THE AMOUNT AND SPECIATION OF TRACE ELEMENTS TRANSPORTED FROM RICE FIELD TO CANAL DURING A FLOODING EVENT

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Abstract. Trace element pollution of soils, sediments and surface water can pose a risk for the local population and the environment of Viet Nam. Rice fields can be affected by storm events, which cause the release of trace elements into surface water and transport them into drinking wells. The aim of this study was to investigate if dissolved and suspended As, Pb and Zn concentrations in surface water of a paddy rice fields and an irrigation canals increased during a flooding event and exceed the threshold values issued by the Viet Nam national technical regulation on surface water quality and WHO Guidelines for Drinking-water Quality. The study site is a rice field area in the Thanh Hoa province in Central Viet Nam, which experiences an average of 2.4 storms every year causing overflow of streams and low-order canals. Concentrations of As increased during the flooding event with dissolved As being the prevailing fraction, which followed a late flush behavior. Lead showed no significant difference in concentration over time. Zn concentrations only increased significantly in the canal upstream the field in the morning of the first day. Suspended Zn dominated at that time, following the first flush behavior of TSS concentrations. Concentrations of As, Pb and Zn did not exceed the threshold values issued by the Viet Nam national technical regulation on surface water quality or WHO Guidelines for Drinking-water Quality (Fourth edition, 2011) at any time and they are therefore of no concern for the health of the local population.

Keywords: Trace element; rice field; flooding; release.

Classification numbers: 3.2.1, 3.4.2, 3.6.2.

1. INTRODUCTION

In Viet Nam, an increase of trace element concentrations in soils, sediments, surface water has been found in the recent years [1-3]. Exposure to trace elements can have a negative effect on the health of humans, animals and ecosystems [4]. Since surface water in Viet Nam is used as
drinking and irrigation water, as well as for other domestic purposes, increased concentrations of trace elements pose a risk for the health of the local population which is dependent on this water source [3].

In the Thanh Hoa province in Central Viet Nam, 90 % of the population lives in rural areas with low income, and paddy rice fields are one of the main land use forms [5]. Every summer, storm events with heavy rainfall, leads to flooding of the area with water levels of up to 2 m [5]. The storm events and flooding increase the concentrations and transport of trace elements in surface water [6].

During greater flooding, surface water can additionally find its way into drinking wells. Since rising trace element concentrations can increase the risk for local populations, the objectives of this study were: (1) to investigate if concentrations of As, Pb and Zn increased in surface water of a rice production area, (2) to determine the distribution between dissolved and suspended concentrations, and (3) to compare the concentrations with the threshold values issued by the Viet Nam national technical regulation on surface water quality (QCVN 08:2008/ BTNMT/B1) and WHO Guidelines for Drinking-water Quality.

2. MATERIALS AND METHODS

2.1. Sampling site

The sampling site is a Viet Nam typical lowland rice field area next to the village Thang Long in the Nong Cong district, Thanh Hoa province (19°35'59"N, 105°39'43"E) (Figure 1).

The climate in the Thanh Hoa province is a tropical monsoon climate. The precipitation in this area is high, especially in the summer months with its maximum of around 400 mm in September. The Thanh Hoa province experiences an average of 2.4 storms every year. Frequently, there are strong storms leading to high precipitation and wind speeds. The consequences are dyke and dam breaches and major flooding of the area [5].

In the rice field area, a low order canal runs along the fields to supply irrigation water or cart away redundant water. The canal flows through the Thang Long village before passing through the fields and ends in the Muc River. The rice fields are flood irrigated with a water level of around 10 cm during most of the rice crop cycle. For the study, one paddy rice field alongside the canal in the center of the rice field area was selected.

![Figure 1. Sampling site map in Thanh Hoa.](image)

2.2. Sampling strategy
Water samples were taken once before and seven times during a storm event. The storm event consisted of three days with rain from the 16th September till the 18th September 2015 and the resulting storm flood lasted for around four days till the 20th September. The water level increased about 30 cm during the flooding. The sampling before the storm flood was carried out at the 2nd September 2015, when the rice on the sampling field was flowering. During the storm event, there were only stubbles left on the field, since the farmer harvested between the first sampling and the storm.

Sampling was carried out at four different points (Figure 1). During the whole storm event the flow direction on the field was towards the canal. In the field two sampling points were chosen: Point F1 was selected close to the water inflow from an elevated field to have an estimate of trace element concentrations and the physiochemical status of water entering the selected field. Point F2 was chosen in the selected field to estimate the conditions of the surface water. The two other sampling points were chosen in the canal: Point C1 was taken upstream of the runoff from selected field and point C2 downstream of the runoff to investigate the effect of the water entering from the field into the canal (Figure 2).

2.3. Trace element analysis

The water used to prepare solutions was MiliQ water (Purelab Chorus), the acid used for standard preparation was 69.0 – 70 % nitric acid (J. T. Baker, USA).

In the field, 50 ml water was sampled in sterile polypropylene tubes (Almeco A/S) with three replications for each sample. Immediately after sampling, 15 ml of the 50 ml sample were filtered through 0.45 μm nylon filters (Mikrolab) for determination of the dissolved element concentration. The remaining 35 ml were used for the determination of acid extractable element concentration. The acid-extractable element fractions in this study was defined as the dissolved fraction plus the extractable element fraction from suspended solids [7]. The samples were preserved with 65 % nitric acid to an acid content of approximately 0.2 %. The samples were sent to the University of Copenhagen for the analysis.

**Figure 2.** Schematic plan of the sampling area with locations of the sample points.

The concentrations of these selected trace elements were determined by Graphite Furnace Atomic Adsorption Spectroscopy (GF-AAS). External calibration was used including six standards and a blank. Recalibration was done after every tenth sample using a blank and the second standard.
Since As concentration in the samples was in the lower μg/l range, the limit of detection (LOD) was determined to 0.39 μg/l. The determination was done according to Harris [8].

Acid-extractable Pb concentrations were determined only before the flooding and in the morning of the first and the third day. Dissolved Pb concentrations were determined before flooding and in the morning of the second, third and fourth day due to time constrains.

2.4. Data analysis

*Suspended element concentrations:* The suspended concentrations of As and Zn were calculated as the difference between the dissolved and the acid-extractable fraction. Since acid-extractable and dissolved Pb concentrations were only measured for some days, it was not possible to calculate the suspended concentrations.

*The Anova-Test:* Analysis of Variance (Anova) was used to identify if the flooding event had a significant effect on the trace element concentrations. The single factor Anova test was performed in Excel (Microsoft Office, 2007).

*Amount of elements per m² soil:* To account for the dilution effect at high water level, the amount of elements per area were calculated for each point and time. In order to do so, the concentration values calculated to mg per cm³ were multiplied with the height in cm of the flooding level. The results were calculated into mg per m².

3. RESULTS AND DISCUSSION

3.1. Arsenic

Concentrations of acid-extractable As ranged between 1.62 and 5.29 μg/l in the canal, and between 1.19 and 7.41 μg/l in the field (Figure 3).

Before the flooding event, the acid-extractable As concentrations were low with 1.62, 1.66, 1.39 and 2.35 μg/l for C1, C2, F1 and F2, respectively. In the canal, the concentrations increased during the third and fourth day and reached 3.92 and 5.29 μg/l for C1 and C2. The Anova test showed only a significant difference in concentrations over time for C2 with a p < 0.001 level (Table 1). The R(t) plots for C1 and C2 in Figure 4. A run close to the 1:1 plot during the whole flooding event, which shows that concentrations of acid-extractable As in the canal were proportional to the water flow. In the field, concentration at the sampling point F1 remained low during the first 1.5 days, but afterwards rose steadily up to 7.41 μg/l. The increase can further be seen in the late flush behavior for F1. The Anova test showed a significant difference over time for F1 with a p < 0.01 level. At the sampling point F2 the standard deviations were high, when concentrations were high and the Anova test showed no significant difference during the flooding event.

Dissolved As concentration ranged from 0.98 to 3.99 μg/l in the canal, and from 0.39 to 6.30 μg/l in the field (Figure 5). The dissolved As concentrations in the water, determined prior the flooding were low for all four sampling points with 0.98, 1.09, 0.62 and 1.21 μg/l for C1, C2, F1 and F2, respectively.

During the first two days of the flooding event, the dissolved As concentrations at all four sampling points remained low, but began to rise during the third day. They further increased during the fourth day up to 3.06, 3.99, 6.30 and 4.63 μg/l for C1, C2, F1 and F2, respectively. The increase in dissolved As was thereby higher in the field than in the canal.
Table 1. Results of a single-factor Anova test for all the trace elements.

<table>
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<th>Extractable</th>
<th>Dissolved</th>
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<tr>
<td>Fe</td>
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<td></td>
<td>C1 *</td>
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<td></td>
<td>F1 ns</td>
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<tr>
<td>As</td>
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<td>C1 ns</td>
<td>C2 ***</td>
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<td>C2 ***</td>
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<td></td>
<td>F2 ns</td>
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<td>Pb</td>
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<td>C1 ns</td>
<td>C2 ns</td>
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<tr>
<td></td>
<td>C2 ns</td>
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<td></td>
<td>F2 ns</td>
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<tr>
<td>Zn</td>
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<tr>
<td>C1 **</td>
<td>2 s</td>
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<td></td>
<td>2 s</td>
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<td>F1 s</td>
<td>2 s</td>
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The Anova test showed a significant difference over time for all four sampling points with a p < 0.01 level for C1 and F2, and a p < 0.001 level for C2 and F2 (Table 2). The increase during the end of the flooding event can also be seen in Figure 4B, which showed a ‘late flush’ behavior for all four sampling points.

The amount of dissolved As per m² rose steadily over the whole flooding event. In the canal, dissolved As elevated from 0.41 and 0.57 mg/m² for C1 and C2 to 1.29 and 1.59 mg/m². In the field, the amount rose from 0.03 and 0.07 mg/m² for F1 and F2 to 0.69 and 0.46 mg/m².

Suspended As concentrations ranged between 0.15 and 2.40 μg/l in the canal, and 0.24 and 3.39 μg/l in the field (Figure 3). They were low during the first and the third day of flooding for C1, F1 and F2, but peaked during the second day with 2.40, 3.39 and 3.21 μg/l, respectively. During the fourth day of flooding they started to rise again. As the suspended element concentrations were calculated as the difference between the acid-extractable and the dissolved concentration, it was not possible to conduct an Anova test. Therefore, no statement can be done regard the significance of the data. The plots of C1, F1 and F2 for suspended As concentrations in Figure 4C showed neither a first nor a late flush behavior. Suspended As concentrations at the sampling point C2, however, showed a clear first flush behavior. The concentrations rose during the morning of the first day to 2.07 μg/l and then decreased again during the second day.

The dissolved As fraction predominated over the suspended fraction during the whole flooding event except for the second day (Figure 5). The data for amount of acid-extractable and suspended As per m² showed no different trend than the concentration data for all three fractions.
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Figure 3. As concentrations before and during four-day flooding event. The full columns show the acid extractable concentrations. The filled part displays the concentration of the dissolved fraction, the lined part displays the suspended fraction.

Figure 4. Plot of R(t) for acid-extractable (A), dissolved (B) and suspended (C) As concentrations during the four-day flooding event. The 1:1 lines indicated that the mass fraction Yt equals the flow volume Yt during the whole flooding event. Plots above the 1:1 plot show a first flush event. Plots below the 1:1 plot show a late flush event.

Figure 5. Amount of dissolved As per area during a four day flooding event. The base flow concentrations were determined two weeks before the flooding event.
Acid-extractable As concentrations in the field clearly followed a late flush behavior (Figure 4A): the concentrations in the water samples remained low in the beginning of the flooding event and increased mainly during the last two days. At the sampling point F1, this led to a significant increase of concentrations in the water during the flooding event (Table 1). The field may be a major source for As, since the canal showed no flush behavior, but concentrations at the sampling point C2, situated downstream the field, showed a significant increase over time in contrast to C1.

For most of the flooding event, dissolved Arsenic predominated the acid-extractable concentrations. This result is consistent with the findings of Zonta [9], which reported As to be mainly transported during flooding events in dissolved form. However, another study found As to be mainly transported in suspended form [6]. The speciation of trace elements thereby can depend on the prevailing chemical conditions as well as on the texture of the suspended particles [10, 11].

Like the acid-extractable concentrations in the field, dissolved As showed a clear late flush behavior (Figure 4B) with a significant difference in concentration over time at all four sampling points. This late increase of dissolved As concentrations in the water during the flooding event could be due to a dilution effect or be associated with redox conditions. As previously mentioned, it is assumed, that during the second day the redox conditions in the soil and sediment changed from oxidized to reduced conditions. This process is known to release trace elements due to the reduction of Fe and Mn hydroxides [12]. Since As has been reported to be mainly associated with Fe hydroxides in soils and sediments [13], the change from oxidized to reduced conditions during the second day, could have led to the release of dissolved As into the water from the soil. These findings are consistent with the results from Takahashi [14], who determined As in paddy rice field to mainly bind to Fe hydroxides under oxidized conditions and to be quickly released into solution when reduced conditions emerged. However, the amount of dissolved As in mg per m² rose gradually during the whole flooding event (Figure 5), which could indicate that dissolved As is released during the whole flooding event, but because of the higher water mass, the concentrations were diluted. It should further be mentioned, that similarly to acid-extractable As the concentrations at the sampling point C2 again showed a higher rise than concentrations at C1. This supports the assumption, that As concentrations were released from the field and transported into the canal.

The suspended As concentrations are negligible for the release of As during the flooding event, since they were only prevailing during the second day of the flooding event (Figure 3).

Even though a clear increase in As concentration could be seen during the flooding event, the concentrations at no time exceeded the threshold values issued by the Viet Nam national technical regulation on surface water quality (QCVN 08:2008/BTNMT/B1), the WHO Guidelines for Drinking-water Quality, nor average background concentrations (Table 3). As is therefore of no concern for the health of the local population.

3.2. Lead

Concentrations of acid extractable Pb in the water samples ranged between 1.27 and 3.82 μg/l in the canal, and between 0.50 and 1.30 μg/l in the field (Figure 6A).

Before flooding, acid-extractable Pb concentrations were 1.27, 2.98, 0.91 and 0.77 μg/l for C1, C2, F1 and F2, respectively. During the flooding event, the concentration at the sampling points C2 and F1 declined continuously until the third day to 1.34 and 0.55 μg/l. The acid extractable Pb concentrations at C1 and F2 peaked during the first day with 3.82 and 1.30 μg/l,
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but decreased afterwards until the third day. It should be noted, that the standard deviations of high values were always high. Furthermore, the Anova test showed no significant difference over time for any of the four sampling points (Table 2).

Dissolved Pb concentrations ranged between 0.03 and 1.80 μg/l in the canal, and between 0.01 and 2.18 μg/l in the field (Figure 6B).

Before the flooding, concentrations were lower in the field with 0.15 and 0.06 μg/l for F1 and F2, and higher in the canal with 1.73; 1.20 μg/l for C1, C2. In the field, the dissolved Pb concentrations peaked during the third day with 1.65 and 2.18 μg/l for F1 and F2. However, the Anova test showed a significant difference over time only for F2 with a p < 0.01 level (Table 2). In the canal, concentrations for C1 declined towards the second, but peak on the third day. For C1, they decreased during the third and fourth day to 0.03 μg/l.

**Figure 6:** Acid-extractable (A) and dissolved (B) Pb concentrations before and during the first three of a four day flooding event. The explanation of the sampling points can be found in Fig. 2. The base flow concentrations were determined two weeks before the flooding event.

The amount of acid-extractable and dissolved Pb per m$^3$ did not show any different trend from the concentration. Acid extractable Pb concentrations showed two contrary behaviors. While concentrations peaked during the first day at the sampling points C1 and F1, they decreased continuously during the whole flooding event at C2 and F2. The dissolved fraction is negligible during the flooding, since it only prevailed during the third day. During the first day of the flooding, suspended solids would be expected as dominating fraction, which is consistent with findings from literature [9,15].

However, the concentrations of Pb were in the lower μg/l range and the standard deviations in were high for the higher concentrations. Hence, it would be necessary to determine the limit of detection to identify, whether these low concentrations are significant. Since the Anova test showed no significant difference over time except for dissolved Pb at the sampling point F2 (Table 2), it can be assumed that no changes of Pb concentrations in the water occurred.
Furthermore, the determined Pb concentrations at no time exceeded the threshold values issued by the Viet Nam national technical regulation on surface water quality (QCVN 08:2008/ BTNMT/B1), the WHO Guidelines for Drinking-water Quality, nor average background concentrations (Table 3). Pb is therefore of no concern for the health of the local population.

3.3. Zinc

Concentrations of acid-extractable Zn ranged between 2.87 and 9.06 μg/l in the canal, and between 3.08 and 7.81 μg/l in the field (Figure 7). Before the flooding, acid-extractable Zn concentrations were lower for C1 and F2 with 4.97 and 3.91 μg/l, and higher for C2 and F1 with 7.75 and 6.40 μg/l. During the first day, acid extractable Zn concentrations in the canal reached their maximum with 9.06 μg/l for C1 and 8.08 μg/l for C2. They showed another smaller peak at the fourth day. In the field, acid-extractable Zn concentrations remained high for F1 and showed a small peak for F2 during the first day of flooding. Like in the canal, the concentrations in the field show another peak at the last day. The R(t) plots for C1, C2 and F2 showed a first flush behavior for the acid-extractable Zn concentration (Figure 8A). It should be noted that all sample points showed high standard deviations and that the Anova test showed a significant difference for acid-extractable Zn concentrations only for the sampling point C1 with p < 0.001 level (Table 2).

Table 3. Guideline concentrations.

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<tbody>
<tr>
<td>As</td>
<td>10 μg/l</td>
<td>10 μg/l</td>
<td>10 μg/l</td>
</tr>
<tr>
<td>Pb</td>
<td>20 μg/l</td>
<td>10 μg/l</td>
<td>5 μg/l</td>
</tr>
<tr>
<td>Zn</td>
<td>500 μg/l</td>
<td>20 μg/l</td>
<td>20 μg/l</td>
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The dissolved Zn concentration in the water samples ranged between 2.20 and 8.12 μg/l in the canal and between 2.84 and 9.06 μg/l in the field. Concentrations before the flooding event were 4.78, 2.98, 6.81 and 3.91 μg/l for C1, C2, F1 and F2, respectively. They peaked for C2, F1 and F2 during the first day with 5.89 μg/l for F2 in the morning, and 5.96 and 7.82 μg/l for C2 and F1 in the afternoon. Afterwards the dissolved Zn concentrations declined and remained low until the afternoon of the third day, where they rose again. Dissolved Zn concentrations at the sampling point C1 showed a small peaked in the morning of the third day and then further increased to 8.12 μg/l in the morning of the fourth day. The R(t) plots for dissolved Zn in Figure 8B show neither a first nor a late flush behavior. Furthermore, it should be noted that the standard deviations were high for all 4 sampling points, that the Anova test showed no significant difference for dissolved Zn (Table 2).

The suspended Zn concentration in the water samples ranged between 0.00 and 4.77 μg/l in the canal and between 0.00 and 3.01 μg/l in the field (Figure 7).
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Figure 7. Zinc concentrations before and during a four day flooding event. The full columns show the acid extractable concentrations. The filled part displays the concentration of the dissolved fraction; the lined part displays the suspended fraction. The base flow concentrations were determined two weeks before the flooding event.

Figure 8. Plot of R(t) for acid-extractable (A), dissolved (B) and suspended (C) Zn concentrations for the four day flooding event. The 1:1 lines indicated that the mass fraction Yt equals the flow volume Yt during the whole flooding event. Plots above the 1:1 plot show a first flush behavior. Plots below the 1:1 plot show a late flush behavior.

Before the flooding, concentrations were low for C1 and F1 with 0.19 and 0.21 μg/l, high for C2 with 4.77 μg/l and could not be detected for F2. During the flooding, suspended Zn concentrations in the field were only detected during the first day. At this time, they were highest for the sampling point F1 with 3.01 μg/l in the morning and for the sampling points F2 and C2 with 2.89 and 4.12 μg/l in the afternoon. The R(t) plots for suspended Zn in all sampling points shows a clear first flush behavior (Figure 8C). As the suspended element concentrations were calculated as the difference between the acid-extractable and the dissolved concentration, it was not possible to conduct an ANOVA test.
Therefore, no statement can be done regard the significance of the data. For the sampling points C1, F1 and F2, the suspended fraction only prevailed during the first day of flooding. In the point C2, however, the concentration of extractable Zn from suspended solids showed a high share during the afternoon of the second and the morning of the third day (Figure 7).

The data for amount of Zn per m² showed no different trend than the concentration data for all three fractions.

Zn concentrations showed a significant change during the flooding event only for the acid-extractable fraction at the sampling point C1 (Table 2), where concentrations were significantly higher during the morning of the first day. This increase is especially influenced by the suspended Zn fraction, which showed a first flush behavior at the afore mentioned sampling point. These finding are consistent with the results of Sanden [16], which reported suspended Zn to increase during a rise of discharge and decline afterwards.

Since Zn concentration only rose significantly at the sampling point C1, which was located upstream of the field, but no increase could be seen for the point C2, F1 and F2, it can be assumed that the Zn originated not from the field. Furthermore, the inflowing Zn-poor water and solids from the field most likely led to a dilution effect in the canal, which would in turn mean a decrease of Zn concentrations downstream the field. A possible source for the increasing Zn concentrations at C1 could be due to runoff from the village, which lays upstream the rice field area. Even though acid-extractable Zn concentrations in the canal rose during the flooding event, the concentrations at no time exceeded the threshold values issued by the Viet Nam national technical regulation on surface water quality (QCVN 08:2008/BTNMT/B1), the WHO Guidelines for Drinking-water Quality, nor the average background concentrations (Table 3). Zn is therefore of no concern for the health of the local population.

4. CONCLUSION

The aim of this study was to assess the effect of a flooding event on dissolved and suspended concentrations of As, Pb and Zn in the surface water of paddy rice field and low order irrigation canal. Concentrations of As increased significantly during the flooding event with dissolved As as prevailing fraction. The increase thereby followed a late flush behavior due to the redox-sensitivity of dissolved As. Furthermore, the field acted as a source of As for the canal. Pb showed no significant difference in concentration over time. However, Zn concentrations significantly increased in the canal upstream the field during the first day. Suspended Zn was the prevailing fraction. Since concentrations in the field itself as well as downstream did not change significantly, the field was not a source for Zn.

Concentrations of As, Pb and Zn did not exceed the threshold values issued by the Viet Nam national technical regulation on surface water quality (QCVN 08:2008/BTNMT/B1) or WHO Guidelines for Drinking-water Quality at any time and they are, therefore, of no concern for the health of the local population. However, TSS concentrations however exceeded the Viet Nam Surface Water Quality Standards by a factor of seven in the field and by a factor of 10 in the canal.

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