

An Investigation into Organic Water Pollution in the River Adur Using the Winkler Test for Dissolved Oxygen

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Abstract

In recent times, pollution has been at the forefront of many people's minds regarding the Worthing-Shoreham coastline and the River Adur, after a major sewage leak event in 2012. In this investigation I set out to quantify the level of organic pollution of the river water (due to sewage, insecticides, etc.), to put local people at ease, although mainly to explain the strangely stark change in water colour along the 7km stretch of river between Upper Beeding and Shoreham.

I collected 6 sample points (with two 500ml bottles of water being taken for each), and analysed the water twice (5 days apart) using the Winkler method for dissolved oxygen, in order to determine the BOD of the water at those 6 points - an indicator of organic pollution.

Results showed a positive correlation between the distance of sample points from a reference point (r) on the river in Shoreham and the BOD of those samples' water; in other words, the water became increasingly polluted with increasing distance from the town, with water in Upper Beeding measuring over 700% the BOD values adjacent to the reference point in Shoreham.

However, due to time constraints on the amount of analysis which could be done, and the precision which could be obtained without taking chemicals and specialist equipment out of the lab, the error uncertainties in the BOD values undermined any clear correlation, meaning few conclusions could be reached regarding the research question. The results did, however, demonstrate that the BOD (and thus, the level of organic pollution) was higher on average nearer to Upper Beeding, than to Shoreham – in support of the original hypothesis.

(graphics created with Blender3D)

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Introduction

The River Adur is a tidal river, which, towards its mouth, flows through Upper Beeding, and finally through Shoreham Harbour. The river and the surrounding coastline are home to many species of wildlife (notably, also to the RSPB Adur Estuary Nature Reserve), and often attract many swimmers, kayakers, and beach-goes. However, during a 2012 pump failure at East Worthing waterworks (located approximately 10 km east of the mouth of the Adur), raw sewage was pumped into the sea, and the public was warned to stay out of the water temporarily, as the sludge reached as far west as Shoreham beach. [3]

So, when I was first introduced in class to BOD (biological oxygen demand) and the Winkler titration, which, combined, enable the measurement of organic compounds dissolved in water, I was immediately reminded of the pollution of the Worthing-Shoreham coastline, and the River Adur thereon.

The Winkler test for dissolved oxygen is a titration, which is used to determine the concentration of oxygen in water and can therefore be used in the process of determining BOD. BOD is defined as the quantity of dissolved oxygen used by the aerobic organisms in a given water sample, over a period of 5 days, as the said organisms break down organic material in the water sample; thus, BOD is an indicator of organic pollution. This organic pollution can be caused by detergents, petroleum compounds, insecticides and sewage, among other things. [1][2]

I decided to utilise the Winkler method to determine the BOD of water samples at various points along the River Adur, to address the following research question:

How will the BOD of water samples from the River Adur vary with those samples' proximities to Shoreham Town/Harbour (measured by distance along the centre of the river).

By investigating the relationship between the river water's geographical location, and its organic pollution level, I hoped to establish whether (or not) the river was polluted beyond recommended levels for swimming, as a result of the 2012 leak, or of others like it. If this was the case, I would expect to see an abnormally high level of organic pollution* remaining uniform regardless of sample position.

However, my main motivation for pursuing this question changed when I observed the stark contrast in the colour and opacity of the river water, which slowly changed from almost colourless in Shoreham, to a murky brown in Upper Beeding (see Figure 1), suggesting increased levels of organic pollution.



(a) Shoreham harbour



(b) Upper Beeding

Figure 1: See above photos (both my own) – note drastic difference in colour and opacity of water

This observation initially puzzled me, as I had assumed that the water quality would *improve* with increased distance from the harbour/town if at all, but I hypothesised:

The water samples' measured BOD values will correlate positively with those samples' proximities to Shoreham Town/Harbour.

My justification for this proposition was that I suspected insecticides and other organic pollutants from the farmland surrounding Upper Beeding were contaminating the river and causing the darkening in colour, and an increase in organic pollution levels, possibly beyond safe levels for recreation *.

* see Appendix A for literature BOD values

Method

As mentioned above, BOD is a measure of the amount of dissolved oxygen which is used by the aerobic organisms in a given water sample, as the said organisms break down organic material in the water sample over an incubation period of 5 days. It is, therefore, effectively the amount by which the concentration of dissolved oxygen reduces over those 5 days, which can be found by performing the Winkler titration (to determine oxygen concentration) twice on the water sample: once immediately (or as soon as possible) after collection, and once again 5 days later.

To investigate the variation in BOD along the river, I took two 500ml samples at each of 6 points - A, B, C, D, E, and F (see Figure 2). The sample points were approximately distributed at 2km intervals along a 7.5km stretch of river, from the bridge at Upper Beeding, to a sharp turn in the river, just outside of Shoreham harbour.

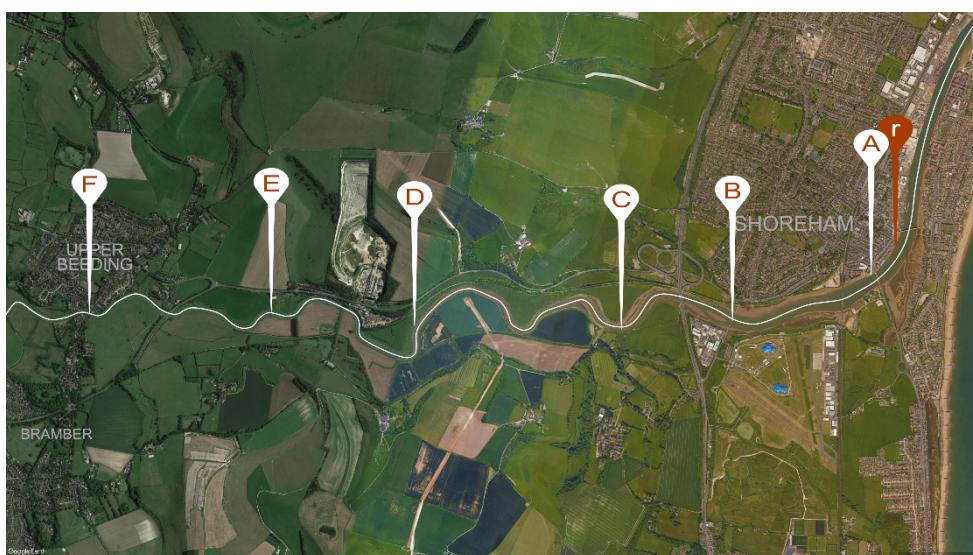


Figure 2: Map of sample points A, B, C, D, E, and r, the reference point from which the distance of the sample points to Shoreham were measured

However, because I feared that organic pollution levels from slower-moving/stagnant sections of the river would not be representative of majority of the (moving) river water at those points, I prioritised taking samples from bridges and jetties*, and on the outside of meanders in the river when none were close-by. At each sample point I noted down my location (as longitude and latitude – see Appendix B), using a smartphone.

Ideally, the first sample at each point would have its oxygen concentration frozen immediately, by adding manganese (II) solution, alkaline potassium iodide solution, and concentrated hydrochloric acid. However, these substances could not be taken out of the lab (see Figure 7), so extra precautions were required to ensure that a minimal amount of extra oxygen dissolved into the water before analysis in the lab. These included removing air bubbles from the sample bottles, avoiding any aeration of the water where possible, and transporting and incubating the bottles under a dark plastic bag, to prohibit any photochemical reactions, which might affect the concentration of dissolved oxygen, from taking place.

Ensuring a minimal amount of trapped air within sample bottles would have been trivial, had I been able to access the river water directly (in a boat for example): I would have simply secured the bottle caps underwater. However, due to the high banks and strong currents characteristic of the Adur (see Figure 4), as well as financial limitations, this was not possible, so I developed a pumping system.

This consisted of a manual fluid pump, attached to a 5m hose pipe and shorter output pipe (both of radius 12mm), the former of which I directed into the river using either a rock (when sampling from a bridge) or using a modular pole system** (when sampling from the river bank), and the latter of which I directed into the sample bottles (see Figure 3)

* Especially at low tide, although I took care to collect samples at a roughly consistent tidal water height (see Appendix B)

** Which I constructed out of bamboo sticks and oak, and which could be dismantled for transportation before being assembled using duct tape at each sample point.

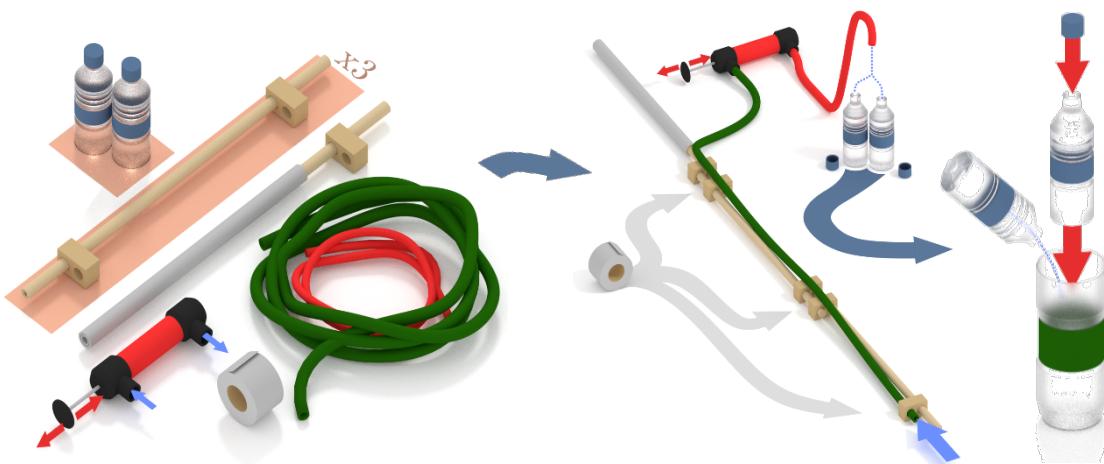


Figure 3: Sampling procedure, using pump system

Besides the twelve 500ml bottles which I purchased to contain the samples (2 from each of 6 sample points), I also used 1 extra 500ml bottle, as well as a larger 1L bottle, with the top cut off so as to allow the sample bottles to slide inside completely, with a few centimetres space on top. For each of the 12 sample bottles, I filled up both that bottle and the spare to almost the very top, before placing the sample bottle in the 1L outer container. I then slowly filled the outer container with the water from the spare bottle, gently allowing the water to fill the inner sample bottle, ensuring that all bubbles within were released. I then fastened the cap of the inner sample bottle under the water held by the outer container, again ensuring not to introduce air bubbles. This method (see Figure 3) reduced the size of trapped bubbles within the sample bottles to a few millimetres in diameter, compared to simply filling the sample bottles directly.

See Figure 4 (below) for the risk assessment of the above procedure.

Figure 4: Procedural risk assessment

Procedure	Hazards			Control Measures
ALL	Researchers should remain together in a group, with mobile devices on their person at all times.			
Water Collection	Water-borne disease; notably →	Illness	Symptoms	<p>Researchers should be cautious not to ingest any river water; a syphon pump and extension tubing should be used wherever possible, in order to limit exposure.</p> <p>Hand soap should be used when collection is complete, in order to remove pathogens on the hands as quickly as possible.</p> <p>Collection should pause to seek medical attention if any skin is broken.</p> <p>Researchers should regularly check themselves and colleagues for symptoms listed (left): if identified, medical attention should be sought immediately.</p>
		Weil's Disease (Leptospirosis)	lethargy, diarrhoea, headaches, vomiting and muscle pain; often fatal if untreated	
		E. Coli	vomiting and diarrhoea	
		Botulism	blurred or double vision, vomiting and abdominal cramps; high temperature and respiratory failure can occur	
		Cryptosporidiosis	lethargy, vomiting, headaches, diarrhoea, and a rash about the abdomen	
	Strong tides [falling into river]			Researchers should avoid submersion in river, especially if unable to swim. If this occurs and the person is in immediate danger, emergency services should be called.
	Collision with watercraft			Wherever possible, collection should be performed a suitable distance from any docked boats, and not in the immediate vicinity of any large/moving vehicles.
	Quicksand/mud			Collection on soft river bank should be avoided where possible: if anyone becomes stuck and is in immediate danger, emergency services should be called.
Transportation	Transportation of high volume bottles by foot or cycle, causing collision with other road vehicles, or loss of samples			Samples should be transported by car

Determining Concentration of Dissolved Oxygen (adapted from CLEAPSS method [5])

I then performed the Winkler titration twice for each sample point- a total of 24 times. This was done to determine the concentration of O₂(aq) in the water before and after the incubation period. The chemicals and equipment required for this process are listed in full (along with a diagram of one stage of my lab setup) in Appendix C. Equipment was rinsed copiously with distilled water throughout procedure.

I prepared the following solutions, A and B, prior to sample collection, to reduce the amount of lag time between sampling and analysis.

Manganese (II) solution – Solution A

I measured 80.0cm³ ± 0.5cm³ of distilled water, using a 150cm³ measuring cylinder, and poured it into a 100cm³ beaker.

I weighed out 39.00g ± 0.01g of manganese (II) sulfate (VI)-1-water using a balance, and gently poured it into the beaker of water. The manganese sulfate did not immediately dissolve despite rigorous heating and mixing using a magnetic stirrer but did so after a 24h period left untouched.

I transferred the solution back into the measuring cylinder and made the solution up to 100.0cm³ ± 0.5cm³, before transferring the solution to a labelled darkened bottle.

Potassium iodide solution – Solution B

I measured 70.0cm³ ± 0.5cm³ of distilled water, using a 150cm³ measuring cylinder, and poured it into a 100cm³ beaker.

I weighed out 4 lots of 8.00g ± 0.01g of sodium hydroxide (NaOH) pellets into 4x 10cm³ beakers using a balance. One by one, I dissolved these beakers of NaOH pellets into the beaker of distilled water, mixing (using the magnetic stirrer) and cooling the solution to below 20° (using the ice bath and thermometer) after adding each one.

Using a funnel, I transferred the solution back into the measuring cylinder, and made the solution up to 100.0cm³ ± 0.5cm³, before transferring the solution back to the 100cm³ beaker.

I then weighed out of 14.00g ± 0.01g of potassium iodide, and carefully added it to the solution. Once I had confirmed that the solution had cooled below 30° (using the ice bath and thermometer) I mixed the solution thoroughly and transferred it to a labelled darkened bottle.

Next, I prepared the water samples, by transferring the water from one of the 2 500ml bottles for each of the 6 sample points into 2 labelled 250.00cm³ ± 0.15cm³ volumetric flasks (the other six bottles were kept stored under the bin bag). However, because it was hard to fill the flasks accurately, I estimate the volume of solution used in each titration to be 250cm³ ± 1cm³.

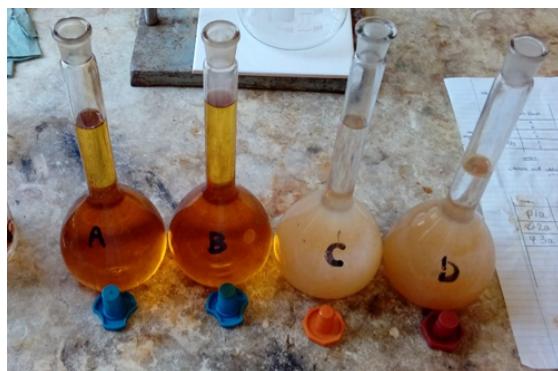


Figure 5: Flasks A, B, C, and D with Sol. A & Sol. B, added to water flasks A & B with conc. HCl also

I then added 1.00cm³ ± 0.15cm³ of Solution A, 1.00cm³ ± 0.15cm³ of Solution B, and 1.50cm³ ± 0.15cm³ of concentrated sulfuric(VI) acid (see Figure 5), using separate pipettes for each solution to avoid forming precipitates in the pipettes.

Next, one by one, I transferred the solutions to the 500cm^3 conical flask, topped up the sodium thiosulfate in the burette, and titrated the solution in the conical flask against the sodium thiosulfate until the solution in the conical flask lost most of its colour (dark-orange to straw-coloured; i.e. was near the end point). I then added $2.00\text{cm}^3 \pm 0.15\text{cm}^3$ starch solution (causing the solution to turn extremely dark blue), using a pipette, and continued to titrate the sodium thiosulfate against the solution until it turned colourless (see Figure 6).

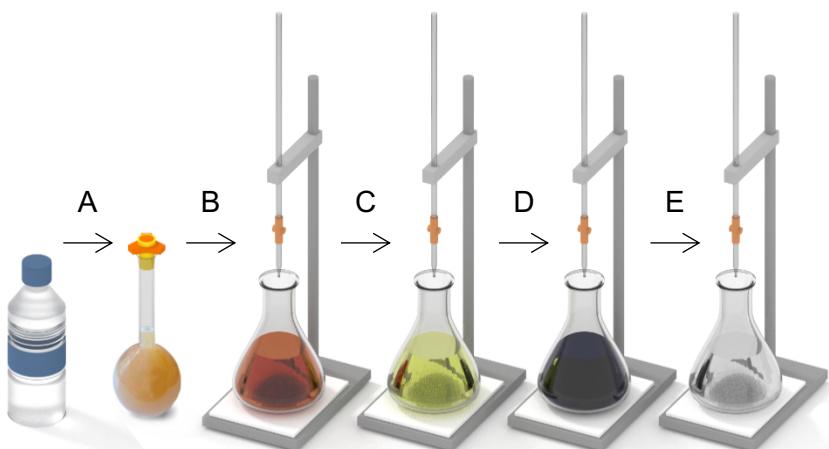


Figure 6: titration diagram – see list below

- A. transfer half to vol.flask; add Sol.A, Sol.B
- B. transfer to conical flask; add conc. HCl
- C. titrate against sodium thiosulfate
- D. add starch indicator (near endpoint)
- E. titrate against sodium thiosulfate

I repeated the above procedure for the other 6 of the sample bottles 5 days later, in order to determine the BOD of the water. See Figure 7 (below) for the risk assessment of the above procedure.

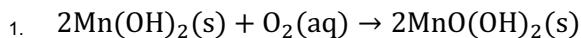
Figure 7: Chemical risk assessment; *ps* = *per sample*

Substance in Use	Amount	Hazards	Control Measures
Manganese (II) Sulfate (VI)	39 g	Serious hazard to health: may cause damage to organs through prolonged or repeated exposure.	Wear eye protection Avoid raising dust (when using powdered solids)
Manganese (II) solution (2.3M) (Solution A)	100 cm ³ (1 cm ³ ps)	Toxic to aquatic life with long lasting effects	
Sodium Hydroxide (pellets)	32 g	Solid: Corrosive (skin and eyes) Solution: Irritant (skin and eyes)	Wear eye protection; take care to avoid skin contact (use spatula or forceps to transfer)
Potassium Iodide	14 g	<i>Not generally classified as hazardous, however:</i> Causes skin irritation , serious eye irritation , organ damage (through repeated/prolonged exposure) Prepared solution is corrosive .	A lab coat, gloves, and eye protection (goggles) will be worn during the procedure. The procedure will be performed in a fume cupboard, with the transparent
Alkaline Potassium Iodide solution (Solution B)	100 cm ³ (1 cm ³ ps)		Eye protection (goggles) and a lab coat will be worn at all times DO NOT INJECT CHEMICALS
Sodium Thiosulfate solution (0.01M)	titrated ps (~1000 cm ³ total)	May cause skin/eye irritation	Wear goggles, avoid skin contact if possible
Starch solution (1%)	2 cm ³ ps (~60 cm ³ total)	May cause skin/eye irritation	Wear goggles, avoid skin contact if possible
Concentrated Sulfuric Acid	1.5 cm ³ ps (~ 45 cm ³ total)	Corrosive: causes severe skin burns and eye damage . Reacts vigorously with water (exothermic).	Avoid contact with water and humans; In an emergency: Use water to counteract exothermic reaction. Remove contaminated clothing Quickly wipe up/off excess liquid
(river water)	250cm ³ ps (collected in excess)	Water-borne disease; see Figure 4: Water Collection	

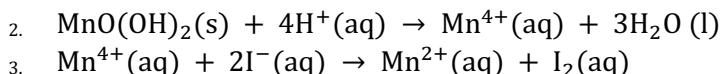
Theoretical Analysis

Firstly, I considered the chemical reactions which occur throughout the Winkler titration [1] [5], in order to create a set of equations, which would allow me to fill in the BOD data automatically, given the titration results.

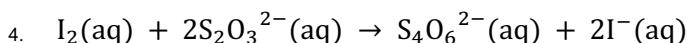
Manganese (II) solution and alkaline potassium iodide solution are added to the sample water, and, under those alkaline conditions, the Mn (II) is oxidised to Mn (IV) by the dissolved O₂, forming a brown precipitate.



Then, concentrated sulfuric acid is introduced, and iodine ions are oxidised to I₂ by the Mn (IV) ions.



This solution is then titrated against sodium thiosulfate, Na₂S₂O₃, using starch to enhance the endpoint.



From the above equations, the following stoichiometric ratio can be derived:



$$\therefore n. \text{O}_2 : n. \text{S}_2\text{O}_3^{2-} = 1:4$$

$$\therefore n. \text{O}_2 = \frac{1}{4}(n. \text{S}_2\text{O}_3^{2-}) = \frac{k}{4}, \text{ where } k = n. \text{S}_2\text{O}_3^{2-}$$

This is the number of moles within a given sample, which is of volume 250cm³ ± 1cm³. Therefore, to find the number of moles of oxygen in 1dm³, we must divide by this volume, in dm³.

$$\begin{aligned} \therefore [\text{O}_2] &= \frac{k}{4} (0.250 \pm 0.001)^{-1} \\ &= k(1 \pm 0.004)^{-1} \end{aligned}$$

Now, k is the number of moles of S₂O₃²⁻,

$$\therefore k = cv, \text{ where:}$$

$$c \approx 0.01\text{M}*, \quad v = 10^{-3}(x \text{ cm}^3 \pm 0.06 \text{ cm}^3) \text{ dm}^3$$

where x is the titration result in cm³

$$= [x \cdot 10^{-3} \pm 6 \cdot 10^{-5}] \text{ dm}^3$$

$$\therefore k = 10^{-2} \cdot (x \cdot 10^{-3} \pm 6 \cdot 10^{-5})$$

$$= [x \cdot 10^{-5} \pm 6 \cdot 10^{-7}] \text{ mol}$$

$$\therefore [\text{O}_2] = \frac{x \cdot 10^{-5} \pm 6 \cdot 10^{-7}}{1 \pm 0.004}$$

$$= \frac{x \cdot 10^{-5} \pm (\frac{6}{x})\%}{1 \pm 0.4\%} = x \cdot 10^{-5} \pm \left(\frac{6}{x} + 0.4\right)\% \text{ (mol dm}^{-3}\text{)}$$

$$m = M_r \cdot n = 32x \cdot 10^{-5} \pm \left(\frac{6}{x} + 0.4\right)\% \text{ (g dm}^{-3}\text{)}$$

$$= 0.32x \pm \left(\frac{6}{x} + 0.4\right)\% \text{ (mg dm}^{-3} = \text{ ppm)}$$

$$\pm \left(\frac{6}{x} + 0.4\right)\% = \pm 10^{-2} (6 + 0.4x)$$

* I estimated that the uncertainty of the concentration of the sodium thiosulfate was negligible.

The above calculations give the concentration of dissolved oxygen in a given 250cm^3 ($\pm 1\text{cm}^3$) water sample and its uncertainty, both as a function of its titration results. The BOD could then be calculated by taking the difference between the $\text{O}_2(\text{aq})$ concentration of the initial sample, and that of the incubated one; taking care to add the absolute uncertainties.

However, I still had the problem that not only were my incubation periods not 5 days, they were not all the identical in length- a consequence of lab availability. Fortunately, I had noted down all the times of sampling and of analysis (see Appendix B), so I decided to extrapolate/interpolate the measured result.

For a given incubation period, t (hrs):

$$\text{BOD}_{120h} = \frac{120}{t} \cdot [\text{BOD}_{\text{measured}}]$$

I also added some more uncertainty to account for the air bubbles in the sample bottles, and in the volumetric flasks. The air bubbles left in the bottles were approximately 5mm in diameter (on average), and I estimate approximately 0.5cm^3 of oxygen was dissolved inside the volumetric flask.

$$\begin{aligned} V_{\text{bubble}} &= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(0.5 \cdot 5 \cdot 10^{-3})^3 \quad (\text{assuming spherical bubble shape}) \\ &= 6.54 \times 10^{-8} \text{ m}^3 \end{aligned}$$

$$\therefore V_{\text{total}} = 6.54 \times 10^{-8} + 0.5 \times 10^{-6} \text{ m}^3 \approx 2 \times 10^{-6} \text{ m}^3$$

(V_{bubble} of negligible volume)

$$PV = nRT \therefore n = \frac{PV}{RT}$$

where: $P = 101 \times 10^3 \text{ Pa}$, $V = 0.5 \times 10^{-6} \text{ m}^3$, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 293\text{K}$

$$\therefore n \approx 2.1 \times 10^{-5} \text{ mol} \rightarrow 8.4 \times 10^{-5} \text{ mol dm}^{-3}$$

$$= 2.7 \text{ ppm} \rightarrow \sim \pm 1 \text{ ppm}$$

Now, assuming that my estimation of the volume of extra dissolved oxygen is correct, either all of that dissolved, or none of it did, so ideally, I should add half of that on to each O_2 concentration and increase the uncertainty by the same amount. However, seeing as the error was consistent (and so shouldn't affect any potential correlation too much), I decided not to include it initially in my calculations.

Results

The main results table (see Figure 8)* consists of the start of, end of, and change in the titrant for each of the two trials per sample bottle, as well as the average change for each sample bottle. The concentration of dissolved O_2 (as well as the percentage uncertainty, and absolute uncertainty) is then calculated using the function derived earlier (see *Theoretical Analysis*). The standard deviation (σ), an amount within which 95% of normally distributed data lies, was also calculated, and the larger of the standard deviation and the absolute uncertainty was used as the uncertainty going forward (and was highlighted green).

Next, the average change in the concentration of dissolved O_2 was calculated by subtracting the O_2 values of the two bottles for each sample point and adding the uncertainties together. Finally, the 5-day BOD was determined by using the other function derived above – considering the actual time between the analysis of the first bottle and that of the second bottle.

I measured the samples' distances to the reference point, R (see Figure 2), along the centre of the river using the polygon tool in Google Earth Pro. This process is extremely accurate, but I estimated the uncertainty to be around $\pm 0.01\text{km}$ due to human error.

I identified 3 clear anomalies and highlighted them with bold red font – not taking them into account when calculating the average for that bottle and using the absolute error instead of the standard deviation (which would have been 0).

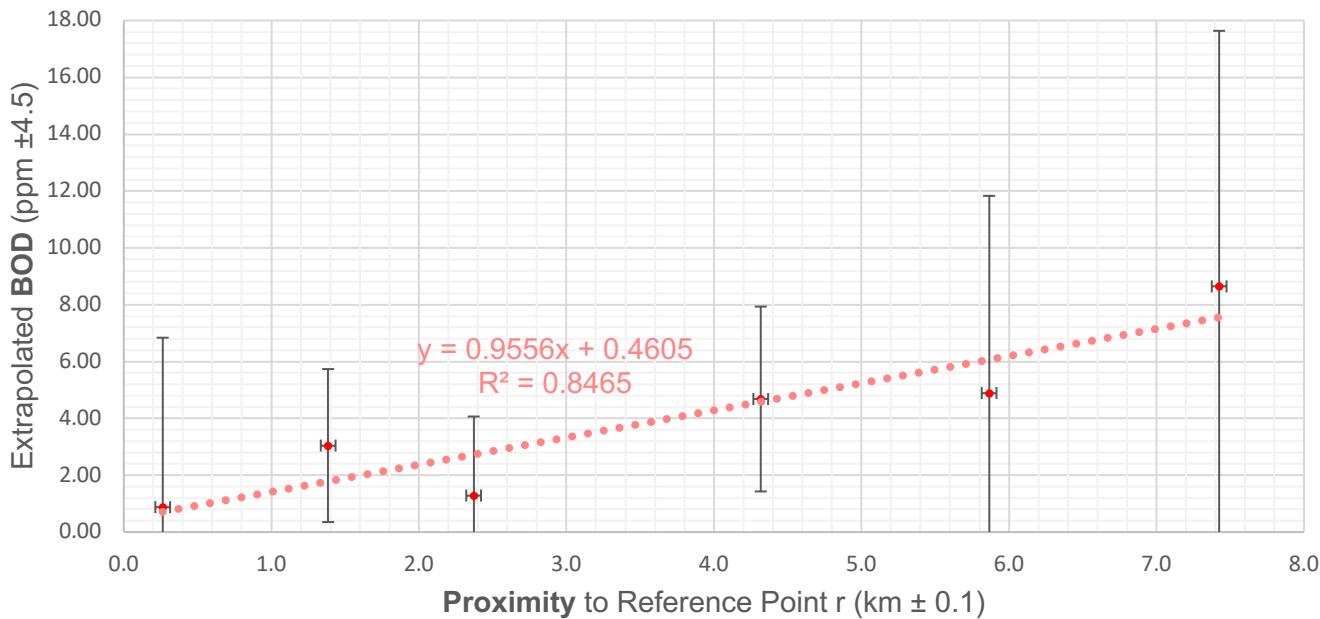
* This table consists of all data directly relevant to the research question. See Appendix B for rest of data collected.

Bottle		Start (cm ³)	End (cm ³)	Δ (cm ³)	avg. Δ (cm ³)	[O ₂] ppm	±%	±	±σ	Δ[O ₂] ppm	±	BOD (ppm)	±	T(h)	Proximity (km)
A	1	4.95	31.55	26.60	25.60	8.19	0.63	0.16	1.41	0.69	4.67	0.88	5.96	23	0.26
		0.35	24.95	24.60										117	
	2	0.60	26.35	25.75	23.45	7.50	0.66	0.15	3.25	2.36	2.09	3.05	2.69	15	1.39
		0.15	21.30	21.15										108	
B	1	1.20	38.95	37.75	36.60	11.71	0.56	0.21	1.63	2.36	2.09	3.05	2.69	15	1.39
		0.65	36.10	35.45										108	
	2	1.35	30.90	29.55	29.23	9.35	0.61	0.18	0.46	1.01	0.30	1.29	0.38	22	2.37
		1.20	30.10	28.90										116	
C	1	1.50	25.70	24.20	24.20	7.74	0.65	0.16	10.75	1.01	0.30	1.29	0.38	22	2.37
		5.15	44.55	39.40										116	
	2	0.75	21.80	21.05	21.05	6.74	0.69	0.14	10.96	3.51	2.44	4.68	3.25	3	4.32
		21.80	58.35	36.55										93	
D	1	2.50	35.75	33.25	34.28	10.97	0.58	0.20	1.45	3.51	2.44	4.68	3.25	3	4.32
		1.10	36.40	35.30										93	
	2	12.65	36.65	24.00	23.30	7.46	0.66	0.15	0.99	1.01	0.30	1.29	0.38	22	2.37
		9.30	31.90	22.60										116	
E	1	0.75	39.55	38.80	38.80	12.42	0.55	0.22	14.32	3.79	5.38	4.89	6.94	16	5.87
		0.15	59.20	59.05										109	
	2	1.25	24.55	23.30	26.95	8.62	0.62	0.17	5.16	6.66	6.93	8.65	8.99	17	7.42
		0.65	31.25	30.60										110	
F	1	1.45	48.75	47.30	47.40	15.17	0.53	0.25	0.14	1.01	0.30	1.29	0.38	22	2.37
		0.00	47.50	47.50										116	
	2	0.55	31.85	31.30	26.58	8.50	0.63	0.17	6.68	3.51	2.44	4.68	3.25	3	4.32
		2.05	23.90	21.85										93	

Figure 8: Main table of results

I then graphed the BOD against distance to the reference point, r. I estimated the measurement error cited on the BOD axis by taking an average of the uncertainties of the BOD.

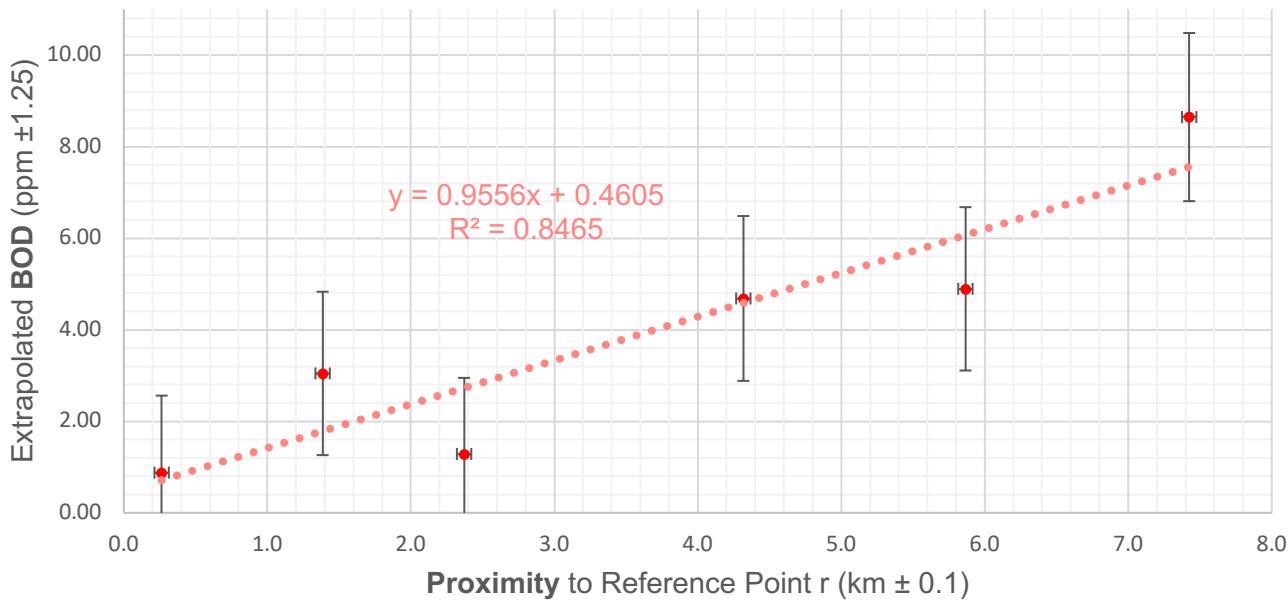
Figure 9: River Adur Water BOD and Proximity to Town (by σ)



Although the error bars reflected the poor precision in the titration results, I decided that the calculated error for point C did not reflect the true uncertainty (because it was so small compared to that of the other values, and to the huge range in titration values), so for the error drawn in the graph, I used a percentage error calculated by averaging that of the other points.

I was still sceptical, that such wide error bars had nonetheless produced a correlation, and so I reasoned that it was likely that the standard deviation did not properly reflect the true level of uncertainty. I therefore recalculated the BOD uncertainty by propagating the absolute uncertainty for the concentration of O₂(aq), and factoring in the extra oxygen uncertainty I mentioned in the *Theoretical Analysis* section, which I had previously omitted – creating a revised graph (see Figure 10 below), which had smaller error bars, which were closer to the line of best fit, than the previous version.

Figure 10: River Adur Water BOD and Proximity to Town (by abs. error)



To get a better sense for the geographical distribution of the BOD, I mapped the regression line equation onto the bird's eye view from Figure 2 – see Figure 11. To achieve this, I created a colour scale based on the literature values for BOD and water quality (see Appendix A), with red indicating moderate pollution, and green/blue indicating pristine water quality.

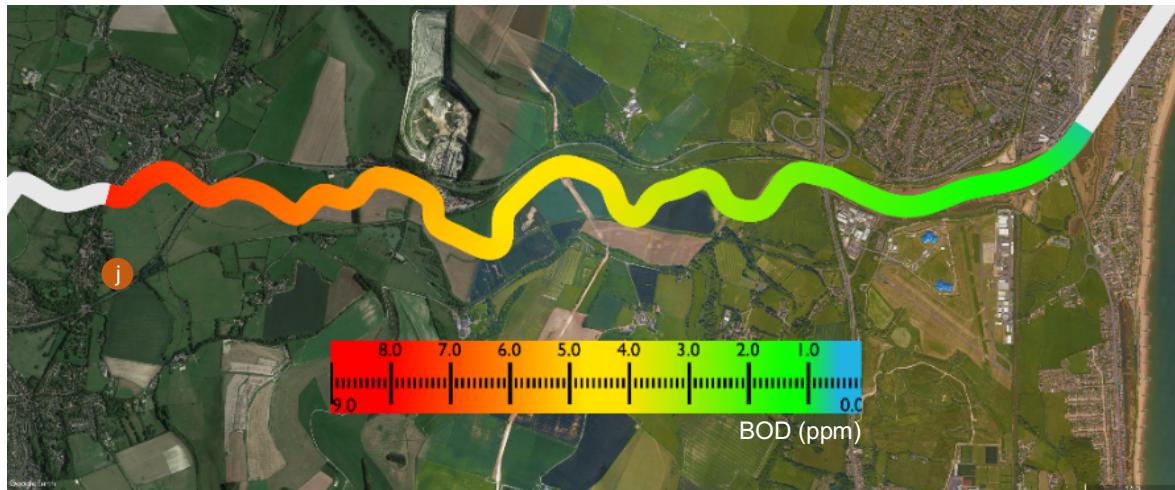


Figure 11: Bird's eye view of geographical distribution of BOD along Adur River.

Conclusion

Not only did the BOD values I determined match what I had expected based on the literature values, they also seemed to correlate positively with the samples' distances from the reference point, with an R^2 value of 0.85 (see Figures 9/10); ignoring the values' uncertainties, this correlation corroborates my hypothesis – that the level of organic pollution increases with increased distance across the 7km stretch I investigated, due to agricultural activity.

Figure 11, in particular (although the data shown is simply a spectral rendering of the regression line in Figures 9/10), demonstrates that the BODs of the water increase as distance from the town increases, and as distance to the flood plains and farmlands (towards the left of the map) increase. See Figure 12 (following page): an image I took to demonstrate the rural terrain, taken at point j (shown on Figure 11).

A possible explanation (as afore-mentioned) for the suggested increase in organic pollution, could be the insecticides, pesticides, and animal waste which are carried into the river from the farmlands by streams and through the groundwater.



Figure 12: Stream flowing through the flood plains located to the south of the Adur (see point j: Figure 11)

The correlation would also contradict my initial idea, that the organic pollution level would be uniform due to constant sewage pollution, setting those suspicious of sewage pollution at ease. Further, if the results were statistically sound, I would have been able to conclude that my observational hypothesis was correct, and that the organic pollution was indeed significantly higher in Upper Beeding – where it would fall into the *somewhat polluted* category: information which could have served to advise people on their choice of swimming/kayaking location, while not being too problematic for wildlife conservationists.

However, my errors and uncertainties cannot be ignored. Although the absolute uncertainties as I calculated them (shown in Figure 10) would not undermine the correlation too much, I think that the huge standard deviation uncertainties (shown in Figure 9) demonstrate that there are even more systematic uncertainties than I had properly accounted for. These include:

- Air trapped in the storage bottles, and thus allowing surplus oxygen to dissolve
- Air trapped in the volumetric flasks – aerating the solutions so much that a visible froth formed
- Potentially unstable sodium thiosulfate, which wasn't standardized (due to time constraints)

Problems with standard deviation rely on normally distributed random variables, but it is hard to tell if this was the case for the titration results, given that some may have been anomalous; if more time were available, increasing the amount of sample points, and the amount of titrations performed on each would have greatly improved the validity of the data – perhaps enough water should have been taken that concordant results could be obtained. Another problem is that environmental systems are far too complex to define with 24 titrations. Tide, weather, and time of day should all have been controlled for, probably over years of research. I wouldn't have been able to conduct such a long-term investigation, and my results were therefore inconclusive.

Not to mention, that presumably the reduction in O₂ concentration is not completely linear with time. Therefore, having slightly different length incubation periods as well as starting them at the same time could have had a huge effect on the results, even though I extrapolated to control for different incubation lengths.

There are, however, several other ways in which I could have improved the experiment within the timescale provided. Using a boat/kayak and filling the bottles up underwater would have prevented aeration by the pump, and extra oxygen from dissolving. The sodium thiosulfate *could* have been standardized, with some extra planning, and the volumetric flasks could have been filled right to the top to avoid further oxygen being dissolved. Also the incubation period should have been started immediately after sampling, and lasted for 5 days exactly, although this would have involved taking hazardous chemicals out of the lab.

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Appendix A

Literature values: how clean water of each BOD category is [1] [2] [4]

BOD Category (ppm)	Water Quality (organic pollutants)
BOD < 2	Good quality
2 ≤ BOD < 5	Moderately clean (unpolluted)
3 ≤ BOD < 10	Somewhat polluted
200 ≤ BOD < 600	Untreated sewage

Appendix B

Results data *not* included in Results Section, see Figure 8.

Sample	Coordinates		Geodesic Proximity (km)	River-Line Proximity (km)	Time	Date Taken	River Height (m)	Date Frozen	Time From Sampling				
	λ (N) °	φ (W) °							(h)	(d)			
A	1	50.8826	-0.3067	6.0933	7.42	1935	20/06/2018	4.7	21/06/2018	17			
	2								25/06/2018				
B	1	50.8708	-0.3013	4.7209	5.87	2030	20/06/2018	3.8	21/06/2018	16			
	2								25/06/2018				
C	1	50.8406	-0.2883	1.3160	1.39	2140	20/06/2018	2.5	21/06/2018	15			
	2								25/06/2018				
D	1	50.8325	-0.2798	0.2359	0.26	1250	27/06/2018	5.4	28/06/2018	23			
	2								02/07/2018				
E	1	50.8477	-0.2928	2.1456	2.37	1340	27/06/2018	4.5	28/06/2018	22			
	2								02/07/2018				
F	1	50.8612	-0.2985	3.6628	4.32	1300	28/06/2018	5.7	28/06/2018	3			
	2								02/07/2018				
		50.8311	-0.2773										
Reference point, r													

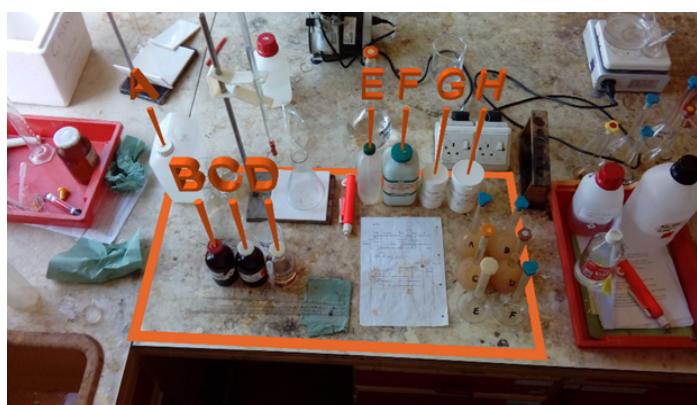
Appendix C

Substances

- distilled water (plenty)
- manganese(II) sulfate(VI)-1-water (39 g)
- sodium hydroxide pellets (32 g)
- potassium iodide (14 g)
- 0.01M sodium thiosulfate solution (~1000 cm³)
- 1% starch solution (2 cm³ x 24 = 48 cm³)
- concentrated sulfuric(VI) acid (1.5 cm³ x 24 = 36 cm³)

Equipment

- 150cm³ measuring cylinder (± 0.5 cm³)
- analytical balance (± 0.01 g)
- 2x 250cm³ volumetric flask (± 0.15 cm³)
- 2cm³ pipette (± 0.15 cm³)
- 1.5cm³ pipette (± 0.15 cm³)
- 2x 1cm³ pipette (± 0.15 cm³)
- 50cm³ burette & stand (± 0.03 cm³)
- 100cm³ beaker
- 4x 10cm³ beaker
- magnetic stirrer
- 500cm³ conical flask
- 2x >100cm³ darkened bottle
- Thermometer $\pm 0.3^\circ\text{C}$



part of lab setup (see list below for corresponding letter)

- A. 0.01M sodium thiosulfate
- B. manganese (II) solution
- C. potassium iodide solution
- D. concentrated sulfuric acid
- E. distilled water
- F. manganese(II) sulfate(VI)-1-water
- G. sodium hydroxide pellets
- H. potassium iodide