

# Part II Aqueous Geochemistry Report

## Nutrients, Life and Tides in the Great Ouse and Associated Waterways, Norfolk



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Due: 17/01/2024

## Abstract

This project aimed to constrain Methane concentrations in the Great Ouse. Due to methodological failings, this was not possible. Instead, the associated nutrients, industrial inputs, tidal variation, and spatial gradients were investigated, in order to provide better basis for future work into dissolved CH<sub>4</sub> concentrations. We found that Salinity is dominated by the temporal tidal cycle, though there is some dependance on location, especially due to the St Germans pumping station. The impermeable Kimmeridge Clay bedrock prevents any groundwater effects, including allowing Alkalinity to behave conservatively. Nutrient concentrations vary according to flow rate and location of tributaries. Industrial input provides negligible changes in this area. More work is needed to spatially constrain CH<sub>4</sub> concentrations.

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# 1 Introduction

## 1.1 Catchment and Context

### Motivation

The effect size of local land-use and salinity on the dissolved gases and biological activity in river water is poorly constrained (Upstill-Goddard and Barnes, 2016). From Downham Market to the Ouse estuary, this area provides a variety of fluvial environments, including the artificial waterway of the *Great Ouse Relief Channel* (RC), which may record a more eutrophied environment. There also are a small number of industrial outflows along the

Ouse, most notably from Palm Paper and their associated Natural Gas power plant, which may also change the river chemistry. (Environment Agency, 2016)

Tidal variations and proximity to the sea mean that the chemistry here must record a dynamic environment. Especially near Kings' Lynn, the high tidal range provides a site for measuring the impacts of salinity on the chemical properties of the river, specifically as this relates to dissolved gases.

Methane and pore-water chemistry in the fenland soils surrounding Kings' Lynn and the Ouse are important as a carbon sink, and are useful for conservation reasons (Garget, 2023). Therefore, the aim of this report was to help place the large waterways into this broader context, while appreciating the temporal and spatial variations associated with salinity in this area.

## Geological Setting

The bedrock geology of the major waterways largely do not vary across our area, with the Ouse estuary, Relief Channel and tributaries all lying on late Jurassic rocks, mostly the Kimmeridge clay formation. Tributaries to the East flow in from the later Tithonian sands, whereas the Western inflows eventually come from the Oxfordian clays and muds. Exposure of these is poor, as Quaternary drift deposits cover much of the bedrock. It can be relatively high in kerogen, a fossil fuel that may provide sulphur, nitrogen and even metals to groundwater. (Gallois et al., 1994)

Drift in the area is slightly more variable; though a significant portion of the area is marked by a succession of tidal clays and silts, the upstream end near Downham market shows some Pleistocene gravels, and more recent ( $2 - 4kyr$ ) peat deposits which may have archaeological significance.

Overall, the geology of the area is not a focus of this report, but some relevant units and their significance are noted below, from the work of Gallois et al. (1994).

### Jurassic Clays and Sands

- Kimmeridge Clay - These are soft and calcareous mudstones. The carbonate content likely controls the alkalinity in this region. The low porosity and permeability of this unit limits the effects of diffuse groundwater sources in our study area. It has a stratigraphic thickness of **95-120m**. Gallois et al. (1994)
- Amphthil Clay and West Walton Beds - Oxfordian mudstones similar in character to the Kimmeridge. These may contain more limestone content.
- Sandringham Sands - These Portlandian fine grained clayey sands are stratigraphically thin at only **5-8m**. They contain minerals such as glauconite that are easily

weathered, perhaps contributing to Silica in local waters.

## **Drift**

- Recent Deposits - a thin layer of mostly sandy material that makes up the Wash and the Fenland. These deposits' soil have been the site of other gas flux sampling.
- Glacial Tills and interglacial solifuction deposits - Several layers of glacial drift are present through the pleistocene. Mostly, this is sand and gravel. The thickest of these beds, which is exposed in the Nar and Gaywood, is a "Chalky-Jurassic Till", which may affect both alkalinity and groundwater movement.

## **Tidal Variation**

The Great Ouse's tidally influenced zone covers all of our area. At King's Lynn the tidal range is quoted at 6m by the Environment Agency (2017). We observed a similar, slightly higher range near Kings Lynn.

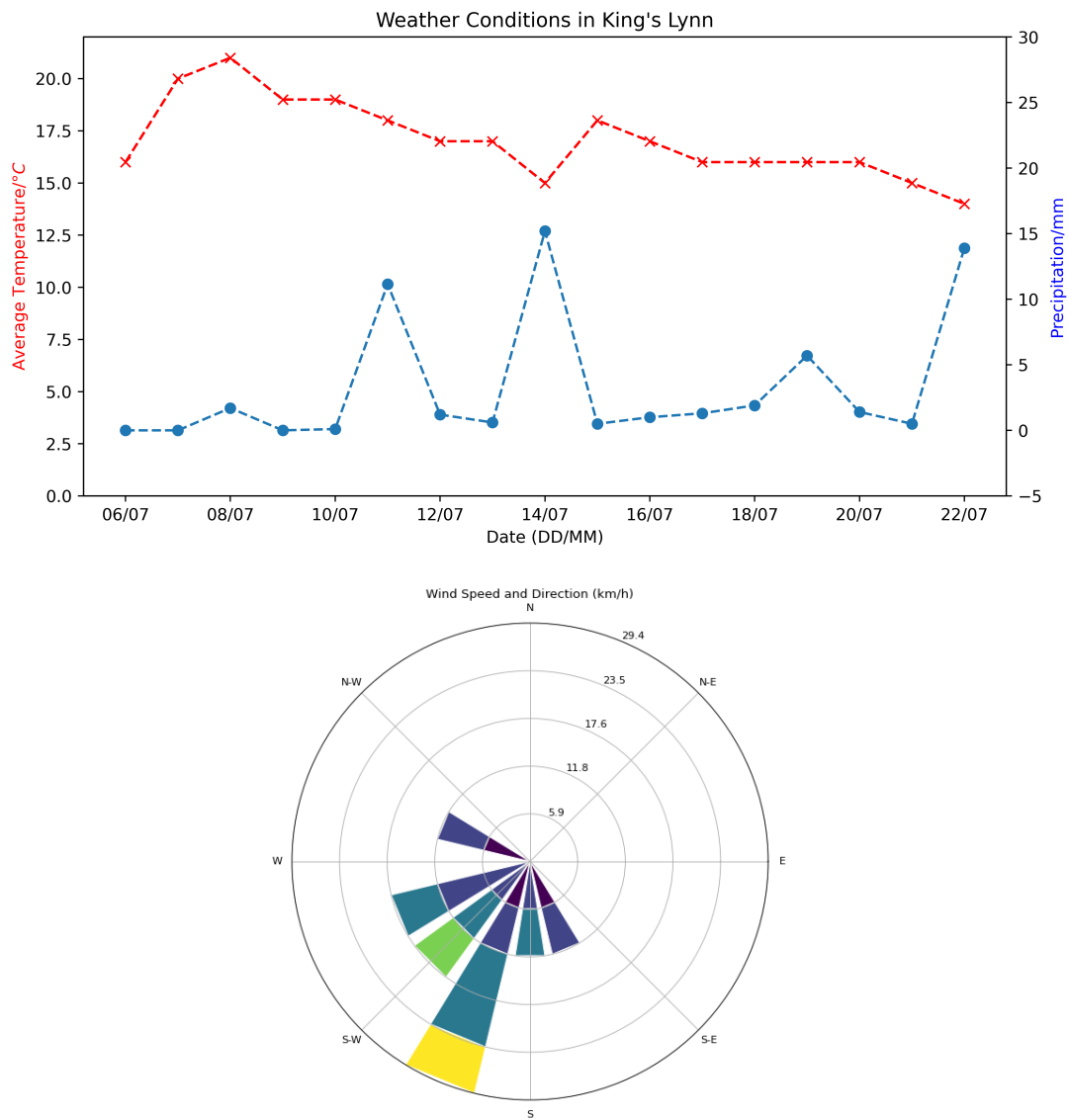
Further upstream, Denver sluice marks the confluence of a series of tributaries which limits the southern extent of this report. At this place, tidal range is quoted as 4m. When tides or flooding conditions are severe, the AG sluice is opened to increase the capacity of the Ouse by adding the Relief Channel.

Tides in the Great Ouse are asymmetric due to the frictional effects, (Kings Lynn Conservancy Board, 2023) though for the purpose of this report, we will normally assume that they are perfectly sinusoidal. Due to the unavailability of local hourly tidal data, daily high and low tides have been recorded from UK Hydrographic Office.

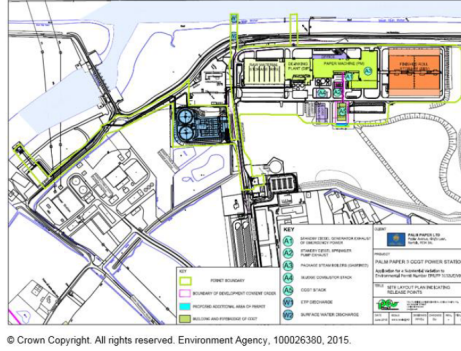
Over the course of the year, tidal flows in the Great Ouse dominate the mixing of nutrients. In summer and spring, it has been suggested that the low freshwater flow changes the character of the primary producers in the Ouse. This likely alters the Nitrogen, Phosphorous and Silica in the water (Rendell et al., 1997).(Neal et al., 2000)

## **Weather**

Weather, including precipitation, average temperature, and wind direction are shown in Figure 1. Rain on the 14/07 and 11/07 increased flow, especially in smaller tributaries. We also expect that the rain on the 14th caused some dilution effects in the slower flowing waterways in the area. Night-time temperatures dropped to around  $9^{\circ}\text{C}$  at their lowest, and there was a sharp decrease in temperature at the relatively late sunsets.



**Figure 1:** Average temperature and precipitation did not vary massively over the course of the study period. Note the rain on 14/07 and 11/07. Wind was dominantly from the SW. Data from Historical Weather (2023)



**Figure 2:** Sitemap of Palm Paper operations near the Tail Sluice. Note the location of abstracting water from the RC, and the two outflows W1 and W2. (Environment Agency, 2016)

## 1.2 Features of Interest

### Relief Channel and Sluices

The major water control infrastructure in our catchment is the Great Ouse Relief Channel, with the A.G. Wright Sluice at its inflow and the Tail Sluice at its outflow. This is primarily used for flood and high tide defences, where it is opened at the Downham Market End. The Tail Sluice is a gravity sluice and discharges water into the Great Ouse in low tide conditions. (Environment Agency, 2017)

Additionally, Wiggshall St Germans is home to the St Germans pumping station on the Middle Level Main Drain. This is a significant inflow, as it reportedly pumped 80,812 megalitres of water in the period October – December 2023. (Burrows, 2024) Comparing this to the discharge from the Ouse, (arc, 2024), 87,869 megalitres are being discharged through the Denver Complex upstream of the pumping station. This means this pumping will have a notable impact on the water chemistry.

### Industrial Inputs

Palm Paper abstracts from the Relief Channel for use both in paper milling and for the combined cycle gas turbine that powers their activities. They emit both into the air and into the water. The water emission is regulated by the Environment Agency, and consists of both a treated effluent outflow (W1) and through uncontaminated surface water (W2). A site map is attached.

These outflows are expected to produce Nitrogen, Phosphorous, Suspended Solids, Metals, and act as a diluant with a flow rate of 15,000m<sup>3</sup> each day. The temperature is expected to be higher, and the pH may also be affected. Environment Agency (2016)

### 1.3 Logistics

Fieldwork was undertaken with Sam Gee. Due to muddy banks and limited sampling area, work was almost always conducted side by side. Where recording and operating the measurement was conducted by Sam Gee, he has been marked in the appropriate data table. Alex Colesmith and Judy Wang conducted a study in the same area with a different initial focus.

We were based out of Kings Lynn, and travel across the area was done via train and by foot. In order to adequately capture a meaningful snapshot of the tidal cycle, sampling times were varied throughout the week. Due to difficulty accessing the river, samples were performed off bridge, or using a half-cut on string.

### 1.4 Preliminary Hypotheses

When initially embarking on this project, we believed we would be able to obtain meaningful data about dissolved methane concentrations. Due to methodological errors detailed in Appendix A, this was not possible. As we initially aimed to constrain this metric, we wanted to quantify the effect of tidal, spatial, land-use and flow-rate variations on dissolved methane, as well as the nutrients and organically affected chemicals in the water. Specifically, we expected the following:

- Methane will be controlled by salinity, both tidally and spatially.
- Industrial input into the Relief Channel and from the Paper Mill will meaningfully affect Nitrogen, Phosphate and Aluminium concentrations in the waterways.
- Phosphate and Nitrate will be increased in slower flowing waterways, and may promote life through eutrophication. This may further increase the Methane production in the river.
- Tidal variations controlling salinity will impact the character of the life in the water, perhaps changing the silica and nutrient relative concentrations.
- Alkalinity will be dominated by Carbonate Equilibria with the underlying Kimmeridge Clay.
- Methane production and nutrient consumption will vary with temperature and sunlight.
- Tributaries coming from slightly different lithologies will have distinct chemical signatures, especially where the flow rate is artificially controlled.



## 2 Methods

Whenever access was possible to the river, we collected water using half-cut bottles. Where access was difficult, a sampler on a string was used to collect samples. From these half-cuts, we were able to measure pH, temperature (T), salinity (S), total dissolved solids (TDS) and conductivity. Filtration was performed with 0.2 $\mu$ m fisherbrand nylon filters, and the filtered samples were used to conduct spectrophotometric analysis. This provided us with the concentrations of ammonium (NH<sub>4</sub>), sulphate (SO<sub>4</sub>), nitrate (NO<sub>3</sub>), phosphate (PO<sub>4</sub>), silica (SiO<sub>2</sub>) and aluminium (Al). 20 samples were selected to bring back to Cambridge for determination of methane (CH<sub>4</sub>) concentration and more accurate ICP-OES determination of ion concentrations including chloride (Cl), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca) iron (Fe), manganese (Mn), strontium (Sr) as well as SO<sub>4</sub>, Al, NH<sub>4</sub> and NO<sub>3</sub> again.

### 2.1 Sampling Strategy

We focused on obtaining two major slices through our area. First, a full spatial section close to high tide, and second, a full temporal section at a single location.

The samples we brought back contained a variety of waterways, across the high tide spatial salinity gradient, as well as 10 samples from the Cut Bridge in Kings' Lynn across a full tidal cycle.

Our aim primarily was to constrain the chemical gradients, so sampling was focused around the saddlebow area where the high-tide salinity gradient was found.

We also attempted to catalogue major tributaries, so that those data could be used to select any that had particularly different chemical signatures.

### 2.2 Overview Metrics

pH, T, TDS and conductivity were all measured with a HANNA HI-991300 Multi-parameter pH meter. Salinity was measured with a HI-98319 Marine Waterproof Salinity Tester, which also measured Temperature.

#### Rationale

pH gives a good indication of different water packages, as well as having a disputed and complicated relationship with CH<sub>4</sub> production (Upadhyay et al., 2023). It additionally is associated with eutrophication, so may show higher values in water containing algal blooms. Temperature, as well as further affecting life, also has been shown to change

Metric	Resolution	Accuracy	Calculated Repeatability
pH	0.01	0.02	0.03
$T/^{\circ}\text{C}$	0.1	0.5	0
S/ppt	0.1	1.0	0
TDS/ppm	1	2%	11
Cond/ $\mu\text{S}$	1	2%	9

Factor	Value	Resolution	Accuracy	Uncertainty
Measuring Cylinder	25ml	0.1ml	0.05ml	0.2%
pH at equivalence	$\tilde{4}.0$	0.01	0.02	0.5%
Pipette Volume	$200\mu\text{l} * 3, 1000\mu\text{l} * 1$	$1\mu\text{l}$	0.5-2.5%	2-10%
Combined				2.7-10.7%

the CH<sub>4</sub> production characteristics of fresh water,(Fuchs et al., 2016) and is good for identifying various water packages.

TDS and conductivity mainly function as an equivalent of salinity, which as previously mentioned has been found to have a clear negative correlation with CH<sub>4</sub> production(Bartlett et al., 1987). Seawater is perhaps the most important water package in this area, so taking plenty of salinity measurements was paramount.

Finally, Alkalinity was measured using a Gran Titration method and the same pH probe. The full data from these titrations is available in Appendix B.

### Uncertainty

The quoted accuracy of the HI-991300 and HI-98319 is tabulated below. The measured repeatability calculated in the field also tabulated. We calculated a theoretical uncertainty for Alkalinity as below. This involved assuming a reasonable value for the equivalence point from which to base our uncertainties. The major source of error in this is definitely the pipetting, as our pipettes were only accurate to within 2.5%, and need to be used several times during a trial.

## 2.3 Chemical Tests

Spectrophotometric tests were conducted on ions we believed would be useful in the field. Specifically, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, PO<sub>4</sub>, SiO<sub>2</sub>, Al were measured using a Hach DR1900 portable spectrophotometer.

## Rationale

Sulphate, phosphate and nitrate were primarily selected as they are nutrients important for biological processes. Additionally, as a major seawater ion, sulphate could serve as a measure of reliability, since we would expect it to correlate well with salinity.

Silica is also important for life, and taking the ratios between Si and N or P can be used to track shifts in species abundances from diatoms to flagellates (Rendell et al., 1997). Ammonium and silica also have the useful property of being diffuse sources through runoff - ammonium from agriculture, and silica primarily from weathering, especially in the glauconite rich sediments to the East.

## Uncertainty

Accuracy as stated by Hach for the chemical test kits provided is listed below.

Interferences for each test are also listed. The only one which may have had an effect was  $\text{NH}_4$ . The chloride concentrations were high enough to have impacted the results.

# 3 Results

## 3.1 Spatial Variability

### Tributaries

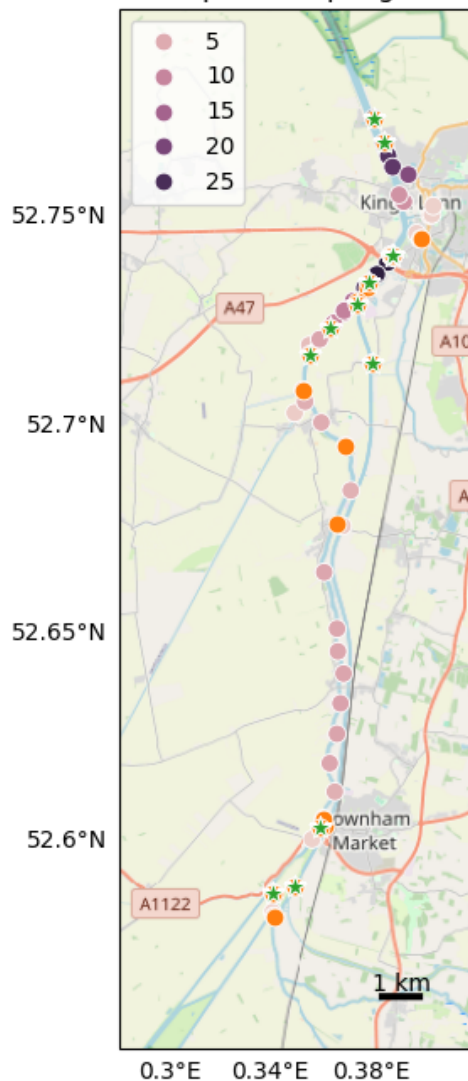
While the overall river picture is formed mostly at the Ouse, there are a variety of water packages that are not the Ouse. The small tributaries all have their own distinct chemical characteristics.

Tributary Name	Avg Characteristics		
	Salinity (ppt)	pH	Alkalinity ( $\mu\text{M}$ )
Nar	AF	AFG	004
Gaywood	AX	ALA	248
Hundred Foot	AL	ALB	008
Ten Mile	DZ	DZA	012
Middle Level Drain	AS	ASM	016
Pur Fleet	AD	AND	020

### Relief Channel

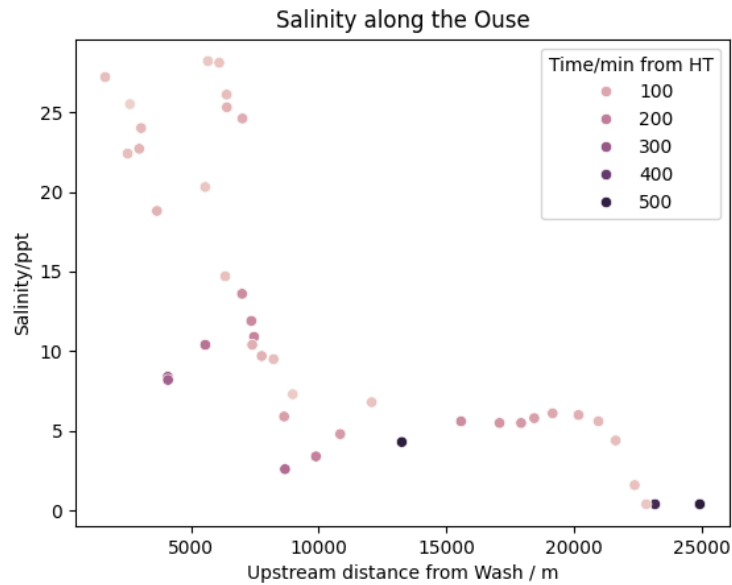
The Relief channel has a lower salinity signal than the surrounding waterways, even those that are upstream of it. There is a salinity gradient across the RC's length, but this seems

Overall Map of Sampling Locations



**Figure 3:** Locations where sampling was conducted. Stars mark locations where samples were collected for analysis in Cambridge (n=20), whereas orange locations had spectrophotometry done (n=39). Other points are coloured purple according to their salinity (n=97).

Upstream distance /m	Sample.ID	pH	T	Cond	TDS	Alk	NH4	SO4	PO3	NO4	SiO2	Al
125.1	0707GH11	8.47	24.6	2356	1172		0.11	122	0.84	3.8		0
125.1	1907GH86						0.16	1150	0.64	3.4	6	0
1411.2	1807GH81	8.58	19.7	2686	1342	3472	0.91	1800	0.29	9.7	9.8	0.007
5409.8	1207GH49	8.24	21.1	2197	1100							
14027.2	0807GH16	8.13	21.3	1150	578		1.32	950	0.91	9.1	2.9	0.004
15601.0	1607GH68	8.2	19.4	1007	504	4142	-1		0.84	2	7.9	0



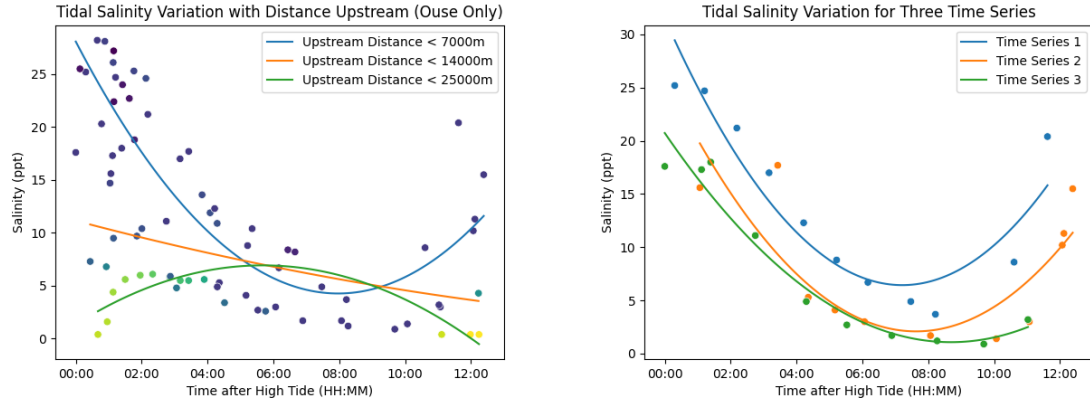
**Figure 4:** Distance along the main channel. It appears to have 3 main segments, and is mostly close to high tide. As you stray from high tide, the points fall downwards off the trend.

relatively slight; going from a TDS of 1172 ppm and a S of 1.2 ppt, to TDS 578 and S of 0.5.

It has a higher Ammonium value than other waterways, including an overrange value, (even without the Chloride interference from section 2.3) except at the downstream sluice. Sulfate is seemingly dominated by the salinity as in the other bodies. Phosphate is surprisingly high for the low salinity, as is Nitrate. This will be discussed in section 4.4. Similarly, there seems to be raised Silica compared to the Salinity. Aluminium is negligible.

### Main Transect

Distance upstream was measured from the beginning of the Wash nature reserve, where the river valley becomes a salt marsh.



**Figure 5:** In order to quantify how this tidal variation related to the distance from the wash, this figure was produced. The effect of tidal changes on salinity visibly drops off as the distance upstream increases.

### 3.2 Temporal Variability

Tidal changes mean that the salinity gradient looks confused if one simply plots distance down river against salinity. Instead, we took 3 time series at the Cut Bridge in Kings' Lynn. Series 1 and 3 were done during primarily daylight hours, whereas series 2 was done at night.

In figure 5, the fit line on the furthest upstream set of points seems misleading, as in reality, the tidal variation just takes longer to reach there, so time after Kings Lynn' high tide doesn't capture the full change.

The relatively straight relationship in the middle, I attribute to both an attenuation of the effect, as well as a delay, causing us to see the most linear part of a near-sinusoidal effect.

### 3.3 Data Table

A full table of all results is shown below. Waterway labels including "TC" indicate that the sample was part of a time series.

X	Y	id	pH	Time	T	S	Cond	TDS	Alk	NH4	SO4	PO4	NO3	SiO2	Al	Op	Rec	Waterway
0.39983783	52.74485098	0607GH1	8.06	13:06	18.5	0.6	871	432	3941							Gee	Hutton	Nar
0.38857748	52.7407914	0607GH2	8.08	14:17	21.7	10.4	-1	-1	3239	1.44	-1		2.8		0.021	Hutton	Gee	Ouse
0.3926657286	52.75376545	0607GH3	8.48	15:17	22.8	8.6	-1	-1								Hutton	Gee	Pur Fleet
0.39321345	52.75377819	0607GH4	8.59	15:22	21.2	8.4	-1	-1								Hutton	Gee	Ouse
0.39130898	52.755436	0607GH5	8.18	15:35	19.2	8.2	-1	-1	3531	0.49	-1		3.3		0	Hutton	Gee	Ouse
0.38669459	52.7391217	0707GH6	7.86	10:21	17.9	28.2	-1	-1								Gee	Hutton	Ouse
0.3824502266	52.73631208	0707GH7	7.98	10:35	18.2	28.1	-1	-1								Hutton	Gee	Ouse
0.3783820966	52.73310168	0707GH8	7.92	10:50	19.3	26.1	-1	-1		2.41	1800	1.14	4.9		0.03	Hutton	Gee	Ouse
0.37755872	52.7330273	0707GH9	7.85	11:27	19.3	25.3	-1	-1								Gee	Hutton	Ouse
0.3749139834	52.72988284	0707GH10	7.91	11:49	19.8	24.6	-1	-1	2541	2.66	2100	0.84	5.8		0	Hutton	Gee	Ouse
0.3747260668	52.72922862	0707GH11	8.47	12:50	24.6	1.2	2356	1172		0.11	122	0.84	3.8		0	Hutton	Gee	RC
0.3730255003	52.72990124	0707GH12	7.86	13:32	22.2	13.6	-1	-1								Hutton	Gee	Ouse
0.36996126	52.72784054	0707GH13	7.97	13:46	21.5	11.9	-1	-1								Hutton	Gee	Ouse
0.36905881	52.72698326	0707GH14	8	13:59	22.2	10.9	-1	-1								Hutton	Gee	Ouse
0.3998298	52.74486176	0707GH15	8.42	14:50	22.7	0.3	671	340								Hutton	Gee	Nar
0.3620791384	52.60366154	0807GH16	8.13	10:36	21.3	0.6	1150	578		1.32	950	0.91	9.1	2.9	0.004	Hutton	Gee	RC
0.361252471	52.60532912	0807GH17	8.19	11:27	22.5	1.6	3150	1535	3691	0.27	300	0.83	4.2	1.6	0.004	Hutton	Gee	Ouse
0.36580414	52.61189667	0807GH18	8.08	11:38	22.2	4.4	-1	-1								Hutton	Gee	Ouse
0.3637974692	52.6187507	0807GH19	8.14	12:00	21.8	5.6	-1	-1								Gee	Hutton	Ouse
0.3666739943	52.62583042	0807GH20	8.14	12:27	21.8	6	-1	-1								Hutton	Gee	Ouse
0.36806429	52.63316653	0807GH21	8.12	12:50	21.9	6.1	-1	-1								Hutton	Gee	Ouse
0.36927359	52.64034329	0807GH22	8.15	13:21	22.4	5.8	-1	-1								Hutton	Gee	Ouse
0.36703777	52.64568007	0807GH23	8.17	13:40	21.8	5.5	-1	-1								Gee	Hutton	Ouse
0.3666951	52.65113594	0807GH24	8.17	13:55	21.9	5.5	-1	-1								Hutton	Gee	Ouse
0.3615778226	52.66471746	0807GH25	8.13	14:24	21.6	5.6	-1	-1								Hutton	Gee	Ouse
0.3663320185	52.67649693	0807GH26		14:46	22.4					0.39	480	0.7	4		0.003	Hutton	Hutton	Ouse
0.39984064	52.74486935	0807GH27	8.15	16:36	21.8	0.4	904	425								Hutton	Hutton	Nar
0.3567791658	52.60046224	0907GH28	7.73	10:09	21.3	0.4	872	437	3170							Gee	Hutton	Ouse
0.34161612	52.58754009	0907GH29	7.95	11:01	21.3	0.4	873	435	3843	0.44	60	1.71	3.1	9.8	0.015	Hutton		Ouse
0.34108367	52.58286784	0907GH30	8.19	12:58	22.6	0.7	1466	735								Hutton		Hundred Foot
0.34160937	52.58189967	0907GH31	8.02	13:13	22.3	0.4	881	442	4259	0.32	60	1.77	3.1	8.8	0.009	Hutton	Gee	Ten Mile
0.3998482241	52.74486053	0907GH32	8.07	15:37	21	0.3	354	708	3195	0.29	76	0.86	5.1	7	0.004	Hutton	Gee	Nar
0.38862491	52.74074719	1007GH33	8.04	10:38	21.5	8.6	-1	-1	3379	0.34	740	0.59	4	4.6	0	Hutton	Hutton	Ouse TC1
0.38863709	52.7407451	1007GH34	7.9	11:39	20.5	20.4	-1	-1	3001							Hutton	Hutton	Ouse TC1
0.38854421	52.74073905	1007GH35	7.94	12:42	21.2	25.2	-1	-1	2743	0.46	-1	0.19	2.9	6.9	0	Hutton	Hutton	Ouse TC1
0.38864399	52.7407526	1007GH36	8.02	13:36	21	24.7	-1	-1	3038							Hutton	Hutton	Ouse TC1

X	Y	id	pH	Time	T	S	Cond	TDS	Alk	NH4	SO4	PO4	NO3	SiO2	Al	Op	Rec	Waterway
0.38864468	52.74075529	1007GH37	7.9	14:35	21.4	21.2	-1	-1	3058	0.76	1350	0.07	2.5	3.1	0	Hutton	Hutton	Ouse TC1
0.3885531923	52.74076422	1007GH38	7.95	15:34	21.2	17	-1	-1								Gee	Gee	Ouse TC1
0.3885571123	52.74078321	1007GH39	8.02	16:37	21.4	12.3	-1	-1		1.08	950	0.56	3.2	5.2	0	Gee	Gee	Ouse TC1
0.3885492724	52.7407571	1007GH40	8.12	17:37	21	8.8	-1	-1								Gee	Gee	Ouse TC1
0.3885845518	52.7407666	1007GH41	8.08	18:34	20.2	6.7	-1	-1		-1	620	0.63	3.4	4.2	0	Gee	Gee	Ouse TC1
0.38862024	52.74074163	1007GH42	8.29	19:52	20	4.9	-1	-1	3729							Gee	Hutton	Ouse TC1
0.3885414326	52.74076422	1007GH43	8.13	20:37	19.5	3.7	-1	-1		0.8	420	0.65	4.1	4.3	0	Gee	Gee	Ouse TC1
0.3885335927	52.74077134	1107GH44	7.98	02:00	19.1	20.3	-1	-1		-1	-1	0.52	2.8	4.2	0	Gee	Gee	Ouse TC1
0.40365626	52.75050807	1107GH45	8.04	21:40	18.7	0.3	772	396								Gee	Gee	Ouse
0.40436605	52.7506863	1107GH46	7.99	21:49	18.7	0.3	766	384								Gee	Hutton	Gaywood
0.40488076	52.75273453	1107GH47	7.99	22:00	18.7	0.3	758	375								Hutton	Gee	Gaywood
0.39826562	52.74618873	1107GH48	8.27	22:36	19.3	0.3	647	324								Gee	Hutton	Gaywood
0.368866376	52.67584926	1207GH49	8.24	14:14	21.1	1.2	2197	1100								Hutton	Gee	Nar
0.3721188	52.68439862	1207GH50	8.4	14:42	20.7	4.3	-1	-1								Gee	Hutton	RC
0.3700863396	52.69514995	1207GH51	8.28	15:48	20.3	6.8	-1	-1	3387	0.51		0.43	3.5	11.2	0.004	Hutton	Gee	Ouse
0.3604595705	52.70073113	1207GH52	8.42	17:56	20	4.8	-1	-1								Hutton	Gee	Ouse
0.3498659981	52.70305213	1207GH53	8.15	18:28	20.9	1	1894	951	3056							Gee	Hutton	Ouse
0.3540071234	52.70571984	1207GH54	8.4	19:08	19.6	4.7	-1	-1								Hutton	Gee	MLM
0.3531714656	52.70855797	1207GH55	8.53	19:24	19.5	3.4	-1	-1								Hutton	Gee	MLM
0.35562931	52.71931529	1207GH56	8.56	20:38	19	2.6	-1	-1	3462			0.62	3.3	2.9	0	Hutton	Gee	Ouse
0.3885465973	52.74078863	1407GH57	8.17	16:56	18.9	15.5	-1	-1	3198	1.17	2750	0.58	6.5	2.2	0	Hutton	Gee	Ouse
0.388589851	52.7407415	1407GH58	8.2	18:00	19	15.6	-1	-1								Hutton	Gee	Ouse TC2
0.3886850093	52.7407415	1407GH59	8.28	19:00	18	11.3	-1	-1		-1	650	0.53	1.5	3.6	0	Hutton	Hutton	Ouse TC2
0.3884380125	52.74089813	1407GH60	8.32	20:21	19.4	17.7	-1	-1								Hutton	Hutton	Ouse TC2
0.3883847874	52.74085354	1407GH61	8.4	21:17	19.4	5.3	-1	-1		0.87	660	0.53	5.1	22	0	Hutton	Hutton	Ouse TC2
0.3883133736	52.74087198	1407GH62	8.49	22:06	19.3	4.1	-1	-1								Gee	Gee	Ouse TC2
0.3883133736	52.74087198	1407GH63	8.46	23:00	19.6	3	-1	-1		0.42	580	0.88	5.9	35.5	0.006	Gee	Gee	Ouse TC2
0.3883133736	52.74087198	1407GH64	8.5	01:00	18.3	1.7	-1	-1		0.78	200	0.49	5	5.8	0	Hutton	Hutton	Ouse TC2
0.3883133736	52.74087198	1407GH65	8.47	03:00	17.6	1.4	-1	-1		0.33	200	0.58	6.1	10.2	0	Hutton	Hutton	Ouse TC2
0.3883133736	52.74087198	1407GH66	8.21	04:00	17.4	3	-1	-1								Hutton	Hutton	Ouse TC2
0.3883133736	52.74087198	1407GH67	8.18	05:00	17.4	10.2	-1	-1		0.52	800	0.72	7.4	20.1	0	Hutton	Hutton	Ouse TC2
0.3497801607	52.58895186	1607GH68	8.2	17:13	19.4	0.5	1007	504	4142	-1		0.84	2	7.9	0	Hutton	Gee	RC
0.3411363615	52.58733102	1607GH69	7.9	18:24	19.5	0.4	874	437	2844	2.13		0.71	3.6	8.4	0	Hutton	Gee	Ouse
0.3599908715	52.60324244	1607GH70	8.25	19:15	19	0.4	889	445	3253	-1		0.95	2.6	7	0	Hutton	Gee	Ouse
0.3885315758	52.74079284	1706GH71	8.17	06:53	16.8	17.6	-1	-1	2774	0.38	1700	0.84	2.1	5.6	0	Hutton	Gee	Ouse TC3
0.3885339425	52.74079295	1707GH72	8.03	08:16	17.3	18	-1	-1	2839		1500					Gee	Hutton	Ouse TC3



X	Y	id	pH	Time	T	S	Cond	TDS	Alk	NH4	SO4	PO4	NO3	SiO2	Al	Op	Rec	Waterway
0.3885339425	52.74079295	1707GH73	8.17	09:38	19	11.1	-1	-1	3079	0.43	1100	0.95	2.8	5.2	0	Gee	Hutton	Ouse TC3
0.3885362038	52.74079327	1707GH74	8.24	11:10	20.4	4.9	-1	-1			450					Gee	Hutton	Ouse TC3
0.3885344558	52.74079105	1707GH75	8.33	12:24	21	2.7	-1	-1	3541	-1	340	0.9	3.6	2.6	0	Gee	Hutton	Ouse TC3
0.3885362038	52.74079327	1707GH76	8.44	13:46	21.5	1.7	3178	1589	3570		160					Gee	Hutton	Ouse TC3
0.3885371701	52.74079362	1707GH77	8.48	15:09	20.4	1.2	2253	1126	3742	0.07	1250	0.98	2.8	2.4	0.006	Hutton	Gee	Ouse TC3
0.3885336849	52.74079117	1707GH78	8.63	16:34	22.8	0.9	1738	870	3541		20					Hutton	Hutton	Ouse TC3
0.3885358237	52.74079432	1707GH79	8.4	17:54	23.1	3.2	-1	-1	2990	0.09	500	0.91	3	5.3	0.007	Hutton	Hutton	Ouse TC3
0.3885358237	52.74079432	1707GH80	8.02	20:24	19.2	17.3	-1	-1	2857		1350					Hutton	Hutton	Ouse TC3
0.3804259301	52.71496886	1807GH81	8.58	19:28	19.7	1.5	2686	1342	3472	0.91	1800	0.29	9.7	9.8	0.007	Hutton	Gee	RC
0.3560188329	52.71703262	1807GH82	8.24	20:22	18.9	7.3	-1	-1	3717	0.15	700	0.48	2.5	19	0	Gee	Hutton	Ouse
0.3637356165	52.72348475	1807GH83	8.2	21:04	18.4	9.5	-1	-1								Gee	Hutton	Ouse
0.3654286343	52.72465816	1807GH84	8.2	21:47	18.2	9.7	-1	-1								Hutton	Gee	Ouse
0.3694895464	52.72756421	1807GH85	8.2	21:56	18.4	10.4	-1	-1								Gee	Gee	Ouse
0.3747260668	52.72922862	1907GH86		08:06														
0.3793469727	52.73429958	1907GH87	8.13	09:11	19.5	14.7	-1	-1		0.16	1150	0.64	3.4	6	0	Hutton	Gee	RC
0.3597790652	52.72074218	1907GH88	8.23	11:01		5.9	-1	-1		0.12	1300	0.47	3.1	3.6	0.002	Hutton	Gee	Ouse
0.3999396543	52.74484868	1907GH89	8.28	19:01	18.6	0.3	625	308								Hutton	Hutton	Ouse
0.385075004	52.76788002	2007GH90	8.01	08:50	19.6	25.5	-1	-1		-1	2100	0.41	1.8	2.2	0	Gee	Hutton	Nar
0.3812502653	52.77385154	2007GH91	8.01	09:52	23.4	27.2	-1	-1		-1	2150	0.36	1.6	4.1	0	Hutton	Gee	Ouse
0.3860741262	52.76629485	2107GH94	8.07	10:24	18.7	22.4	-1	-1								Hutton	Gee	Ouse
0.3870006603	52.76475439	2107GH95	8.04	10:40	19.2	24	-1	-1								Hutton	Gee	Ouse
0.3887843893	52.76209347	2107GH96	8.04	10:52	19.4	22.7	-1	-1								Gee	Hutton	Ouse
0.3950103937	52.76024991	2107GH97	8.23	11:02	19.2	18.8	-1	-1								Gee	Gee	Ouse

## 4 Synthesis

### 4.1 Overview

We will systematically evaluate our hypotheses by looking at evidence for seawater conservative mixing, the shape of the tidal cycle, the various water bodies, the paper mill industrial inputs, and how alkalinity relates to lithology. Finally, we will attempt to predict where Methane may be found in the case of future research.

### 4.2 Seawater Mixing

In order to construct a mixing line, we require a conservative tracer. The most basic of these is salinity vs distance down stream. As such, an annotated version of Figure 4 is shown. Additionally I verified that temperature is not a good tracer, as the well-mixed surface waters tend to thermally equilibrate with the atmosphere. (c.f. Figure 2).

Figure 6 shows very clearly that the St Germans pumping station is moving sufficient water to constitute the other end member in a conservative mixing model. Further upstream, I suggest that the St Germans station is causing a gradual migration upstream of the higher salinity water it pumps, and so essentially the whole green line is fairly uniform at high tides.

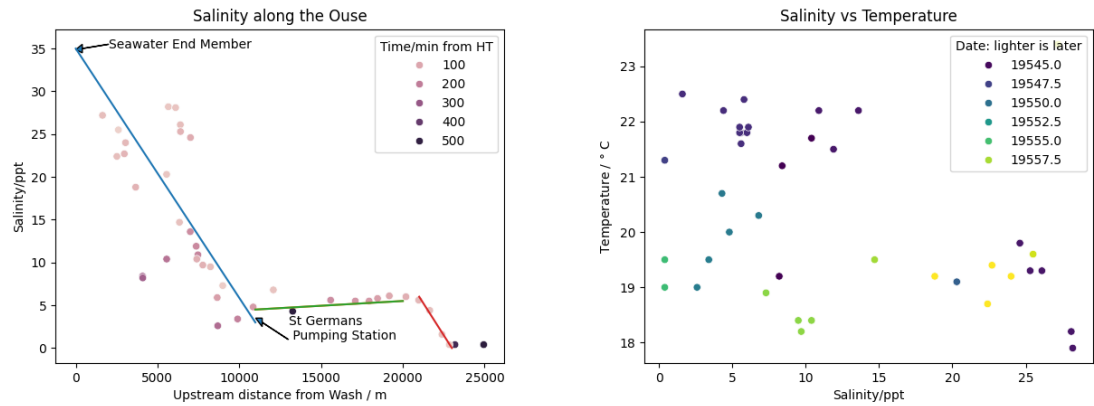
As expected the Salinity vs Temperature graph is not as simple. By comparing it with the average weather data from Figure 2 (Historical Weather, 2023), it seems that the later, colder air temperature dates, are also recording lower water temperatures. This might be due to the lengthy sampling process in areas with limited access giving time for water to equilibrate but more likely, the constant movement of the river keeps the temperature in accordance with the atmosphere.

More chemically rigorous tracers are possible. From our field measurements, we are able to use alkalinity to check for conservative mixing behaviour, though it's important to note that alkalinity may be affected by carbonate equilibria as discussed in section 4.7.

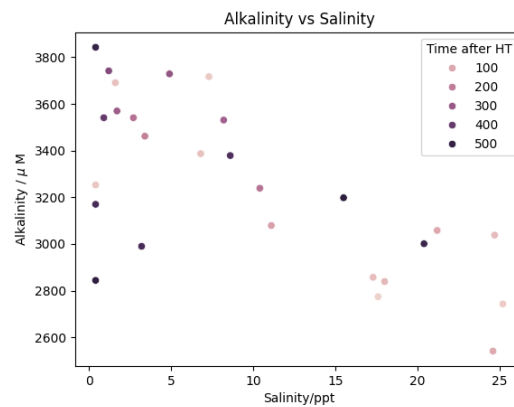
Alkalinity along the main Ouse channel might be a straight line, but at low tides the points with low salinity seem to indicate some sort of removal of alkalinity that makes this relationship non-conservative.

### 4.3 Tidal Influences

The major ions vary with the tides, as shown in our three tidal time series. Silicate to Nitrate ratios are also plotted in this section, as we hypothesised that tidal variations could affect the character of the life within the river.



**Figure 6:** Salinity works well as a conservative tracer. These figures only use data from the main Ouse channel, and seem to show a clear trend. The temperature does not work well, and is very similar to the atmospheric temperature.



**Figure 7:** In the Ouse, the later after high tide, the less conservative Alkalinity seems to be. Perhaps this is due to exposure of carbonates in the lower drift.

Over the course of a tidal cycle, ions vary. Sulphate naturally follows the salinity (cf: fig 8). Interestingly, ammonium mostly follows the tidal cycle, which we attribute to fertiliser runoff being carried by tidal flows.

Phosphate, on the other hand, seems to be inversely related with the tides, though this is especially prominent in the first repeat. This can be attributed to the fact that salinity can induce binding to soil particles. [5]

At night, silica and nitrate are both enriched, which indicates something about the biological life which would otherwise be consuming the nitrate. These photosynthesisers are likely diatoms, then, as the silica to nitrate ratio is not changing, and silica is being significantly uptaken during the day normally.

Aluminium was almost never recorded, as it must be on the lower end of our kits' range.

## **4.4 Impact of Water Management**

The ion data provides convincing evidence for the eutrophication of the Relief Channel, and the inflows from the St Germans pumping station seem to significantly impact Salinity and other concentrations.

St Germans pumping station has recently been outputting large amounts of water, which closely compare to the total discharge from the whole Great Ouse system. This has significantly diluted the downstream region of the Ouse.

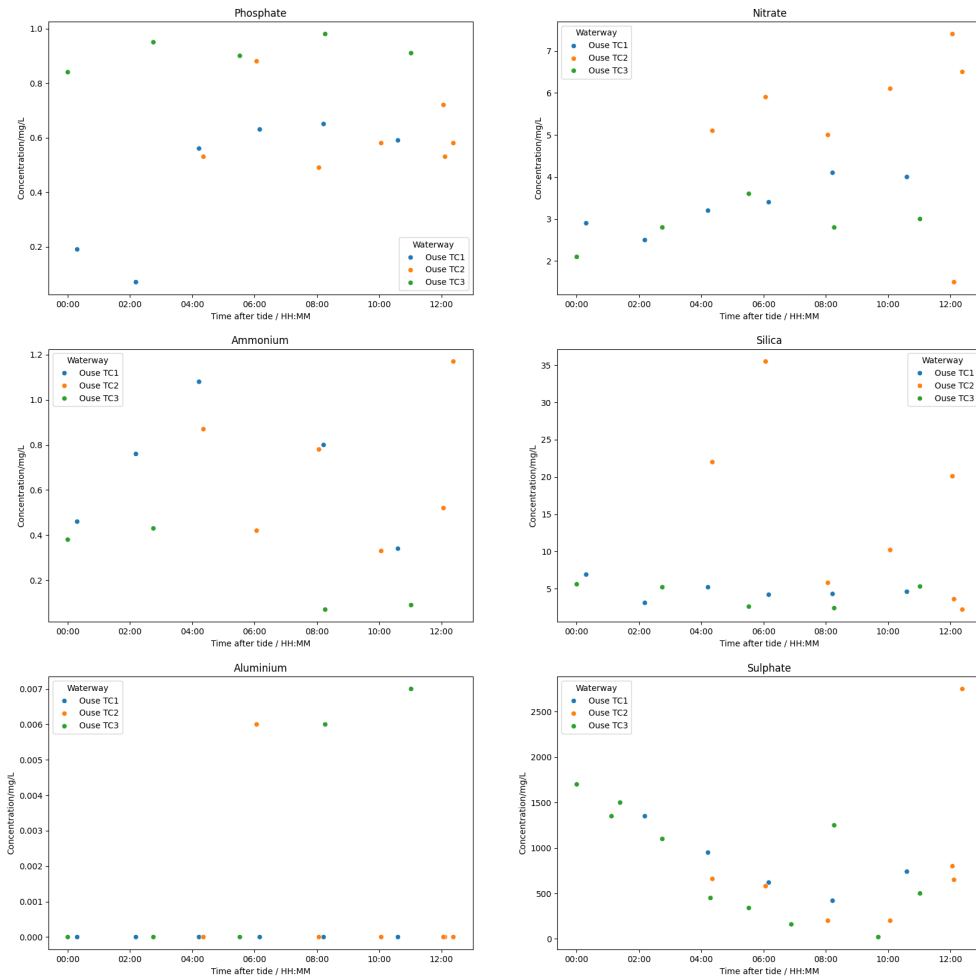
## **4.5 Tributaries and the Relief Channel**

By taking an average of the high tide readings we had for each location, we could produce comparisons between the overall nature of these bodies of water.

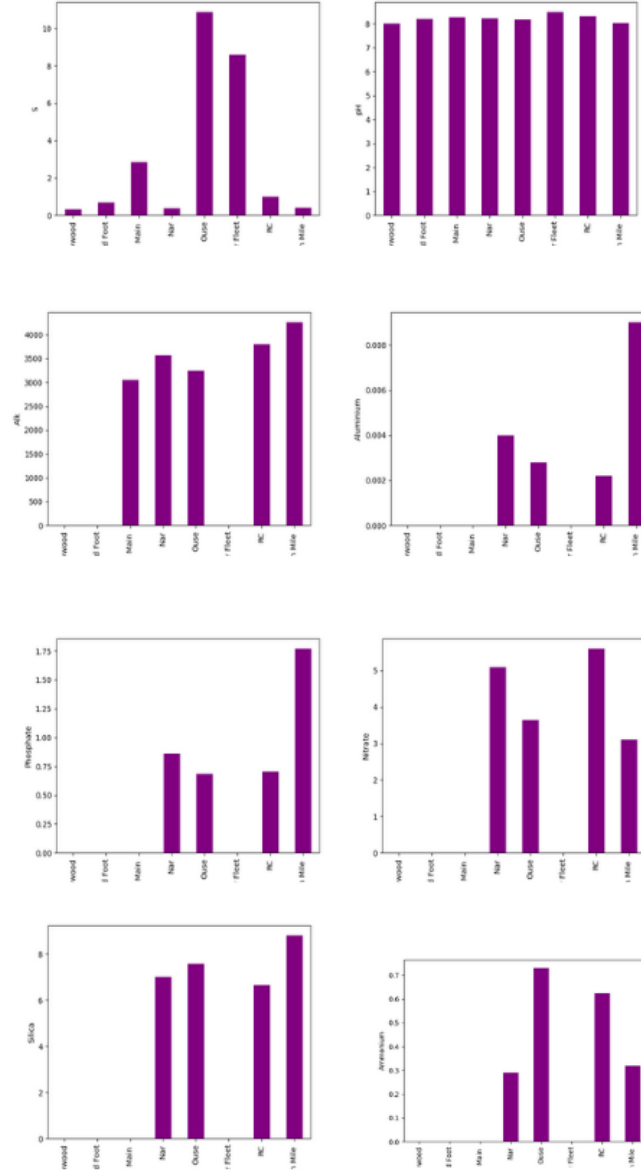
pH is slightly higher in the RC and the visibly eutrophied Pur Fleet. RC also has elevated levels of Nitrate, which further indicates eutrophication. This could have been related to increased Methane productivity. [3]

Alkalinity is highest in the 10 mile river and the Nar, both tributaries which flow in from more carbonate rich bedrock. That could indicate dissolution. Phosphate and Aluminium are both very high in the 10 mile river, which might indicate some effluent inflow further upstream, though we did not observe or find this recorded.

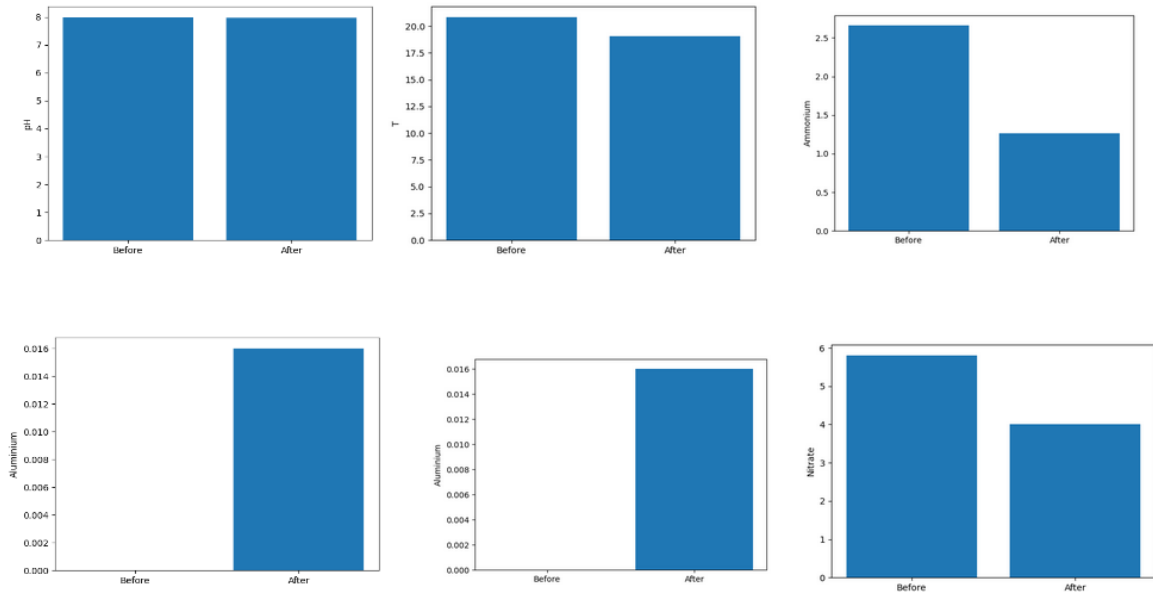
Ammonium is most prevalent in the Ouse itself. This is likely related to land use. The land between the RC and the Ouse is almost all plant agricultural, and therefore would produce significant amounts of fertiliser runoff. This is reflected by the RC also being high in this. As it's a diffuse source, no other individual tributary has recorded this.



**Figure 8:** From our single location tidal cycles at the Cut Bridge, we found changes in ion chemistry.



**Figure 9:** The various tributaries and waterways in our catchment have different chemical profiles. Salinity seems almost entirely confined to the Ouse, which makes sense, as many of the tributaries are either very small or quite far up stream.



**Figure 10:** The major industrial inflow is the Palm Paper Mill which has been extensively regulated by the Environment Agency.

## 4.6 Industrial Inputs

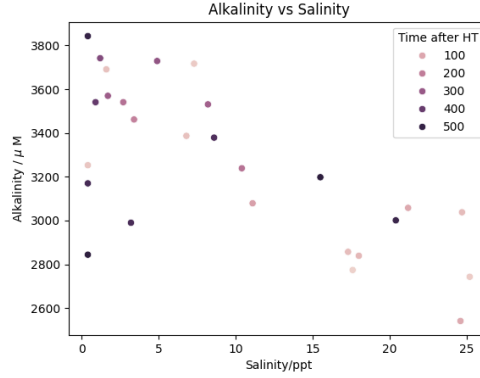
Concentrations are shown immediately before and after the location of the paper mill outflow detailed in section 1.2. The Environment Agency (2016) suggests that this outflow site is likely to produce:  $\text{NO}_3$ ,  $\text{PO}_4$ , metals and suspended solids.

It seems that despite expecting higher pH, higher T, more Nitrate and Ammonium, we did not observe any of those. The outflow was visible during our fieldwork, so it seems likely that the treatment is better than reported. Aluminium, which was not detectable in any sample within 1km upstream, was present after the outflow, so this seems a plausible link.

The Palm Paper Mill takes in water from the Relief Channel, which is relatively low salinity and low concentrations in phosphate, so this might be why the outflow seems to have no measurable effect. It also is possible that the volume outflowing was not sufficient to be detectable.

## 4.7 Lithological Controls

Alkalinity looks very nearly conservative, except for in the Nar, Middle Level Main Drain, and at points close to them in the Ouse. This is likely due to the varying sediment carbonate once you get further away from the main channel. The Nar flows through Tithonian carbonate rich muds, and so could increase its alkalinity; and then decrease it



**Figure 11:** The Ouse’s alkalinity behaves conservatively, likely because the impermeability of the Kimmeridge clay makes it hard for the river to dissolve the rocks beneath it.

due to flow rate changes.

Broadly though, the Ouse’s alkalinity behaves conservatively, likely because the impermeability of the Kimmeridge clay makes it hard for the river to dissolve the rocks beneath it, or allow groundwater to mix with the river channel.

## 4.8 Predicted Methane Concentrations

As detailed in Appendix A, our methane concentration measurements did not show any variation; this means we have to rely on previous research and scientific reasoning to predict CH<sub>4</sub> concentrations across the catchment.

Methane is likely to be present in the partially eutrophied Relief Channel, as well as in the less saline areas. Additionally, the high nitrate in some areas of the Ouse would be ideal for CH<sub>4</sub> producers.

## 5 Conclusion

Salinity in the Great Ouse is dominated by two gradients, the temporal tidal cycle, especially in the area up to the St Germans pumping station; and the spatial distance to the sea. The St Germans pumping station has a significant impact on diluting the seawater end-member. Sulphate follows salinity, as it’s a major ion in the ocean, whereas phosphate binds with soil particles and is removed at high salinities. Silica and Nitrate are enriched at night, as the primary producers do not consume as much. The fact their ratio is constant on our timescales indicates that the species composition isn’t changing and it’s more likely to be diatoms. Alkalinity is mostly conservative due to the impermeable Kimmeridge clay, but some tributaries record changes due to Carbonate dissolution and



precipitation. Industrial input from the Palm Paper mill are negligible and were not detectable. More work is needed to help associate this nutrient information with CH<sub>4</sub>. We predict that increased Nitrate and higher pH (such as is present in the Relief Channel) would promote CH<sub>4</sub> production.

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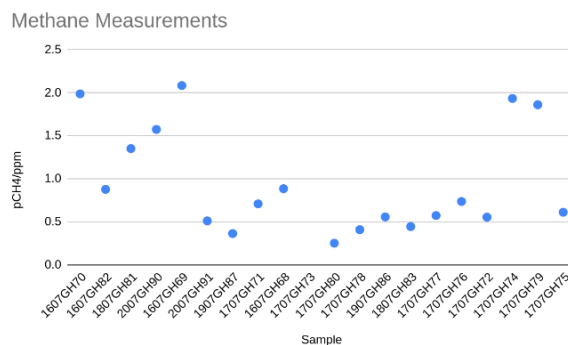
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## Appendix A Methane Measurements

Methane concentration measurements taken on this project were found to be contaminated with atmospheric air. We believe that the filters used encouraged equilibration with the atmosphere which is why almost all the CH<sub>4</sub> is at atmospheric 0.5ppm levels, despite the proximity to the CH<sub>4</sub> rich fens.



**Figure 12:** These concentrations are all near atmospheric

We initially chose to filter these samples because of the length of time between collection and recording, as we knew the microbes would continue to alter the gas properties.

## Appendix B Digital Notebook Resources

- Alkalinity Gran Titration Calculations:  
[https://docs.google.com/spreadsheets/d/17R9hZ8hc0imuU1Jg9i\\_P7VLwGXkn1K\\_rU\\_XBA7VAJpY/edit?usp=sharing](https://docs.google.com/spreadsheets/d/17R9hZ8hc0imuU1Jg9i_P7VLwGXkn1K_rU_XBA7VAJpY/edit?usp=sharing)
- Final Data Table:  
[https://docs.google.com/spreadsheets/d/1H0pfV0QaPXJ\\_1bPAbo8XepHf4pRKPItX33lwo0n-X\\_8/edit?usp=sharing](https://docs.google.com/spreadsheets/d/1H0pfV0QaPXJ_1bPAbo8XepHf4pRKPItX33lwo0n-X_8/edit?usp=sharing)

## Appendix C Abbreviations

- RC = Relief Channel
- Ouse/GO = Great Ouse River
- T = Temperature
- S = Salinity
- TDS = Total Dissolved Solids
- SO4 = Sulphate
- NO3 = Nitrate

- Al = Aluminium
- SiO<sub>2</sub> = Silica
- PO<sub>4</sub> = Phosphate
- NH<sub>4</sub> = Ammonium

“I declare that the submitted work is my own, except where acknowledgement is given to the work of others or to work done in collaboration. I declare that I have read and understood the Department of Earth Sciences statement on plagiarism and that my work could be tested using automated plagiarism software.”