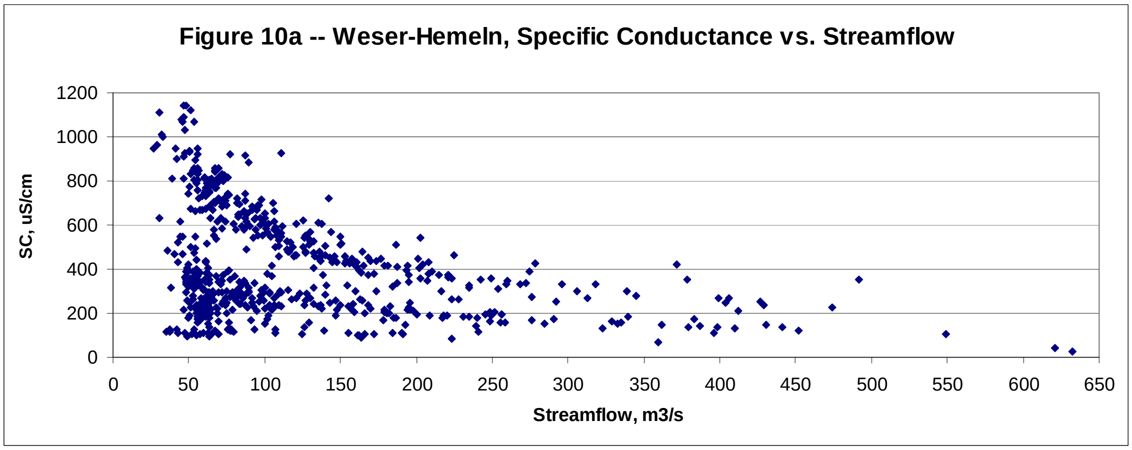
Weser-Hemeln and Weser-Hessisch Oldendorf sites.— For these sites in the middle part of the basin, water-quality conditions increased relative to characteristics described upstream for the Fulda River tributary. Streamflows nearly double those for the monitoring site at Wahnhausen further upstream (average Qs of 123 vs. 67.3 m^3/s). SC over the entire period of record increases at Hemeln by almost an order of magnitude (412 uS/cm v. 44.0 uS/cm upstream); however, a substantial decrease has occurred after unification (Figure 9b).

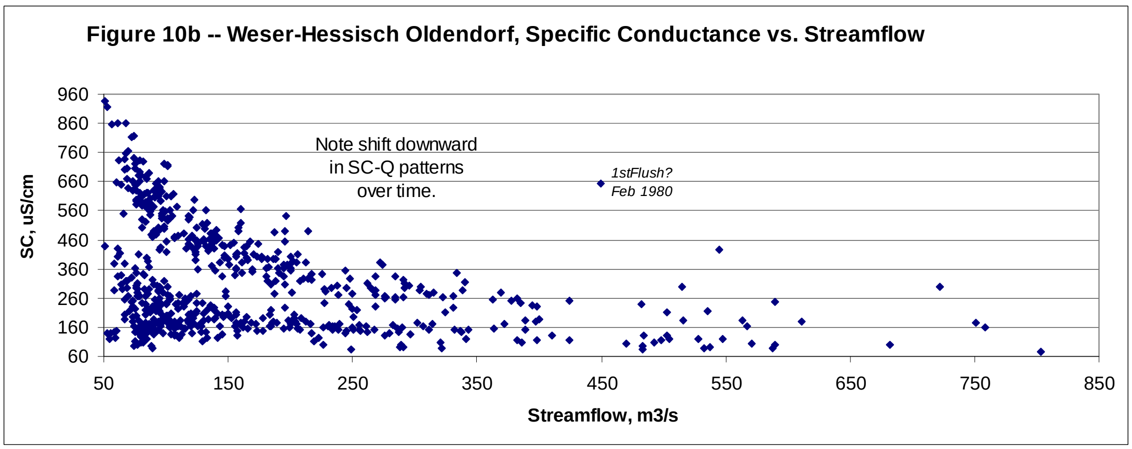


For the Weser-Hessisch Oldendorf downstream (Figure 1), water-quality conditions were higher than at Wahnhausen furthest upstream in the Fulda River tributary but less than average values upstream at the Hemeln site. Average streamflow increases about 40 percent more than that for the second monitoring site at Hemeln upstream (average Qs of 177 vs. 123 m^3/s). SC over the entire period of record some decreases at this site compared to the upstream site at Hemeln (320 uS/cm vs. 412 uS/cm upstream); however, again at Hessisch Oldendorf a substantial SC decrease has occurred after unification (Figure 9c).

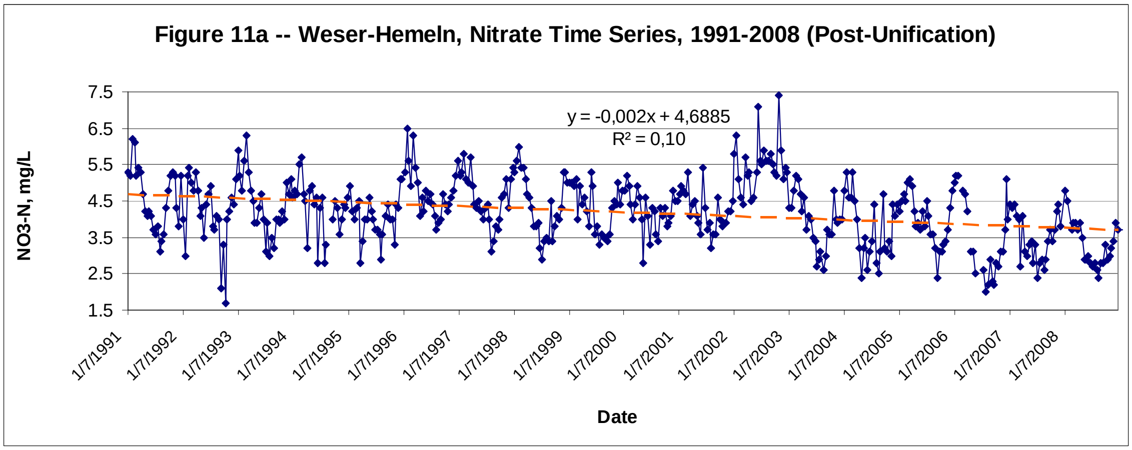


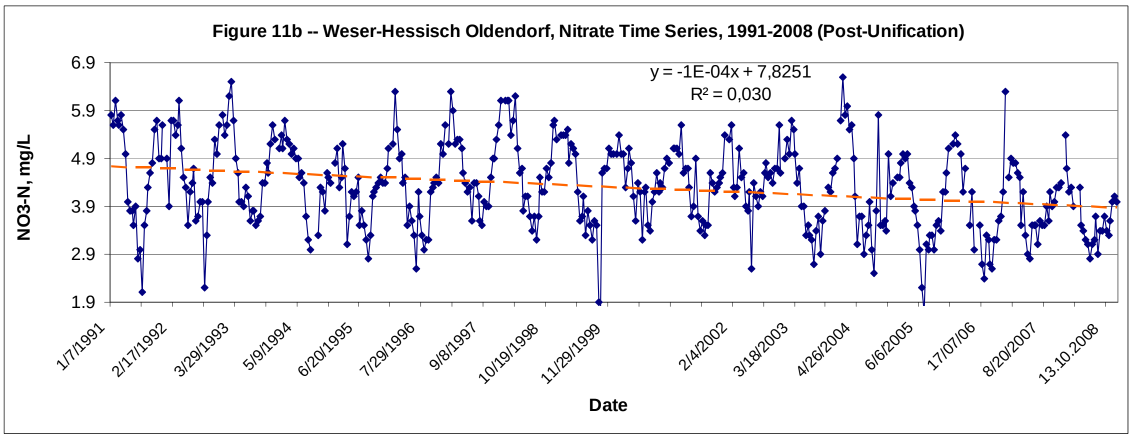
SC vs. streamflow again shows a typical hyperbolic relationship at these two mid-basin locations; however, shifts in SC-Q patterns for Weser-Hemeln result from upstream remediation efforts, causing a distinct separation over time (Figure 10a). This SC-Q shift is observed downstream at Weser-Hessisch Odendorf (Figure 10b) as well. This pattern is in contrast with that observed at the furthest downstream monitoring site (Weser-Hemlingen, see Figure 2a above).





Although considerable scatter is shown, bivariate plots of major ions versus SC indicate general correlation patterns of the interrelationships between these variable pairs. However, in the case of SO4, a few anomalously high values were noted (Steele and Houshang, 2009). However, SC and major-ion concentrations at this location indicate decreasing values over time. For the 30-year available period, NO_3-N shows a seasonally variable pattern but not a time trend until recent years. For the shorter time period since unification of Germany, SC indicates a downward time trend; however, SC data are lacking at this since 2004 (Steele and Houshang, 2009). At present, definitive information is not available to explain possible causes of the SC time-series patterns nor the decreasing time trends in all major and a recent downward time trend in NO_3-N at these two monitoring-site locations (Figures 11a and 11b).





For the Weser's Hemeln and Hessisch Oldendorf sites, SC as well as major-ion and NO3-N concentrations all indicate decreasing values over time. For a shorter time period since unification of Germany, SC indicates a downward shift and continuing decreasing time trend.

<u>Monitoring-Sites Comparisons.—</u> As was highlighted above for this fourth site located furthest downstream (Steele and Houshang, 2009), water-quality conditions continue to decrease slightly relative to characteristics indicated further downstream. The average streamflow increase at Hemelingen is nearly double compared to the third monitoring site at Hessisch Oldendorf upstream (average Qs of 340 vs. 177 m^3/s). SC over the entire period of record indicates some decrease at Hemelingen compared to the upstream sites (202 uS/cm vs. 320 uS/cm at Hessisch Oldendorf and 412 uS/cm at Hemeln upstream). Again, a substantial SC decrease has continued to occur at this downstream site after unification. SC vs. streamflow again shows a typical hyperbolic relationship; however, the shift in SC-Q patterns indicated at the two sites upstream (indicating impacts of reductions in salt-mining sources upstream) are less distinctive at this furthest downstream site (Figure D-1). Although considerable scatter is shown, bivariate plots of major ions versus SC indicate general correlation patterns of the interrelationships between these variable pairs; however, the bivariate Ca-SC plots are relatively nonlinear compared to other major ions at all sites. Time-series plots of streamflow for all four sites indicate no trend. However, SC as well as major-ion concentrations all indicate decreasing values over time. For the shorter time period since unification of Germany, SC and NO3-N concentrations indicate downward shifts and continuing decreasing time trend. At present, information is limited to evaluate possible causes of the SC time-series patterns and the decreasing time trends in all major ions and NO_3-N at this monitoring-site location. Useful information within the Weser River basin

management plan (FGG-Weser, 2009) provides insight as to the economic activities in the river basin as well as beneficial improvements in point-source wastewater treatment plant discharges, agricultural applications of fertilizers, and other remediation actions.

DISCUSSION

The principal anthropogenic impacts affecting water quality in the Weser River basin are described in the river-basin management plan by the Flussgebietsgemeinschaft Weser (FGG-Weser, 2007b), along with associated remedial actions to control these adverse impacts. Key activities involve closing of salt mines, along with point-source controls of high-salinity flows and reductions of nutrients through better use and management of detergents and fertilizer applications on agricultural lands.

Further evaluation should be made of possible streamflow effects, resulting in decreased constituent values with higher flows through dilution. Such effects were noted in the dataset. For certain periods at each site, streamflows, SC values, or water-quality variable concentrations were missing for parts of a given year or an entire year within the period of record. Additional observations and notes regarding water-quality conditions and areal/temporal patterns using data for the four selected monitoring sites in the basin are given in a separate, more detailed report (Steele and Houshang, 2009.

CONCLUSIONS AND RECOMMENDATIONS

The dataset selected for this case study provided useful information. Relatively greater focus was made on time variability for streamflows as well as the various water-quality variables – seasonality and multi-year time trends – for the Weser River monitoring site located at Hemelingen. Possible bivariate-regression functions enable possible data fill-in and/or extrapolation to be made for some lacking data values. Time-trend analyses in several instances indicate effects of changes in human activity impacting water-quality conditions.

This data assessment should be extended to other monitoring sites in the Weser River basin. Priority might be given to those sites having streamflows concurrent with water-quality sample/measurement results. In addition, quantification of seasonal patterns for water temperature should be made using a simple-harmonic function (Steele, 1974). Resultant harmonic coefficients then can be regionalized or otherwise used to assess changes from natural seasonal variability (such as below spill structures or dams).

Further evaluation is recommended regarding the overall water policy and associated components and milestones of the European Union’s Water Framework Directive (Steele and Bongartz, 2006; Steele and others, 2008; Steele, 2009), within the context of management planning for large river basins in Europe. This water policy incorporates in a formalized structure all of the components of watershed plans as promulgated by U.S. Environmental Protection Agency guidance documents. Distinctive positive aspects of the WFD include the integration of different water bodies (groundwater, surface waters, and coastal areas), linkage of biological and ecological characterizations with water quality, and formalized inputs and information transfer with stakeholders and the general public through meetings and outreach.

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