Effects of air pollution on river ecosystems

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Abstract

The inner-city traffic junction “Neckartor” located in Stuttgart, reports the highest air pollution values in Germany. *Monitoring air pollution is key to understand its harm to our environment, but is it possible to detect pollution in the water caused by traffic?*

Our research focuses on water pollution through traffic in the river “Neckar” located in Stuttgart. Not only are we interested in whether local marine wildlife is threatened by tire abrasion or other emissions but also whether a lower flow velocity at restored riverbanks helps to reduce water-pollution.

Water samples are to be taken regularly at various points from the Neckar and analyzed for gas concentration and other parameters. Furthermore, a permanent measuring station, automated via microcontroller, is planned, which will detect and store alterations in water quality. This data will be compared to the concentrations at the “Neckartor air monitoring station”. The parameters are expected not to change simultaneously but delayed in relation to the air measurement values. Additionally, it is assumed, that restored riverbank areas help reduce the particle concentration as the particles sink and are bound in the sediment. As a result, our investigations may detect the need for protective actions of local marine wildlife.

Keywords: Neckar, water pollution, air pollution, restored riverbanks

1. Introduction

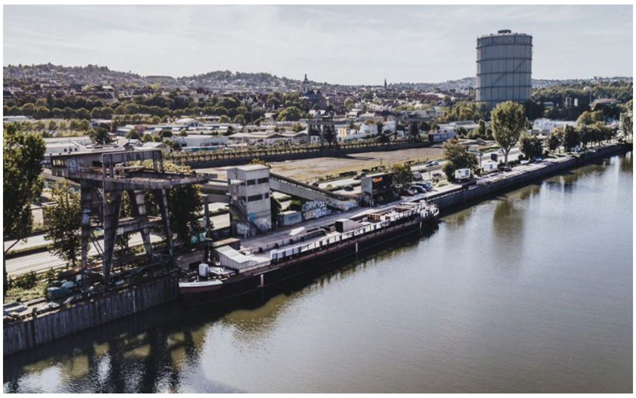
1.1 Water Pollution around Stuttgart

The Neckar is a local river in Baden-Wuerttemberg, which has a total length of 362,3 km. It is located mainly in the south of Germany (picture 1) and has an average flow velocity of 145 m^3/s.

Picture 1, map of the Neckar

Its origin can be found in Schwenningen Moos and the river itself has a long history of inland waterway transport [1]. The combination of this past and other recent influences like industry (picture 2) and sewage treatment plants (499 in total) leave the river with a poor water quality. It was and still is one of the three rivers proving the worst water quality in Germany.

The decisive parameters on which these results are based are defined by the European and National guidelines for water quality, called “Wasserrahmenrichtlinie Deutschland-gewässer”, which are enforced by the German Federal Environment Agency [2].


Picture 2, industrial area at the Neckar riverbank

The poor water quality has been influenced by several factors. Firstly, the once ineffective sewage treatment plants (even though nowadays improvements have been made [3,4]) lead to poor water quality. Secondly, the high density of hydroelectric power plants (29 in total) [5] alongside the Neckar also contributed to worsening the water quality. Furthermore, several sluices and floodgates have been built which resulted in the disappearance of most water animals that depend on running water. Additionally, former alterations regarding the natural riverbed and flow of the Neckar to improve shipping traffic in the past caused further destruction of the nearby ecosystems. This resulted in the disappearance or even extinction of several species in certain areas.

Renaturation projects aim to restore habitats for plants and animals [6]. To improve the condition of the Neckar, the city of Stuttgart introduced several actions (starting around 1970) such as upgrading the sewage treatment plants [7], building turbines and most relevant for our project, restoring bank sides [8]. These were part of the “Renaturierungsprojekt” (renaturalization project) initiated in 2012 by the mayor of Stuttgart [9]. The project proposes to restore about 17 kilometres in total as breeding habitat for typical wetland animals and the redevelopment of a highly canalized and constructed federal waterway into semi-natural wetlands [10]. The project itself succeeded and the location “Poppenweiler” (see pictures 3 and 5) is one example for a restored bank side.


Picture 3, restored bank sides

1.2 Air Pollution in Stuttgart

The measuring point for fine dust “Neckartor” (picture 4) is one of the most important in the city of Stuttgart. Due to the high air pollution, it was set a daily limit on concentration of fine dust PM10. The daily limit is 50 micrograms per cubic meter. During the first six months of 2018 the daily limit for fine dust was exceeded for 46 times. [11] To reduce the values of fine dust in the air the so called “fine dust alarm” was initiated. If, during the fine dust period from 15th October to 15th April, the German Weather Service predicted that the atmosphere would have a limited ability to exchange particulate matter on at least two days in a row, the city of Stuttgart triggered the fine dust alarm. On these days there was an appeal to car owners to use public transportation. In addition to that there was a ban on comfort fireplaces. Because of the fine dust alarm the usage of these fireplaces was banned for several months. [12]

Within the first half of 2022 [13] the daily limit was exceeded for only 3 times in total. The values are better than a few years ago but the situation regarding air pollution in Stuttgart is still worrying. Possible reasons for this might be several industrial zones such as highly congested roads alongside the river leading to high tire abrasion and other emissions.


Picture 4, air measuring station “Neckartor”

1.3 Purpose of the Investigation

The purpose of our investigation is to detect a possible connection between the water quality of the river Neckar and the air pollution in the metropolitan area of Stuttgart that the river Neckar runs through. Furthermore, we wanted to detect whether restored areas of the riverbanks have an influence on the water quality in the river. We therefore compared our own water samples to public data available from federal water and air surveillance canters.

Our expectation was to see some correlations between the concentrations of different substances in the air compared to the corresponding ones in the water. If factor A in the air increases, factor B in the water would increase or decrease subsequently. We assumed that in diagrams showing the time course of the value of one factor there would be direct correlations to the values of another factor, or that one factor would follow the other factor delayed by hours or days.

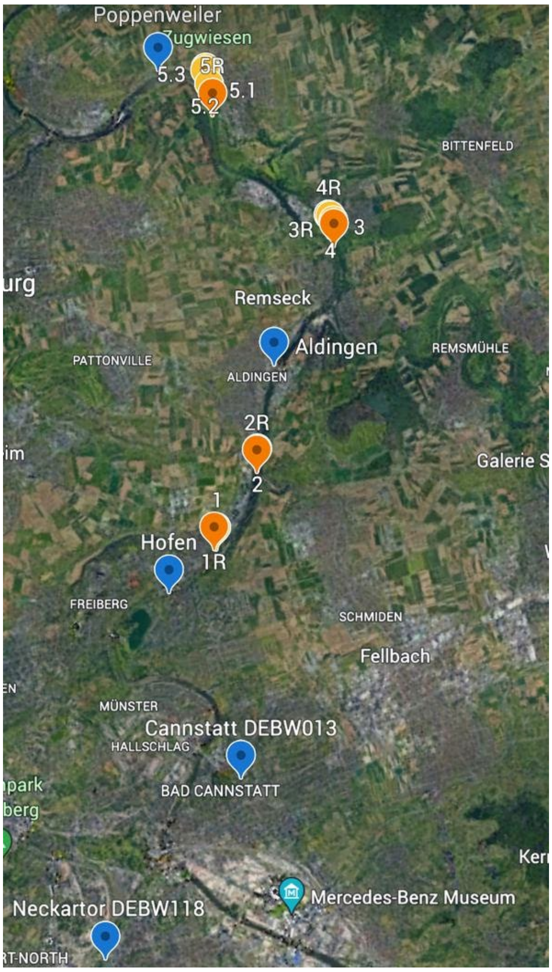
Furthermore, we detected air qualities and compared them to the water samples to find out to what extent connections between water and air conditions can be found. By examining the external factors one can identify their negative and positive man-made influences on the local ecosystem. Subsequently, further actions should be taken to protect the local waters/bodies of water since it is of great relevance for not just the environment near the river but also the whole metropolitan area of Stuttgart.

2. Methods and Material

2.1 Taking Water Samples

To detect the relevance of the restored bank sides water samples at chosen stations were examined (picture 5).

The sites to be studied were chosen according to their accessibility, the possibility of reaching the shore without destroying nature, and whether interesting results could be expected. At location number 5 due to its bigger size even 3 samples plus a reference sample were taken. At each site, a sample was taken from the restored riverbank and a reference sample from a non restored area of the Neckar. The reference sample was taken closest possible to the actual sample site, but outside the area of the renaturalization marked with an R in picture 5.



Picture 5, public measuring stations:
Poppenweiler: measuring station at restored bank sides
Hofen: measuring station at restored bank sides
Aldingen: measuring station near a sewage treatment plants
Cannstatt: air measuring stations
Neckartor: air measuring stations

Before taking the sample, the sample bottles were rinsed several times with the water from the river. This was done a short distance downstream to avoid turbulences and interferences at the sample site. The water was taken with a minimum distance of 40cm to the riverbank in a depth of 30cm below the water surface. Care was taken not to cause turbulence at the bottom of the Neckar as this could have affected the measurement.

Series 1 was taken on August 21, 2022.

Series 2 was taken in the same way as Series one just another day, shortly after a rainfall on August 28, 2022.

In the first series of measurements, two samples and two reference samples were taken. One (the one used for oxygen measurement) was treated with chemicals and then sealed as airtight as possible, unfortunately leaving a small amount of air in the sample container. The samples were then transported home for examination. Some shaking could not be avoided along transport.

Measurements of the oxygen concentration in series 2 were carried out directly to avoid shaking.

For analysis of the water samples, we used a MColortest #1.11151.0001 Merck Millipore compact water laboratory produced by the Merck KGaA Darmstadt, Germany. Testing was done according to the manufacturer's instructions. Testing is based on titration and comparison of color of the solution with a color bar (colorimetry) [14,15].

2.2 Measuring pH Value in Water

pH refers to the Acidity i.e., the concentration of Hydronium (H_3O^+) ions. pH was measured using universal indicator, a solution of multiple indicators covering the entire pH scale in their color changing range. Indicators are themselves weak acids/bases and thus can be (de-) protonated by Hydronium or Hydroxide ions present in the sample, through this process their interaction with light changes, which results in a change in color of the solution. The pH is usually calculated as the negative decimal logarithm of the concentration of Hydronium ions.

$$pH \approx -log_{10}(\frac{c(H_3O^+)}{mol * l^{-1}})$$

Measuring range: 1-14

2.3 Measuring Oxygen Concentration in Water

For measuring of dissolved oxygen concentration, a Winkler titration was used. This works by having the oxygen reduce a surplus of Mn(II), under alkaline conditions, to $MnO(OH)_2$.

$$2\ \mathrm{Mn}^{+}_{2\ (aq)} + \mathrm{O}_{2\ (aq)} + 4\ \mathrm{OH}^{-}_{(aq)} \rightarrow 2\ \mathrm{MnO(OH)}_{2\ (s)} \quad (1)$$

After this excess acid is added which enables the iodide (I^-), also added in step one, to be oxidized to elemental iodine (I_2).

$$\mathrm{MnO(OH)}_{2\ (s)} + 2\ \mathrm{I}^{-}_{(aq)} + 4\ \mathrm{H_3O}^{+}_{(aq)} \rightarrow \mathrm{Mn}^{2+}{}_{(aq)} + \mathrm{I}_{2\ (aq)} + 7\ \mathrm{H_2O}_{(l)} \quad (2)$$

Following this step starch indicator is added, complexes with the iodine and results in a blue coloration of the solution. In the last step this solution is titrated with sodium thiosulfate ($S_2O_3^{2-}$) until decoloration of the solution.

$$2\ \mathrm{S_2O_3^{2-}}{}_{(aq)} + \mathrm{I_2} \rightarrow \mathrm{S_4O_6^{2-}}{}_{(aq)} + 2\ \mathrm{I}^{-}_{(aq)} \quad (3)$$

From reactions (1,2,3) a stoichiometric equivalency emerges, from which one can calculate the approximate concentration of dissolved Oxygen in the original Sample.

Measuring range: 0.1 – 10 $mg * l^{-1}$

2.4 Measuring Nitrate Concentration in Water

Nitrate is reduced to Nitrite, which, together with Sulfanilic acid, forms a diazonium salt. This, in a further step, undergoes azo coupling with 2,5-dihydroxybenzoic acid to form an Orange-Yellow azo dye. Nitrate concentration can then be deduced by color intensity.

Measuring range: 10 – 150 $mg * l^{-1}$

2.5 Measuring Orthophosphate Concentration in Water

Orthophosphate ions (PO_4^{3-}) react with molybdate ions, for example from ammonium molybdate, in an acidic environment to form phosphomolybdic acid. This product is in turn reduced to a molybdenum blue compound, which can be determined colorimetrically.

2.6 Deriving Data of Air Pollution

Data of air pollution could be derived from a federal measuring station that can be accessed publicly online (Luftverschmutzung in Stuttgart Am Neckartor) [16]. The measured values were automatically obtained by a program every hour from public APIs (Application Programming Interface). This time interval was chosen because the water values were equally updated hourly. The water values are taken from the API of the German "Lupo-Cloud" [17] which is among others operated by the "Landesanstalt für Umwelt Baden-Würtemberg" LUBW [18]. The LUBW is a federal institution that deals with environmental issues. This institution operates measuring stations near the floodgates in the Neckar. Recorded data are time, turbidity [FNU], temperature [°C], oxygen concentration [mg/l] and pH-value. In the area observed in this paper the measuring points are "Hofen", "Aldingen", and "Poppenweiler".

The air values come from the air sensors "DEBW013" in "Cannstatt" and "DEBW118" at the "Neckartor". These stations are also operated by the LUBW. However, we obtained the values from the opensource third party service "Luft.jetzt" [19] which translates to "Air.now", because their web applications were easier to use. From the provided values of the LUBW we saved the particle PM10 [µg/m³], the ozone [µg/m³] and the nitrogen dioxide [µg/m³] values, because "Luft.jetzt" only delivered these.

Because all factors were subject to extreme cyclical fluctuations throughout the day, we took an average value per each 24 hours.

2.7 Ozone-Oxygen Cycle [20]

$$O_2 \xrightarrow{sun\ light} 2\,O \quad (4)$$

$$O + O_2 \rightarrow O_3 \quad (5)$$

$$O_3 \xrightarrow{sun\ UV\ light} O + O_2 \quad (6)$$

$$O + O \rightarrow O_2 \quad \text{or} \quad O + O_3 \rightarrow 2\,O_2 \quad \text{or} \quad \text{Eq.(5)}$$

3. Results

3.1 Results from Series 1

Figure 1: Concentration of oxygen in riverwater in mg/l in series 1, August 21, 2022

Location	Sample	Reference Sample
1	11.7 mg/l	10.6 mg/l
2	12.7 mg/l	Ship distortion
3	12.8 mg/l	8.1 mg/l
4	11.4 mg/l	11.1 mg/l
5.1	Ship distortion	11 mg/l
5.2	11.8 mg/l	
5.3	13.6 mg/l	

Figure 2: Comparison of oxigen concentration in sample and reference in series 1

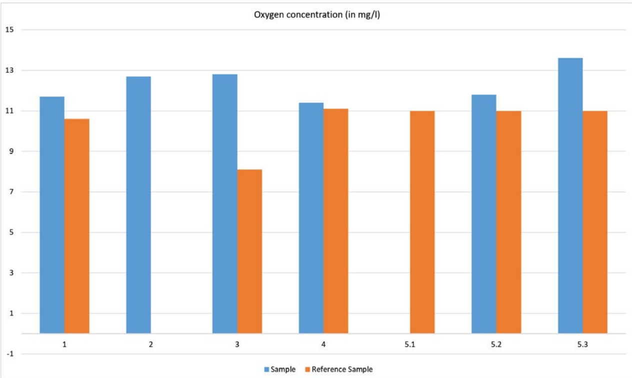


Figure 3: pH-, nitrate and phosphate -values from series 1 according to measuring spots from picture 3

	pH-value	nitrate	phosphate
1	7.75	12	~ 0.4
1R	7.75	11	~ 0.4
2	7.8	11	~ 0.4
2R	7.8	11	~ 0.4
3	7.6	11	~ 0.4
3R	7.6	11	~ 0.4
4	7.6	11	~ 0.4
4R	7.6	11	~ 0.4
5.1	7.5	10	~ 0.4
5.2	7.8	9	~ 0.4
5.3	7.5	10	~ 0.4
5R	7.5	11	~ 0.4

3.2 Results from Series 2

Figure 4: Concentration of oxygen in riverwater in mg/l in series 2, August 28, 2022

Location	Sample	Reference Sample
1	5.8 mg/l	5.0 mg/l
2	4.8 mg/l	4.1 mg/l
3	4.3 mg/l	3.6 mg/l
4	3.4 mg/l	3.4 mg/l
5.1	4.3 mg/l	4.5 mg/l
5.2	5.4 mg/l	
5.3	6.4 mg/l	

Figure 5: Comparison of oxigen concentration in sample and reference in series 2

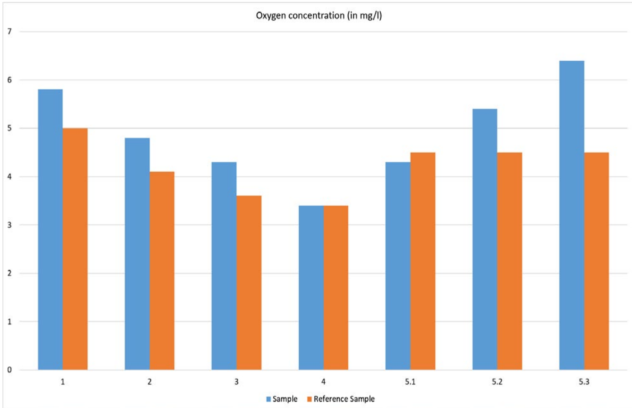
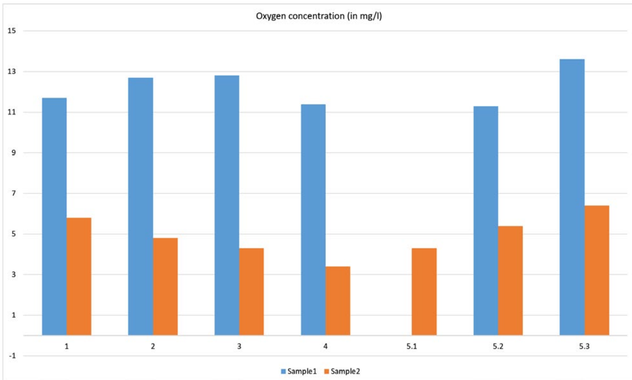


Figure 6: Comparison of oxigen concentrations in samples of series 1 and series 2



3.3 Data from Federal Measuring Points

Figure 7: pH-Value of the Neckar as measured by the LUBW between 27-7-2022 and 28-8-22

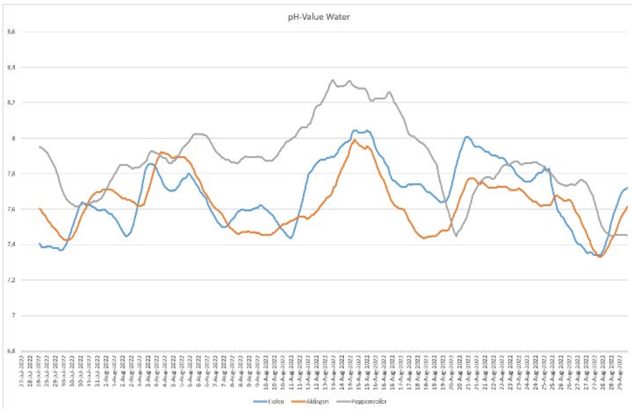


Figure 8: Oxygen concentration in water and Ozone Concentration in air as measured by the LUBW between 27-7-

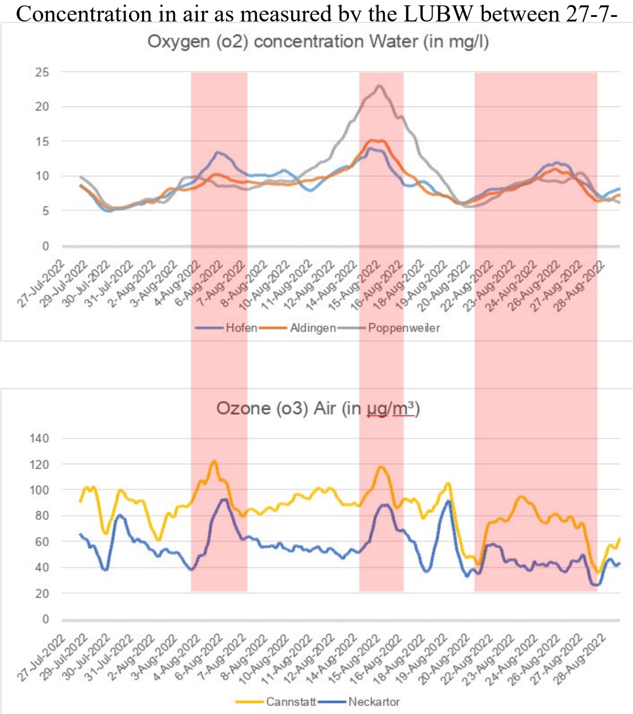


Figure 9: Comparison of turbidity in the water and particulate matter in the air as measured by the LUBW between 27-7-2022 and 28-8-2022

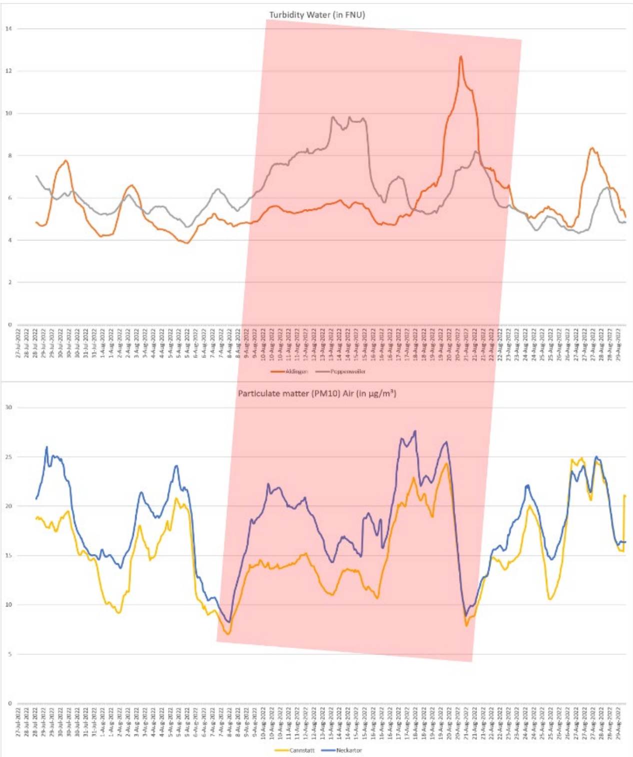
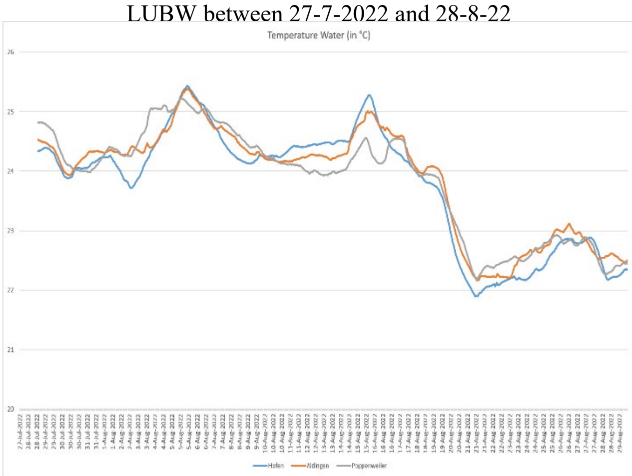


Figure 10: Water temperature in the Neckar as measured by the LUBW between 27-7-2022 and 28-8-22



4. Discussion

As seen in figure 3 sample values of pH, nitrate and phosphate did not differ significantly from each other in sample and reference of series 1. There was either no change in these values or our testing method was not sensitive enough to detect changes. As these values base on titration and comparison of the color of the solution with a color bar (colorimetry), all values are influenced by human subjectivity. We therefore concluded that our method simply was not enough sensitive for what we wanted to detect. We therefore decided not to repeat these measurements in series 2. Our methods of testing simply seemed to be insufficient for these measurements. No meaningful statements could be derived from these results in terms of comparison of sample and reference. However, if comparing the different locations of sample taking, it can be stated that the pH value drops downstream the Neckar with increasing distance to Stuttgart. As drinking water has a pH value around 6.5 this drop is to be interpreted as an improvement in water quality. Our hypothesis that the restored areas lead to a decrease of particles and thus improve the water quality could be a part in this. On the other hand, there are other rivers flow into the Neckar on its course from sample point one through five that might also contribute to the better water quality at point five.

The samples taken for this paper were taken in a quickly changing environment with biasing factors such as occasional events and natural factors. Occasional events as passing ships mixing water and mud were to be seen as an unpredictable factor. Samples taken a few minutes after a ship passed were cloudier and there was a smaller difference in oxygen concentration between the sample and its reference. However, the fact that the passing of ships led to an all over lower oxygen concentration showed their negative impacts on the environment in terms of wildlife and fauna if a high oxygen concentration is seen as a positive factor for the latter.

Series 2 was taken shortly after a rainfall. Oxygen concentrations of that series (figures 2 and 5) were significantly lower than in the first series for both, samples and reference samples. Rain therefore seems to have a major impact on the oxygen concentration in the water.

In almost all cases the oxygen value in the sample is higher than the value in the reference sample (figures 2 and 5), i.e., in the restored area the oxygen concentration is higher than in the non restored areas (figure 6). This can be interpretated as a clear benefit for fauna and flora in the restored areas. Renaturalization therefore needs to be further pursued in the area and can be recommended for other metropolitan areas with likewise problems of water pollution.

It was not possible to obtain data about the correlation between particle concentration in the water at the restored areas compared to the non restored areas, but the difference in oxygen concentration might be influenced by many different factors including pollution particles. This is subject to further investigations and shows that our data are not suitable for detection of an impact of air pollution on water pollution.

Our own data was far too inaccurate and too little to allow clear statements on our questions. We could not answer the question whether water pollution is directly connected to air pollution. The comparison of the public data allowed on the other hand more detailed analysis and statistically based statements. We could see that rising water temperatures (figure 9) correlate with a) rising ozone values in the air (figure 8), with b) a rising oxygen concentration in the water (figure 8) and c) a rising pH value in the water (figure 7). This gives reason to suspect that the air and the water are connected and influence each other´s pollution. The correlation between oxygen concentration in the water and ozone concentration in the air (figure 8) can possibly be traced back to the ozone-oxygen cycle (picture 6).

We also investigated the correlation between the particulate matter concentration in the air and the turbidity of the water (figure 9). The curves seem to follow each other to a certain extent. It is, however, difficult to know, whether this is a direct impact of one another, or whether it is a multi-factoral phenomenon with high temperatures in air and water (figure 10), high water evaporation, no rain, low water levels and other factors influencing each other respectively, including particulate matter concentration and turbidity of the water.

The complexity of this research and the difficulties of evaluation and extracting data show that the balance between water and air is a very sophisticated ecosystem that needs to be further studied and protected.

Our experimental setup was not suitable to raise valid data with our means of examinations. With our data it was not possible to detect an influence of air pollution on water pollution. We were discussing other methods and experimental set ups to extract biasing factors. Our idea was to place a bucket with water beside a very busy traffic road. The bucket should, however, be covered for rain protection, as we learned that rain might change the outcome. Furthermore, it should be protected from wind, as wind influences the water surface and temperature. This experiment needs to be thought through more precisely if executed. The advantage with our current experiment is, however, that it was executed in a more natural surrounding and not in a theoretical background as the one described with the bucket. We therefore could make some guesses about possible linkages that might not have been possible in a completely experimental surrounding.

5. Conclusion

As we engaged into the subject, it can be found out that our means of investigation are too basic to answer our primary questions. However, we could see that oxygen concentration in the river Neckar is higher in restored areas compared to non restored riverbanks and thus the river and its ecosystem benefit from these restored areas. We also could see that water and air parameters seem to influence each other and therefore need to be further investigated. Better methods and larger data volumes are needed for better understanding and statistically significant statements. Other experimental setups that eliminate many factors could help to focus on singular parameters while studying the complexity of the impact of air pollution on water quality.

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All diagrams were created by the writers of this paper.