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Environmental Presence of Heavy Metal Contamination of Industrial Tributary in a Rural River Catchment.

-A case study on Trönningeån stream in Southern Sweden.

Mohamed Irshad kk

Master Student, Department of Applied Environmental Science, Halmstad university, Halmstad, Sweden

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Abstract - *Heavy metal pollutants are a worldwide concern. It causes negative effects on aquatic organisms and human health. Heavy metals concentration and transport of copper, zinc and cadmium were investigated in high and low flow conditions in Trönningeån River, southern Sweden. A total of 33 surface water samples collected from the river and Kistingebäcken tributary were analyzed. Concentration (high to low) of heavy metals in the Trönningeån river and its tributary were- copper(Cu) > zinc (Zn) > cadmium (Cd). The concentration of Copper was found to be high in low flow condition whereas in the case of zinc, high concentrations were found in both the flows (high and low). Study further showed that, the tributary has high pH and conductivity. And finally, the study concluded that there is high concentration and transport of heavy metals in the above-mentioned industrial tributary.*

***Key Words*: Heavy metal pollution, Heavy metal transport, Industrial tributary, Trönningeån river.**

1. INTRODUCTION

This study aims to assess heavy metal pollution in the stream Trönningeån in southern Sweden. The study could be a possible addition to the LIFE GOOD-STREAM project which is currently, focusing on the complete catchment area of the rural stream Trönningeån, southern part of Sweden [fig1] and installation of wetlands. According to the VISS database (Vatten Information Systemet Sverige); a database for classification of all Swedish waters according to the European Water Framework Directive), the rural stream has a moderate to poor water quality [1]. The LIFE GOOD-STREAM project is mainly concentrated on retention of nutrients using wetlands. Assessment of heavy metals is expected to be an added benefit to the already undergoing LIFE GOOD-STREAM project.

2. BACKGROUND

According to World Health Organization, zinc, copper and cadmium are among 10 toxic heavy metals with major issue [2]. Heavy metal pollution in river and streams is primarily caused due to industrialization [3] [4]. Industries such as - textiles industries, diaries, recycle facilities, fertilizer industries, tin and drug industries located besides, the river catchment are the primary causes for heavy metal pollution [5]. River sediments become the storage of heavy metals, which in turn becomes the potential secondary source of metal pollution to the connected aquatic systems [6]. As the nature of heavy metals are non-degradable and toxic, heavy metal pollution in rivers has been the subject of several studies and hence has drawn global attention towards it [7].

Heavy metals are deposited in the river sediments during the process of adsorption, precipitation and hydrolyzation [8]. Also, it has been observed that the mechanical disturbance of the sediments increases the risk of contamination when they are re-suspended [9]. Toxicity of zinc, copper and cadmium [10] [11] in the aquatic environment increases the risk of entering in to the living systems directly or indirectly, causing serious health issues [12] [13]. Long term zinc, copper and cadmium exposure leads to health problems such as physiological problems in blood production and liver malfunction.

Also, zinc and cadmium intake through food and water could cause metal poisoning for which appropriate medical care must be taken to avoid further damage [14]. A previous study has identified traces of heavy metal (Zn and Cu) samples in teeth dentine of humans, that could have toxic effect. The study concluded that the teeth dentine tests can act as a possible biomarker for environmental pollution [15].

Figure 1:Trönningeån catchment area.

A study observed that aquatic systems are prone to heavy metal pollution especially in fishes like *Tilapia nilotica*. Fish liver contained traces of Zn and Cu [16]. As per this study, heavy metal concentration in different parts of the fish varied with the growth of the fish and that the heavy metal concentration in the edible parts of the fish were under permissible safety level. Similar case was found in another study where the subject was the muscle of a commercial shrimp (Metapenaeus affinis) found in the muscle, liver and gills of two fish species (*Thryssa vitrirostris* and *Johnius belangerii*) taken from Arvand river in the northeast Persian Gulf [17].

An initial monitoring performed within the LIFE-GOODSTREAM project indicated that the water quality in two tributaries to the stream Trönningeån was strongly influenced by industrial activities [18]. This included indication of heavy metal pollution (unpublished data) suggesting that the LIFE-GOODSTREAM project should not only focus on nutrients or pollution from agriculture, but also the project should focus on heavy metal pollution, towards achieving good water quality status of the whole catchment. The municipality has also showed uncertainty regarding the possibility of heavy metal pollution, because of industries and landfill near the river tributary Kistingebäcken.

3. OBJECTIVE

This study aims investigate possible industrial pollution of the tributary Kistingebäcken in the catchment of the rural stream Trönningeån. It is done by sampling at strategical points and analyzing water samples, to detect heavy metals such as zinc, copper and cadmium among the group of heavy metals, in addition to pH and conductivity of water.

Some of the important research questions for the study are:

1. Can concentrations of heavy metals be found in water samples of Kistingebäcken tributary?
2. Can we detect that industrial activities and landfill situated at the Kistingebäcken is responsible for the heavy metal pollution in Kistingebäcken tributary by collecting water sample only?
3. Is Kistingebäcken tributary responsible for the heavy metal pollution in Trönningeån main stream?

4. MATERIALS AND METHODS

The Trönningeån catchment area [Fig1] is about 32 km^2 with the stream of length of 12 km. Forest constitute 42% of the surrounding area with close to 50% agricultural land. Remaining 8% of the land [19] situated in the village Trönningeån with a population of 1555 [20]. One of the area of Natura 2000 is situated at the point where the stream leaves Trönningeån village. Natura 2000 is a renowned natural reserve in the territory of European Union. It comprises of Special Areas of Conservation (SACs) and Special Protection Areas. The network includes both terrestrial and marine sites (Marine Protected Areas).

This study is focused on Kistingebäcken tributary [Fig1] which has a length of about 2.9 km with a catchment area of 7 km2. A few industries including recycling industries and a landfill is situated at the area.

Figure [Fig1] shows a Trönningeån catchment area map, from which water samples were collected on 7 locations- 1 is situated close to the landfill. 2 is at Kistingebäcken tributary. 3 represents the point at which '1' and '2' meet. 4 is a point nearby the industry in the Kistingebäcken tributary. 5 is end of Kistingebäcken tributary. 6 is a point in Trönningeån main stream. 7 is the point nearby the intersection of Kistingebäcken tributary and Trönningeån main stream.

Water samples were collected on two different conditions- high flow and low flow. Low flow condition simply means that the water sample was collected before rain on 30th march, 4th April and 16th April of year 2017 respectively. And high flow condition means sample was collected after rain on 11th and 13th of April 2017.

A 100-ml clean glass bottle with 1 ml of nitric acid (HNO3) was used to collect 50 ml water samples using a measurement jar in all the sample locations.

Conductivity and pH of the water samples were measured using a multi meter (HANNA HI991301). The measurement of pH and conductivity were directly done below the water surface.

Flow rate was measured using flow rate meter. Procedure followed was to check the number of rotations per minute. The cross-sectional area of the water sample locations was assessed using the measured length and breadth. The flowrate was estimated from the measured area and rotation from the water velocity calibration chart.

For the analysis of the heavy metals, an atomic absorption spectrophotometer was used in the laboratory at Halmstad University. Sample bottles are arranged based on the sampled location. Water samples are filtered by the addition of 1 ml of HNO3. Further filtration was done only for water sample collected from location 2 using filter paper. Initial set up of atomic absorption spectrophotometer is done. Further calibrations are made in the instrument based on the required heavy metal analysis in the water samples as given below.

The guidance values referred were obtained from the published book- Bedömningsgrunder för miljökvalitet belonging to 'Swedish Environmental Protection Agency'. These guidance values were used as a threshold value to compare with the analyzed sample values [21].

Heavy metal transport refers to the product of concentration of metal found at a location and the rate of water flow. Water samples at location 5,6 and 7 were collected on different days characterized by high and low flow.

Since the concentration of cadmium is very low, it was difficult to detect its presence with the instrument used for the study. Hence for accurate detection, advance instruments will be needed.

5. RESULTS

5.1 pH .value

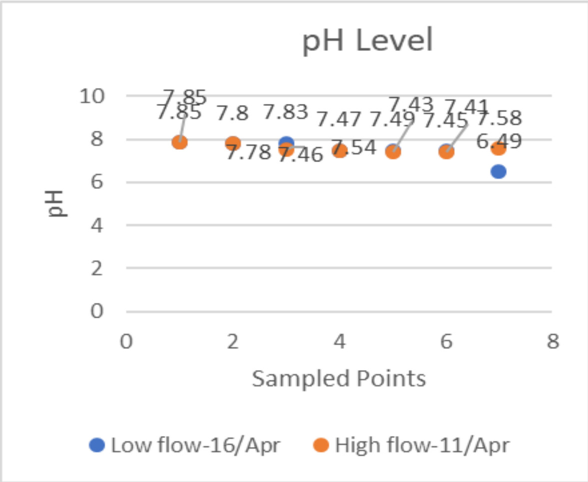

Figure 2: Graph of ph value- for both high and low flow condition (16th April and 11th April)

The pH values for the sampled location for high and low flow respectively were measured. A graph plotted with the values for high flow and low flow for different dates shows that pH value at sample locations 1 and 2 is always higher irrespective of high or low flow. The Ph values in the Trönningeån main stream is showing lower compared to Ph values at Kistingebäcken tributary.

5.2 Conductivity

The conductivity for the sampled location for high and low flow respectively were measured. A graph plotted with the values for high and low flow for different dates show that conductivity value at sample locations 1 and 2 is always higher irrespective of the flow conditions. The results of conductivity measured is like that of Ph. The conductivity values in the Trönningeån main stream is showing less value compared to Ph values at Kistingebäcken tributary.

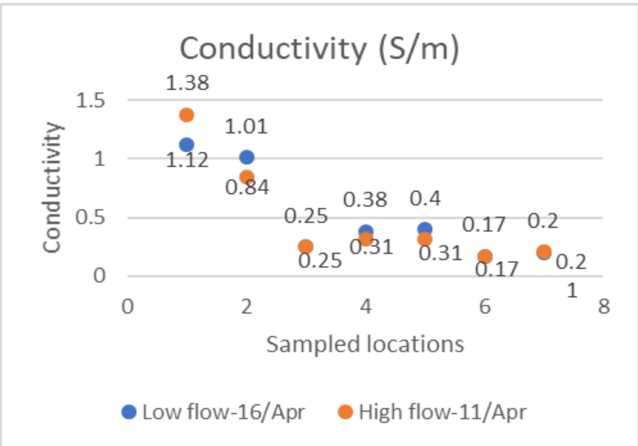

Figure 3 :Graph of conductivity- for both high and low flow condition (16th April and 11th April)

5.3 Copper concentration

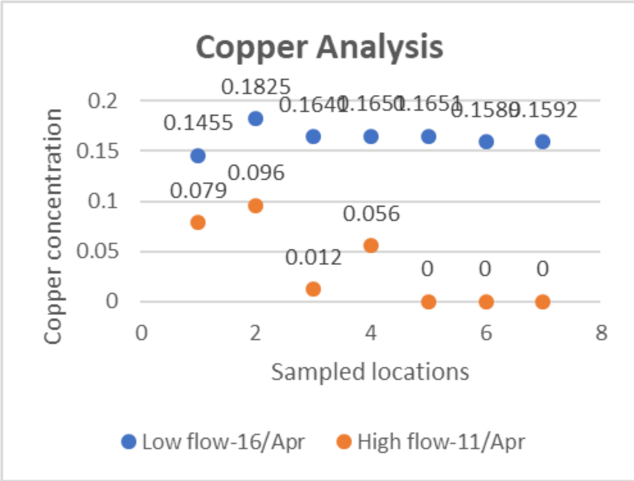

Figure 4: Graph of copper concentration for both high and low flow condition (16 April and 11th April)

When guidance value and obtained values were compared, on a low flow day, it was found that there is high risk of biological effect even with short term exposure in all the locations. Similarly, on a high flow day, locations 1,2 and 4 showed the same result as mentioned before. Location 3 showed increased risk for biological effects. For location 5,6,7 obtained sample values had negative readings, so zero value was considered in all the cases.

The analyzed values indicated that the concentration of copper was bit higher in low flow condition compared to high flow condition. Depicts that the sample values or the concentration of copper metal is higher in the tributary than the main stream. And some analyzed values are comparatively higher than guidance value as shown in the table above.

5.4 Zinc concentration

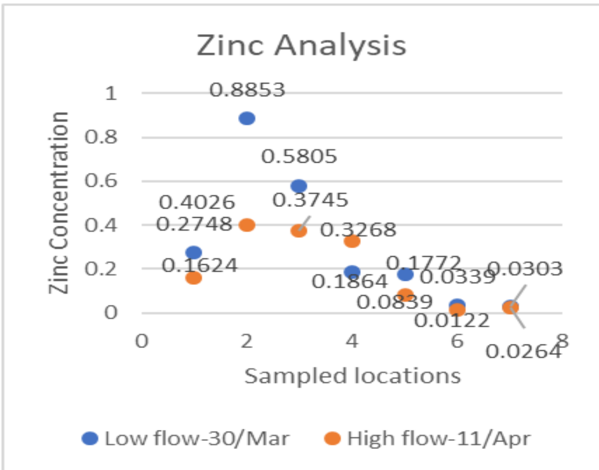

Figure 5: Graph of zinc concentration for both high and low flow condition (30 March and 11th April)

When guidance value and obtained values were compared, on a low flow day, it was found that there is high risk of biological effect even with short term exposure in the locations 2 and 3. Locations 1,4,5 showed increased risk for biological effects. And location 6,7 indicated that biological effects can occur.

Similarly, on a high flow day, locations 1and 4 showed increased risk for biological effects. Location 2,3,4 showed high risk of biological effect even with short term exposure. Location 6,7 showed biological effects can occur.

The analyzed values indicated that the concentration of zinc was bit higher in both the conditions. Depicts that the sample values or the concentration of zinc metal is higher in the tributary than the main stream. And some analyzed values are comparatively higher than guidance value as shown in the table above.

5.5Heavy metal transport

Table 1 : Heavy metal transport of copper and zinc for both high and low flow condition (kg/day) in sampled locations.

Sam. No	High/Low flow	Copper (Kg/day)	Zinc (Kg/day)
5	High	4.156116	2.097654
	Low	**9.720104**	**2.799004**
6	High	2.000609	0.954426
	Low	2.958486	0.954426
7	High	6.432307	1.177805
	Low	9.903514	1.841357

Two days were chosen taking into consideration the two different levels- Low flow level and high flow level respectively. During these two days, water samples were analyzed which were collected from three different locations (Kistingebäcken, Trönningeån and near the intersection point of the former). Samples were collected from both low and high flow levels respectively. High heavy metal flow was found in Kistingebäcken.

5. DISCUSSION

When high pH and conductivity are found in industrial stream, it signifies pollution [22]. Former pH and conductivity values, were found at locations 1 and 2, since they are near to landfill area [23]. This shows that the initial research questions proposed are satisfied with the results obtained.

6.1 Heavy metal concentration

If the concentration of copper found in water sample is high, then it causes heavy metal pollution [24]. Analyzed readings shows of the copper concentration in the water samples at the given locations. figure 5 and 6 shows the graph of heavy metal concentration at locations for both high and low flow conditions respectively. Referring the readings, copper concentration was found to be higher with respect to the guidance values given. In fact, copper concentration was found above the range of Class 5[21] which corresponds to high risk of biological effects. Concentration was found to be clearly higher at locations 1,2 and 3 (i.e., the place close to the landfill) compared to others.

However, concentration is comparatively lower at location 5 i.e., at the Trönningeån mainstream. negative readings were obtained for locations 5,6 and 7 during high flow conditions. Hence, it was marked zero. This could be owed to the fact that as it's been a high flow condition, metal concentrations could have diluted and hence was not detected in the instrument. Also, the instrument used in the study cannot determine low concentrations. From the analyzed results, it can be concluded that Kistingebäcken tributary where industries and landfills are situated contributes to the high concentration levels of copper in to the main stream.

If the concentration of zinc found in water sample is high, then it causes heavy metal pollution [25]. Analyzed readings show of the zinc concentration in the water samples at the given locations. figure 5 and 6 shows heavy metal concentration at respective locations for both high and low flow conditions. With reference to readings, zinc concentration is found to be higher with respect to the guidance values given. Once again, zinc concentration is found above the range of Class 5, which corresponds to high risk of biological effects [21] even with short term exposure at all locations. But, it is significantly higher at location 2 compared to others. However, concentration is comparatively lower at location 5 i.e., at the Trönningeån mainstream.

If the concentration of cadmium found in water sample is high, then it causes heavy metal pollution [26]. The range of cadmium concentration given as the guidance values is very low to be detected, by the instrument used for the in these studies. Hence, cadmium presence could not be detected effectively.

It has been observed that the occurrence of several toxic heavy metals leads to heavy metal pollution [27] Further study can be done on heavy metal concentrations of other metals like lead(Pb), chromium (Cr), Arsenic(As) and nickel (Ni) in the tributary.

6.2 Heavy metal transport

Metal deposits in the rural stream contribute more heavy metal transport to the main stream [28]. Results obtained in the table (1) shows that in high flow, heavy copper mass transport is observed in Kistingebäcken tributary. It is obtained that mass transport of the order of 4 kg/ day and 9 kg/ day in high flow and low flow respectively is present in Kistingebäcken tributary based on the calculations. The copper concentration is only of the order of 2.9 kg/ day in Trönningeån main stream. It is evident that Kistingebäcken stream is responsible for heavy metal pollution in Trönningeån river. From the analyzed results, it can be concluded that Kistingebäcken tributary where industries and landfills are situated contributes to the high concentration levels of copper in to the main stream.

Results obtained in the table (1) shows that in high flow, heavy zinc concentration is observed in Kistingebäcken tributary. Based on the calculations done, the weights are of the order - 2.1 kg/ day and 2.7 kg/ day in high and low flow conditions respectively in Kistingebäcken tributary. The copper mass transport is only of the order of 0.9 kg/ day in Trönningeån main stream. It is evident that Kistingebäcken stream is responsible for heavy metal pollution in Trönningeån river.

There is no cadmium presence observed in the locations. One of the limitation found in this case was, the concentration of cadmium is very low. It was difficult to detect its presence with the instrument used for the study. Hence for accurate detection, advance instruments will be needed.

6. CONCLUSION

Metal concentration and transport present at the Kistingebäcken tributary is the main contributor of heavy metal pollution to the main stream. These results are significantly alarming, concerning the amount of transport of heavy metal into the main stream.

Study gave the analysis of metal deposition with respect to concentration which concluded that the presence of copper is higher than zinc. Cadmium metal mass transport was not traced. High Ph and conductivity value were found at the Kistingebäcken tributary compared to Trönningeån main stream. Further study can be done on heavy metal concentrations of other metals like lead(Pb), chromium (Cr), Arsenic(As) and nickel (Ni) in the tributary.

Finally, study concluded that there is a very high concentration of heavy metal pollution at locations 1,2,3 and 4.

7. RECOMMENDATIONS

Heavy metal mass transportation is analyzed to be high and are even above the range of Class 5 based on the guidance values referred. Steps must be taken to ensure that either wetlands or aeration is created before the water flows into the sea to avoid further damage to aquatic organisms. It is suspected that improper recycling waste deposit at the industrial facility leads to, the heavy metal pollution with storm water. Strict action must be taken by the concerned Municipality. Further studies are required to detect the presence of cadmium. It is also recommended to analyze the presence of other heavy metals like Lead, Chromium, Nickel and Arsenic.

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