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A Benchmark Study on the Malago River's Water Quality

Group I

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Abstract

This report aims to provide new insight into the water quality of the Malago River, south west Bristol, in a benchmark study. 20 water samples were taken downstream, before tests were carried out in the laboratory to investigate the river's water quality. Results suggested that the Malago's water quality is very good in terms of ammonia, nitrite, nitrate and phosphate concentrations when compared to Environment Agency standards (2011). It is anticipated however, that pollutant fluxes will increase rapidly following rainfall events (Higashino and Stefan, 2014). Nitrite and nitrate concentrations increase and decrease respectively preceding a dam on the river, but the effect is not significant on the water quality in accordance with Environment Agency standards (2011). It was expected that microplastic counts would increase before the dam, as seen on large scale dams (Zhang et al., 2015), however this pattern was not reflected on the small scale of the Malago.

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1.0 Introduction

Water chemistry in river catchments has many implications for river health, diversity and biology (Handy, 1994; Reinhert et al., 2002; Gordon et al., 2012). Nitrogen (consisting of ammonia, nitrite and nitrate) and phosphorus are essential nutrients in rivers, being important controls on primary production (Alexander et al., 2007). However, when these are found in excess in river catchments, the river health and biology can be damaged through eutrophication and algal blooms (Smith et al., 1995; Li et al., 2014). In addition, high ammonia concentrations may negatively affect river biology, by depleting fish populations (Lease et al., 2003), whilst excess nitrite can be damaging to plants and can reduce the respiratory abilities of aquatic organisms (Philips et al., 2002).

Whilst nutrients are an important control on river water quality, many research papers have recently focused on the influence of microplastics on catchment health. Microplastic contamination in marine environments and freshwater systems has been an ever-concerning problem since mass production of plastics in the 1940s (Cole et al., 2011; Wagner et al., 2014). In 2009 alone, 230 million tonnes of plastic was produced (PlasticsEurope, 2009), with some, inevitably, being deposited in river systems through dumping or runoff. UV light degrades larger pieces of plastic, converting them to microplastics (< 5mm in size; Gregory, 1999; Erikson et al., 2013). In aquatic systems, organisms confuse microplastics for food (Avio et al., 2017) which can result in bioaccumulation of plastic pollution, putting organisms in higher trophic levels at risk (Farrel and Nelson, 2013).

River water quality studies investigating the influence of both nutrients and microplastics on river health have been conducted at a range of catchment scales. The following report builds on previous understanding of water quality controls with application to a small, urbanised river catchment in Bristol.

1.1 The Malago River

The studied river is an 800m stretch of the Malago River, situated in Manor Woods Valley Conservation Park, Bishopsworth, approximately 2.5 miles south-west of Bristol city centre (figure 1a). The river is immediately surrounded by vegetation and parkland yet resides in an urbanised suburb (figure 1b). The river first flows out of a tunnel beneath a road, and the downstream end flows underground into a culvert, in front of which debris and litter had accumulated. Located approximately half way down the reach are allotments (figure 1b), with large open grassland beyond. A dam, roughly 7m wide and 1.5m tall, features at two thirds of the distance down the river, along with two smaller weirs at approximately 90m and 190m downstream respectively.

The convenor of Malago Valley Conservation Group (a group dedicated to conservation of the area) provided the authors with specific briefs regarding the outcome of the investigation. The first was to provide an updated map of the area, with the inclusion of a previously unplotted footpath running along the wooded southeast bank of the river. The second was to provide an indication of the water quality of the river in reference to water quality standards, and to investigate the dam’s potential control on this.

Figure 1: a) The Malago's location in south west Bristol, highlighted in red (Google Maps, 2018). b) The 800m stretch of river, with the allotments, highlighted in red (DigiMap, 2018).

1.2 Secondary Data

The secondary data relating to the reach which could assist in achieving such aims was limited; a previous report by University of Bristol students (2017) investigated the water quality of the Malago and Pigeonhouse (running parallel to the Malago) streams. This was undertaken in terms of E-coli, which emerges from faecal contamination; excessive quantities indicate increased likelihood of waterborne disease outbreak (Madoux-Humery et al., 2016). The previous report concluded that water quality increases downstream between relatively sparse locations, only one of which was located in the reach in focus of this study. Whilst this study does not directly measure E-coli counts of the river for reasons which will be discussed, it will be possible to use this data to help make inferences about the quality of the river when compared with existing water quality standards. Such standards also exist for nutrients including phosphate, nitrite, nitrate, ammonia (Environment Agency, 2011) to allow classification of water quality with respect to multiple variables. It will be possible to contextualise the water quality findings in terms of rainfall, with comparisons to the Colliters Brook gauging station data (Shoothill Gauge Map, 2018), only approximately 1.5 miles from the Malago River.

1.3 Previous Research and Hypotheses

As mentioned, the river is located near allotments. It also has a mudstone bedrock and is in a relatively urbanised catchment, so most of the ground is relatively impermeable. This increases the potential for pollution inputs to the stream by surface runoff. As explained by Higashino and Stefan (2014), rainfall intensity is a key control on nutrient input to rivers. Therefore, before conducting fieldwork and measuring nutrient concentrations, qualitative meteorological observations were made in the days prior to the fieldwork. This suggested that pollutant fluxes were likely to be low due to limited rainfall over the preceding week, leading to the development of the following hypothesis:

H1: Ammonia, nitrite, nitrate and phosphate concentrations will fall within Environment Agency standards (2011) for high quality water.

With reference to the brief proposed by members of Malago Valley Conservation Group, the control of the dam on water quality is an area of focus within the report. Previous research has suggested that structures causing a build up of water, such as dams, may have implications for water quality due to microplastic accumulation (Zhang et al., 2015). Whilst much research has been applied to large scale river catchments with significantly larger dams, less research has been carried out in small river catchments, such as the Malago. It is hence unknown whether results on large scale catchments may be transferable to smaller catchments, leading to the formation of the following hypothesis:

H2: Microplastics build up in front of the dam on the River Malago, degrading the water quality.

Whilst there has been much research into the impact of excess nutrients on catchment health, considerably fewer papers have looked at the impact of dams on nitrate and phosphate concentrations. It has been suggested however, that sediment build up before dams may cause denitrification in an anaerobic environment, whereby nitrite and nitrate concentrations increase and decrease, respectively, in the presence of low oxygen saturation (Kelso et al., 1997; McGee, 2008). Much of this research has been conducted on dams with similar dimensions to the one on the Malago, such as McGee's (2008) application on five dams lower than 5m in height in central Ohio. It is hence hypothesised that:

H3: Nitrite concentration increases in the sediment rich water before the dam, whilst oxygen saturation decreases.

2.0 Methodology

Prior to data collection, a pilot study was conducted on the river, in which the most beneficial sampling strategy was identified. Qualitative observations of the surroundings and physical characteristics of the river during the pilot study gave an indication of the variables which would be beneficial to the aim of this study and could be feasibly measured. Observations suggested that measurements for heavy metals and digestion were not necessary due to lack of nearby industry and the low turbidity of the river, respectively. It was also anticipated that E-coli would have yielded very high values due to large amounts of dog waste on the ground adjacent to the river, and it was hence not measured. Since coming to this decision, the parameters of the investigation have changed from solely looking at the influence of the dam on the Malago's water quality to looking at the overall health of the river also. Therefore, inferences about the water quality in terms of E-coli will be made from secondary data available from Bristol City Council

(2018). The methods which were used to collect data for variables in the field and laboratory are described below.

2.1 Field Work

2.1.1 GPS Mapping

In order to fulfill the client's requirement of a map of the footpath running along the eastern bank of the river, waypoints were taken every five metres whilst walking its length, using two Garmin Etrex 10 GPS units. The mean of these sets of coordinates was then taken and joined in ESRI ArcMap to create a line feature. This was added to an OS Vector Map Local file (Digimap, 2018) and contours derived from 2005 LiDAR DTM tiles with 1m spatial resolution (Environment Agency, 2015). A scale bar, north arrow and 100m grid lines were added for ease of use when using the map for ecological surveys. The final map can be viewed in section 6.1 of this report.

2.1.2 Water Quality

The 800m reach was systematically split into 20 equidistant sites, providing a dense sample to allow effects of the dam, weirs and changing river channel characteristics to be identified (figure 2). At each of the 20 sites, a 500ml sample of water was taken from beneath the surface of the

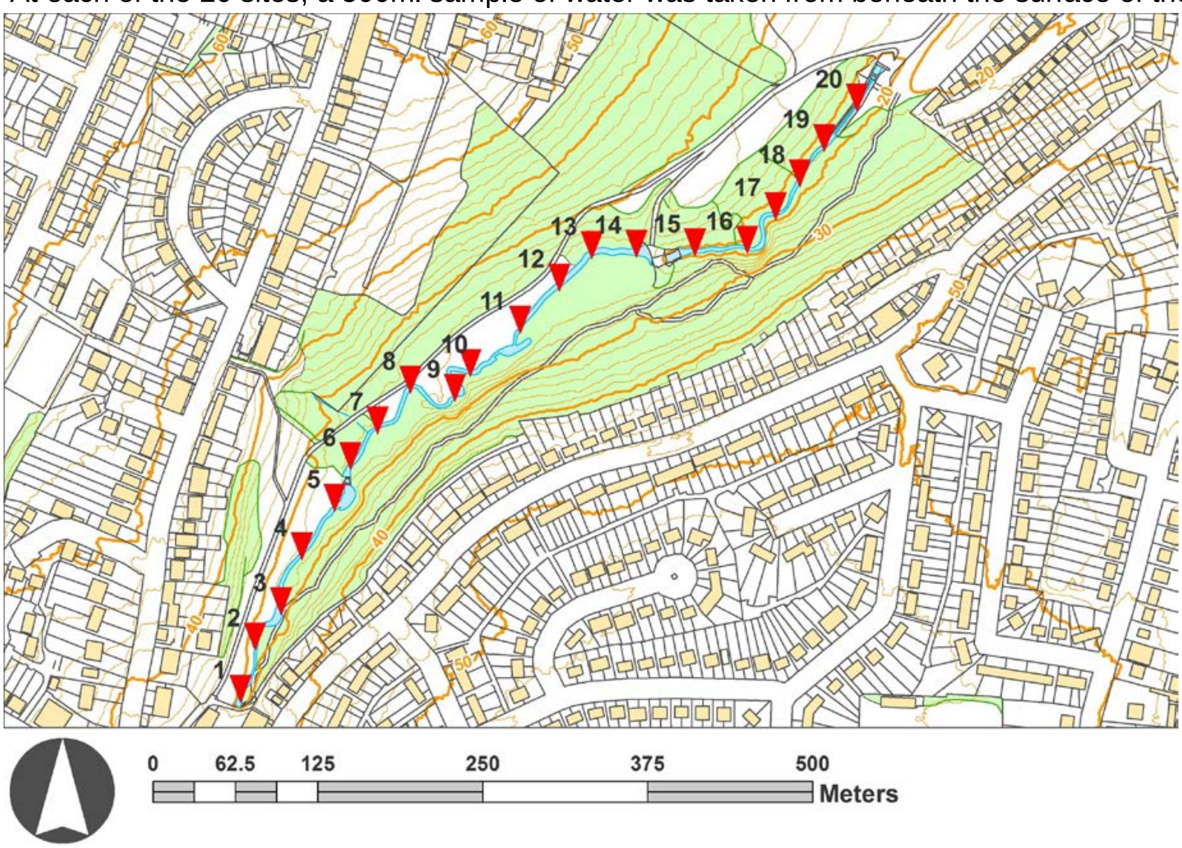


Figure 2: Site locations on the Malago River where water samples were taken and measurements of oxygen saturation, conductivity and pH were made (DigiMap, 2018). In this investigation, site 1 was located at 0m and site 20 was located at 760m downstream.

water to prevent oxygen bubbles interfering with the water in transit between the field and laboratory. Measurements of oxygen saturation, pH and conductivity were taken at each of these sites using probes held upstream of the user. Oxygen saturation would be used to identify potential anoxic locations and to investigate the nitrification process, and pH and conductivity were used as other variables with which the quality of the river could be assessed.

2.2 Laboratory Work

Immediately after returning from the field and in between the undertaking of each test, every sample was placed in a fridge at 5ºc. Due to the nature of some of the variables being measured, certain tests needed to be carried out within a time limit of 48 hours for the results to be valid; these were Biochemical Oxygen Demand (BOD) and chlorophyll. Remaining tests were carried out that week, and microplastics were analysed two weeks later.

2.2.1 BOD

To measure the amount of oxygen used in respiration at each site, the oxygen levels were measured before and after an incubation period of 48 hours at 25ºC. During this time, bottles of sample water, sealed and with air bubbles removed, were wrapped in tin foil to prevent light entering, stopping photosynthesis. This allows the gross respiration to be calculated, rather than the net respiration. The river sites with the greatest decrease in oxygen saturation over the incubation period reflected the areas with highest demand for oxygen and most active microbial life, enabling patterns between biological activity and pollutant and nutrient concentrations to be identified. Limitations associated with equipment availability prevented measurements from being taken in duplicate or triplicate, so this will be considered when investigating the outcomes of this process.

2.2.2 Chlorophyll

At each site, 100 ml of sample water was filtered before covering the filter paper in tin foil and freezing at -20ºC for 24 hours. After this period, a 5mm strip was cut from every sample's filter paper and placed in 10 ml of acetone. This was placed in a centrifuge and spun for 15 minutes before using a spectrophotometer, set at 665 nm to pick up green light wavelengths to quantify the amount of green pigment in the sample. This was used as a proxy for the amount of chlorophyll present. Similarly, this would allow inferences to be made about the effects of pollutant levels on the activity of photosynthesising microorganisms.

2.2.3 Turbidity

To allow the quantification of sediment build up behind the dam and weirs, vials of 5ml of each of the 20 samples were placed in a turbidimeter to measure the amount of sediment in suspension. The scale of measurement was adjusted accordingly, depending on the results presented: the scale from 0-10 (TU) was used for each sample.

2.2.4 Microplastics

To identify to abundance of microplastics in the Malago River samples, a method developed by Maes et al. (2017) and adapted by Owenbridge and Gordon (personal communication, 2018) was used. 50 μL of Nile Red dye was added to 5 ml of each site's sample and put in a rotary shaker for one hour on maximum speed, to allow the plastic to absorb the dye. The samples were filtered through a 0.45 μm, 47mm filter, which were then placed under a UV microscope. The microplastics, having absorbed the dye, glowed blue and so could be counted.

2.2.5 Gallery Data

The concentrations of nitrite, nitrate, ammonia and phosphate were measured from 10 ml samples from each site, using the gallery automated photometric analyser. This was conducted to enable the investigation of the nitrification process and additionally, to examine the water quality.

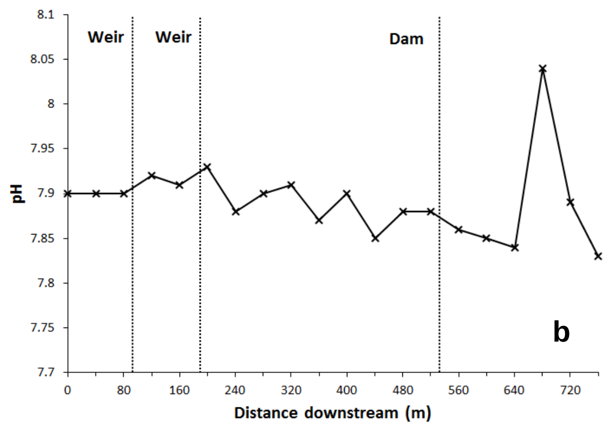
3.0 Results

For the full tabulated dataset, see table A1.

3.1 Variables Discarded from Further Investigation

This study will hereafter not use the results of BOD or chlorophyll to determine the effects of water quality on the biological activity in the Malago River, as the results were inconclusive (figure 3a). Due to the time of year of data collection and its associated lack of activity, conclusions drawn will not be representative of trends in the river throughout the rest of the year. The use of these results was also discouraged following the recording of several negative BOD calculations, indicating an increase in oxygen concentration during the incubation period. Similarly, chlorophyll was discarded from further investigation, as results returned no values.

Despite that pH values recorded on the Malago River lie comfortably within the Environment Agency standards for good quality water of between 6 and 9 (figure 3b; 2011), it was not used as a variable in analysis or interpretation of other results as it does not aid the conclusion of this investigation's hypotheses. A similar scenario was encountered with conductivity results (figure 3c), which lie beneath the Environment Agency standard of 2500 μScm^{-1} for water safe for human consumption (2011). However, this information is also unable to further assist in concluding this report's hypotheses.



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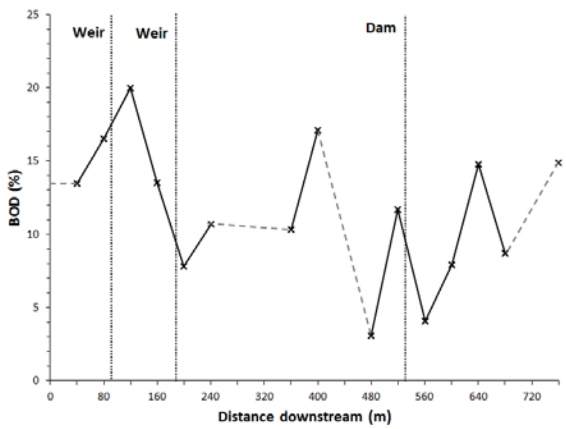

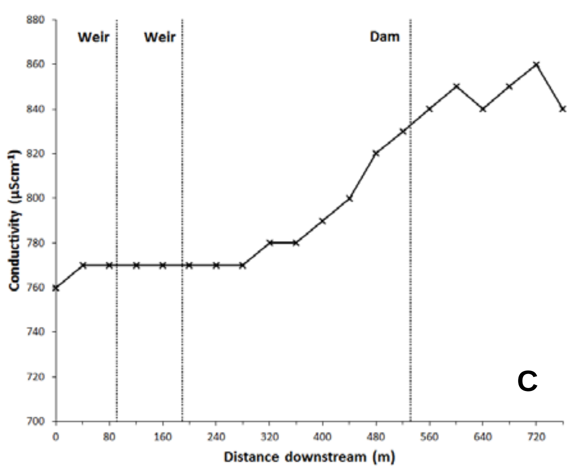

Figure 3: a) BOD in the Manor Woods Valley section of the Malago River. Grey dashed lines represent areas where BOD results were negative, and so removed from the results. b) pH and c) conductivity along the same stretch of river.

3.2 Hypothesis 1

The data for ammonia, nitrite, TON (from which nitrate was calculated) and phosphate concentration obtained from the gallery was very precise. Each measurement is rounded to, and therefore precise to, three significant figures, having taken into account the detection limit and measurement error for each nutrient. These detection limits were 1.3µgL^{-1}, 1.6µgL^{-1}, 7.3µgL^{-1} and 0.8µgL^{-1} for ammonia, nitrite, TON and phosphate respectively, all with a measurement error of ±2%. However, due to time constraints, repeat samples were not carried out and hence, error bars are not included on the graphs. The size of the error bars on each of the nutrients, when taking into account gallery precision data, was so small that this data was considered negligible.

3.2.1 Ammonia

Ammonia standards for inland freshwaters have been calculated by the Environment Agency (2011) resulting in the formation of 5 classes ranging from 'very good quality' to 'poor quality' represented respectively by RE1 to RE5. For ammonia, RE1 has a value of 0.25 mgL^{-1} and so concentrations lower than this would fall into this top category. To fall into the RE2 category, water must contain less than 0.6 mgL^{-1}, with lower classes gradually increasing to a value of 9 mgL^{-1} for RE5.

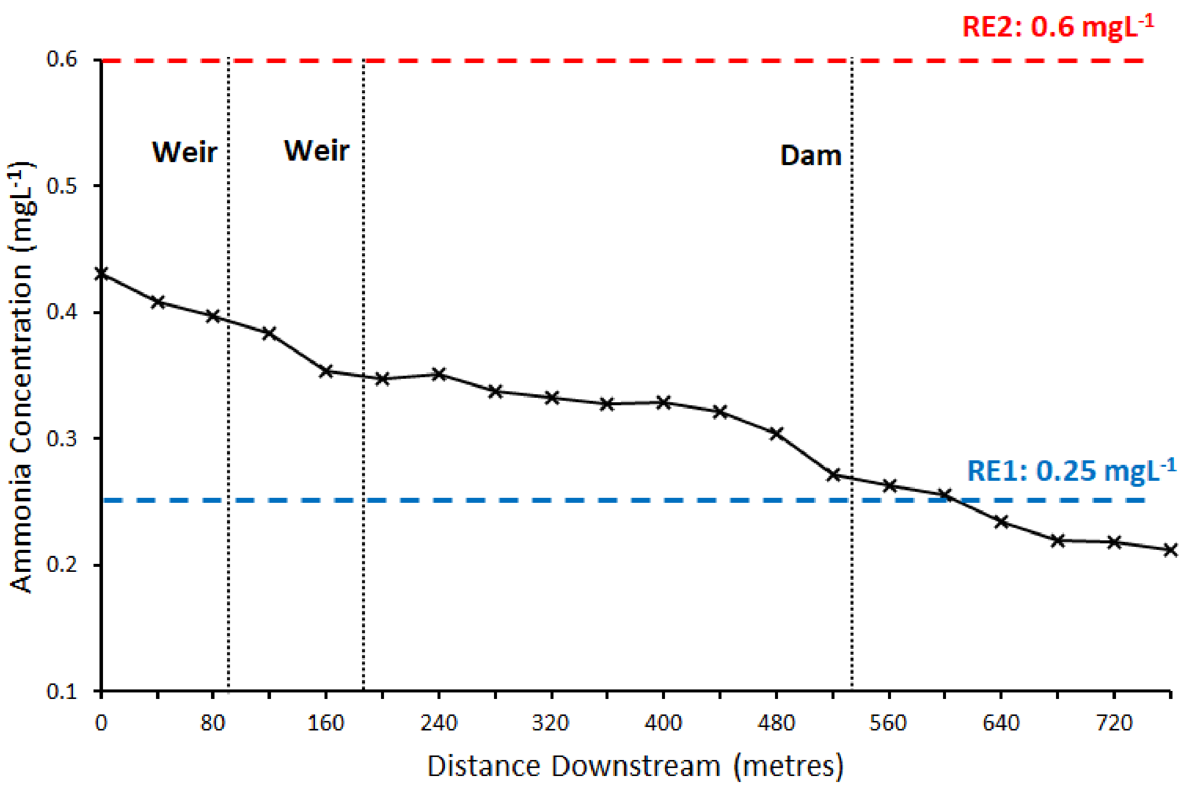

Figure 4: Ammonia concentrations in the Manor Woods Valley stretch of the Malago River, compared to the Environment Agency categories for RE1, 'very good quality', and RE2, 'good quality', of ammonia concentrations (2011).

The entire stretch of the Malago River in the Manor Woods Valley fell into at least the RE2 class (figure 4). The highest ammonia level recorded in the Malago was 0.43 mgL^{-1} falling comfortably into the RE2 standard of 0.6 mgL^{-1}; 'good quality'. Ammonia levels in the reach continuously decreased downstream, and as such the final 160 m leading up to the culvert fell into the 'very good quality' classification, with ammonia concentrations below 0.25 mgL^{-1}. The average ammonia concentration for the entire stretch is 0.32 mgL^{-1}, so overall the water falls into the 'good quality' RE2 category.

3.2.2 Nitrite

As there were no inland water quality standards available for nitrite, drinking water standards were used instead, on the basis that they would be more thorough. In order for the water to be suitable for drinking, nitrite concentrations must be below 500 μgL^{-1} according to the Environment Agency (2011). All recorded nitrite concentrations in the river fell below this value (figure 5), with an average over the reach of 130 μgL^{-1}. Even the highest concentration measured (191 μgL^{-1}), immediately following the dam, is comfortably below this standard.

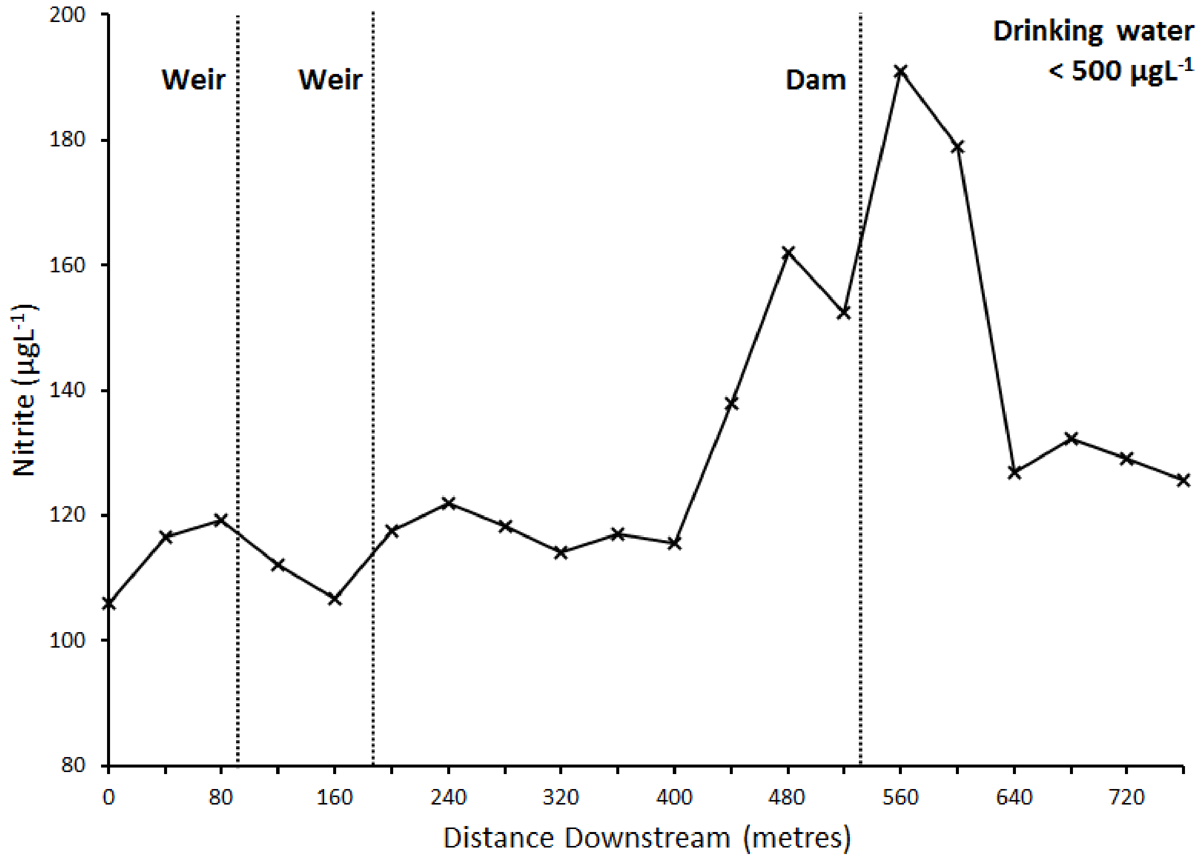

Figure 5: Nitrite concentrations in the Manor Woods Valley section of the Malago River, and associated standards for drinking water (Environment Agency, 2011).

3.2.3 Nitrate

Drinking water quality standards from the Environment Agency (2011) were also used for the assessment of nitrate concentrations. The classes of DW1, DW2 and DW3 represent the highest quality water, suitable for abstraction for drinking water. To fall into the highest nitrate water quality category of DW1 nitrate values must be lower than 50 mgL^{-1}. Nitrate values in the Malago fall comfortably into this top category of DW1 (figure 6). The highest nitrate value recorded was only 5.1 mgL^{-1}, with an average of 4.95 mgL^{-1}, showing the Malago River to be of a very high quality in terms of nitrate.

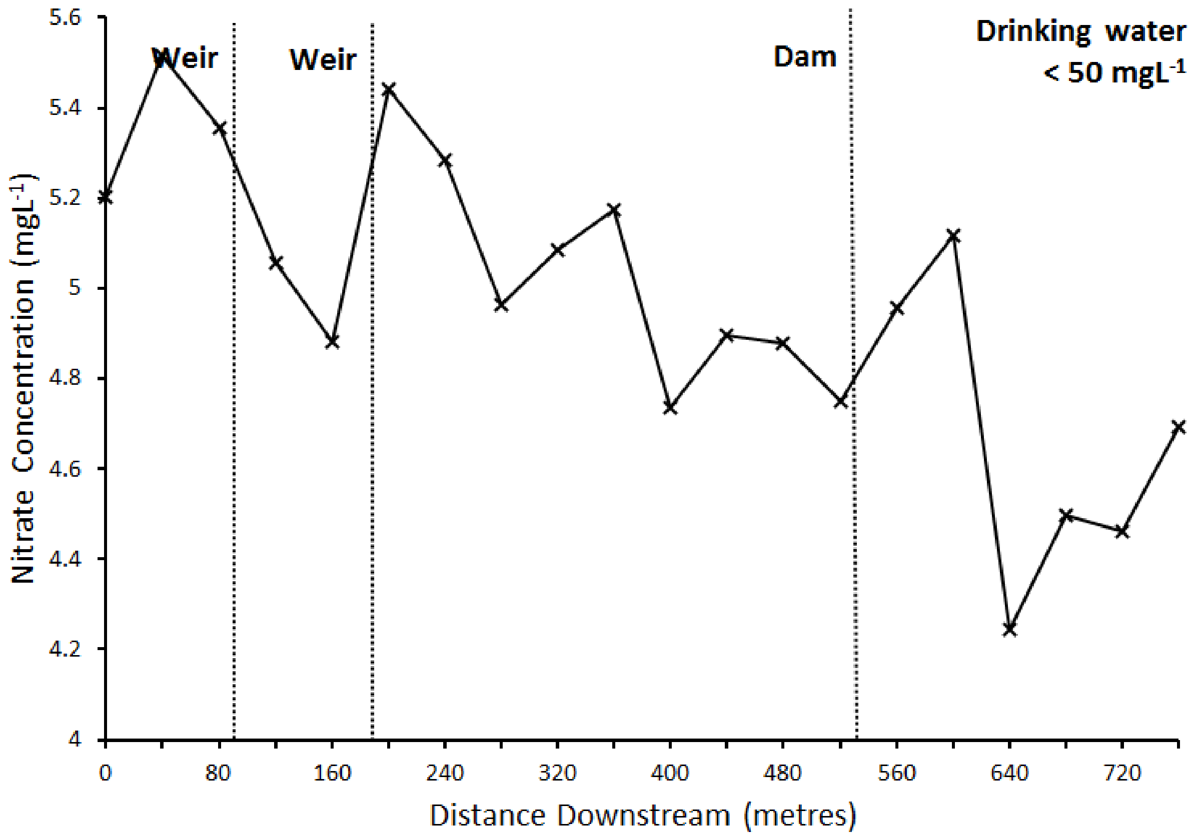

Figure 6: Nitrate concentrations in the Manor Woods Valley section of the Malago River, with the standard for drinking water quality stated above (Environment Agency, 2011).

3.2.4 Phosphate

The Environment Agency (2011) standards for phosphate are split into categories of decreasing water quality, from A1 to A3. Concentrations of phosphate in the A1 category need only simple physical treatment and disinfection in order for it to be safely used for drinking water. In order to fall into the A1 category phosphate concentrations must be below 0.4 mgL^{-1}. The entire reach fell into the A1 category as none of the values rose above 0.4 mgL^{-1} (figure 7). The highest value recorded in the river was 0.07 mgL^{-1}; far below the A1 threshold, showing the water quality in terms of phosphate was very high.

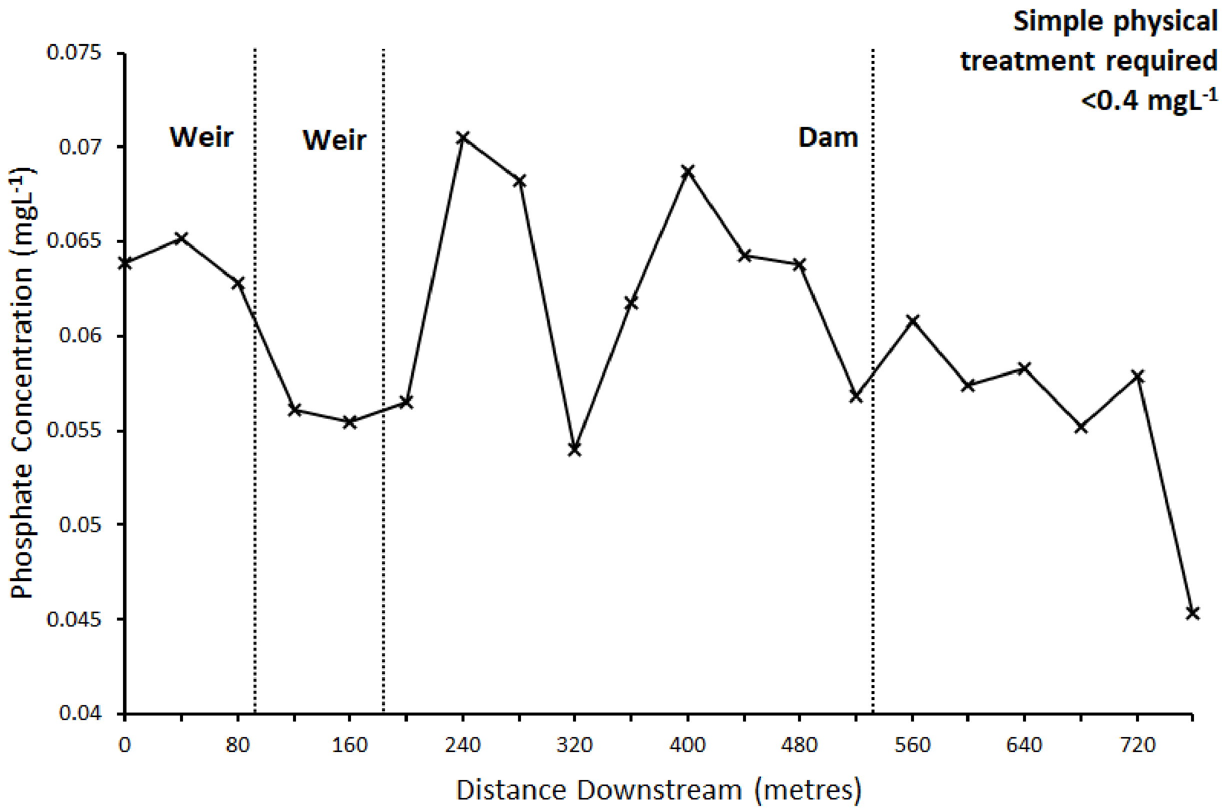

Figure 7: Phosphate concentrations in the Manor Woods Valley section of the Malago River, with the associated standard stated above (Environment Agency, 2011), where only simple physical treatment and disinfection would be needed for drinking water. It must be noted that "simple physical treatment" is the highest standard of water quality stated by the Environment Agency.

3.2.5 E-Coli

In addition to primary data, secondary data has been used to make further inferences about the Malago's water quality. In this investigation E-coli counts were not directly measured, but, having examined secondary data from Bristol City Council (2018), E-coli measurements were found for the Malago river every month since 1995. In 2003 a storage tank was installed, and so E-coli counts were significantly reduced and have been relatively stable since, as a result figure 8 shows only the E-coli counts since 2004. It is evident that E-coli counts in the Malago do not fall below the Environment Agency (2011) standards for bathing water at 10,000 counts per 100ml (figure 8). Instead, E-coli concentrations vary hugely with many of the values recorded rising well above this number. This implies that the water quality in terms of E-coli is highly variable and likely to be unsafe for swimming, however, these measurements were only recorded at a single point in the Manor Woods region and so may not reflect the entire river.

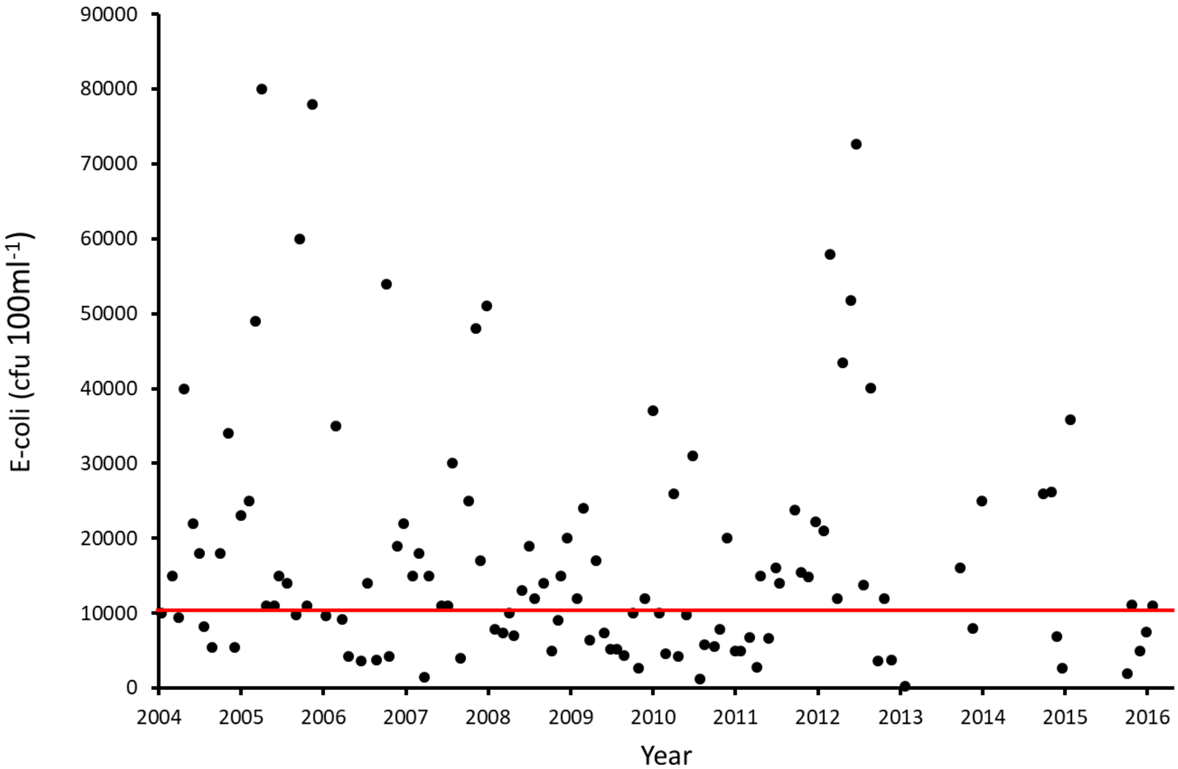

Figure 8: E-coli counts in the Malago River since August 2004, after the installation of the storage tank (Bristol City Council 2018).

3.3 Hypothesis 2

Throughout the stretch of the Malago River in question, there is an overall increase in microplastic counts (figure 9), seemingly doubling between the upstream and downstream ends of the river. The increase is not continuous; there are large fluctuations. The trends observed on either side of each weir mirror each other; microplastic counts immediately increase following the structures, then proceed to decrease with distance downstream. However, the trend associated with the dam is different. Instead of displaying a large increase immediately after the structure, there is a decrease in microplastic counts beginning around 50 metres before the dam, which continues immediately after the dam. Only then does a sharp increase in microplastic counts occur, as seen immediately after the previous weirs. This is when microplastic counts are at their highest throughout the reach, at 31400 counts L^{-1}. However, there is considerable variation in the data, so it is almost impossible to ascertain the exact effect of the dam on microplastic accumulation.

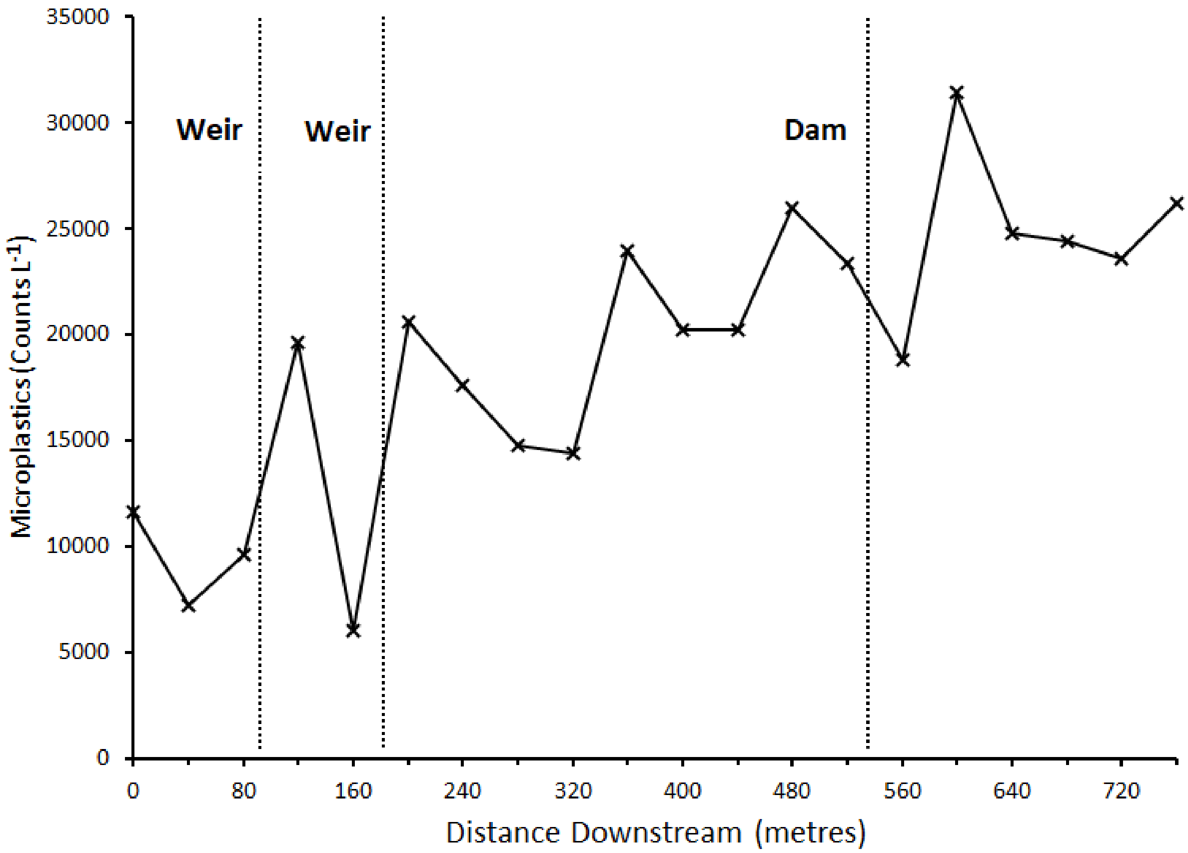

Figure 9: Microplastic counts in the Manor Woods Valley section of the Malago River.

It must also be noted that it is not possible to specify the error of each of the microplastic recordings due to the limitations associated with equipment availability; the samples were only measured once at each site. As such, caution must be taken in the interpretation of these results. However, it is important to note that the method blank used yielded a microplastic count of 12200 L^{-1} (higher than sites 1, 2, 3, and 5). This may suggest that real microplastic counts are actually much lower than those observed.

Despite the dam not appearing to have any significant effect on the accumulation of microplastics, it is worth noting that microplastic concentrations rise significantly along the reach studied. Taking into account that the method blank yielded high results, values change significantly from as low as 6000 counts L^{-1} in the first 200m and 31400 counts L^{-1} just after the dam.

3.4 Hypothesis 3

3.4.1 Turbidity

Upon observation, the water before the dam appeared to be more turbid, which would have suggested higher suspended sediment load, than other areas of the Malago. It was therefore initially thought that the dam may have an important control on the turbidity of the water in the

Malago. Figure 10 demonstrates that in reality this may not be the case. Turbidity fluctuates downstream, appearing to show no significant pattern. It decreases before the dam between 400m and 520m downstream, contrary to qualitative observations. This may be due to limitations associated with the turbidity method or could also be because observations were influenced by the greater depth of the water, making it appear more turbid.

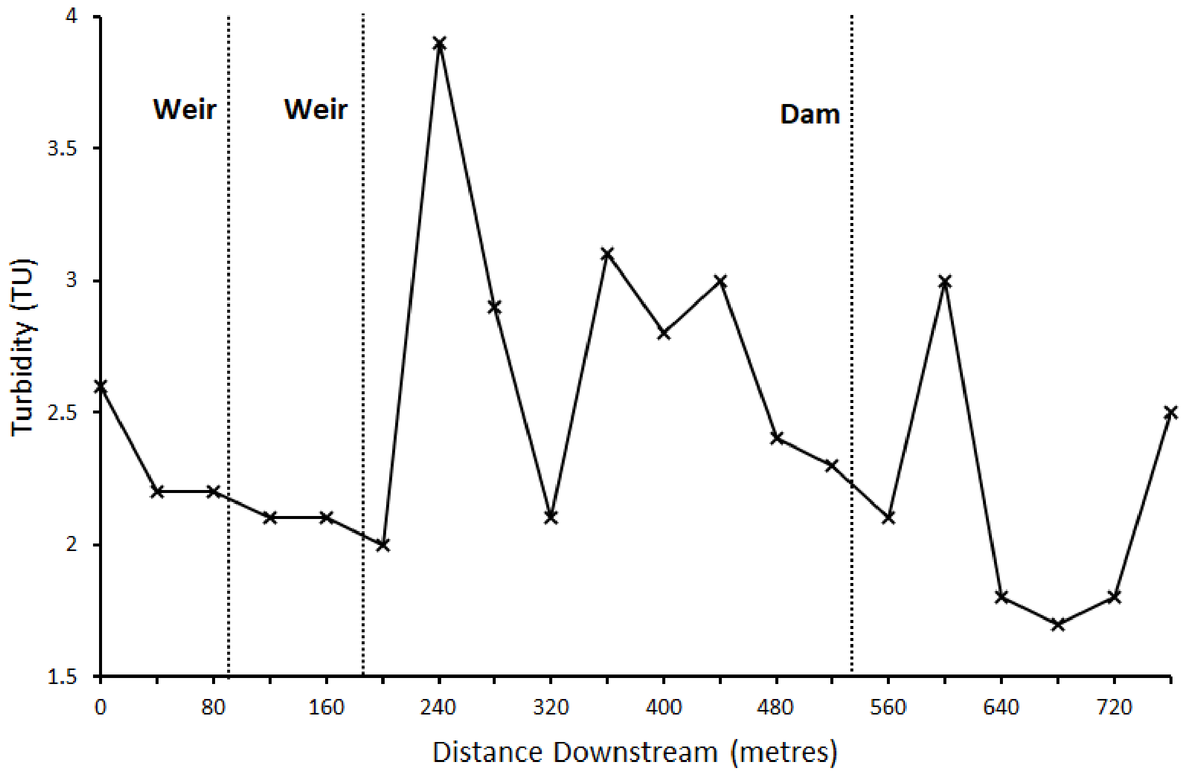

Figure 10: Turbidity (TU) in the Manor Woods Valley section of the Malago River.

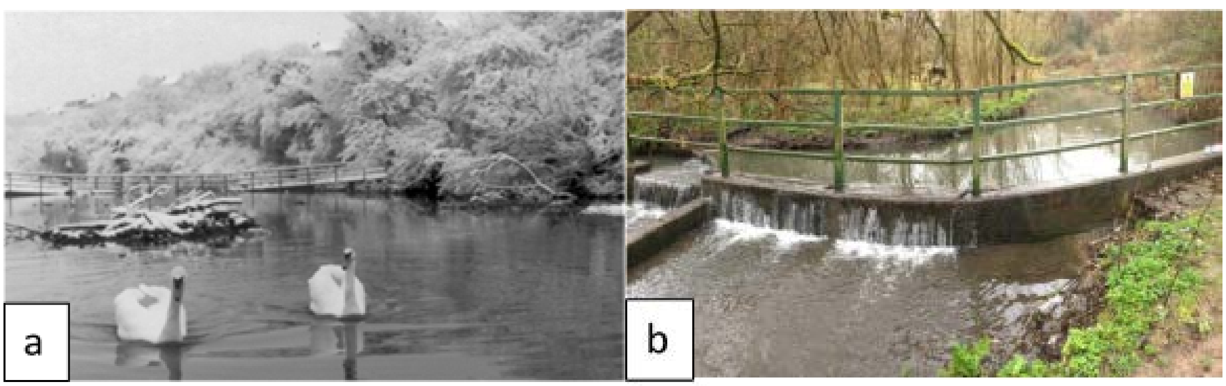

Figure 11: Photographs comparing the water upstream of the dam on the Malago in 1980 (a) and in 2017 (b) (Malago Valley Conservation Group, 2017).

Despite the results for turbidity suggesting otherwise, figure 11 shows evidence of silt accumulation since 1980. Silt accumulation has resulted in the retention lake in 1980 (figure 11a) being filled in over time (figure 11b). This suggests that, although the turbidity results imply that there is little difference in suspended sediment before the dam, there has in fact been significant silt accumulation in the last 38 years.

3.4.2 Nitrite Concentration and Oxygen Saturation

Nitrite concentration showed interesting trends downstream of the Malago River. Between 0m and 400m downstream, nitrite concentration was relatively stable, fluctuating slightly between 106 µgL^{-1} and 122 µgL^{-1}. Between 400m and 480m downstream the concentration begins to dramatically increase to approximately 162 µgL^{-1} before decreasing slightly before the dam (figure 12). Concentration drastically increases after the dam to the maximum value recorded for the stretch at 191 µgL^{-1}. There is a sharp decline in nitrite concentration between 600m and 640m downstream, after which, levels stabilise with values slightly higher but similar to the first 400m of the Malago (figure 12).

In regards to oxygen saturation, there appears to be no overall pattern downstream of the Malago. However, there is some evidence of increasing values after both weirs and the dam (figure 12). The saturation is highest, ranging between 92.5% and 94.5%, between 200m and 400m downstream. There is a sharp decrease in the water preceding the dam before a slight rise immediately in front of it. Results, however, must be interpreted with caution. It must be considered that, although the oxygen meter used in-situ had an accuracy of ±1.5% and precision of ±0.1%, measurements in the field were often problematic with large degrees of measurement fluctuation meaning recalibration was often required.

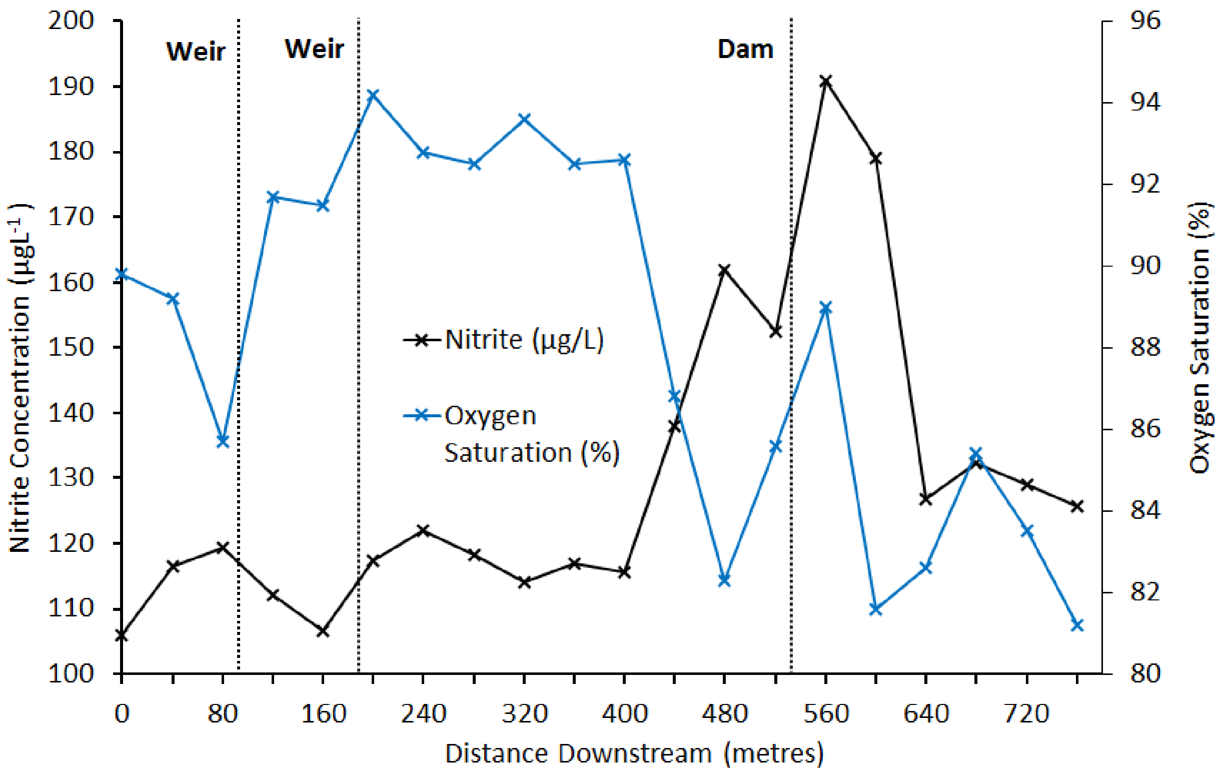

Figure 12: Changing nitrite concentrations and oxygen saturation in the Manor Woods Valley section of the Malago River.

Upon observing figure 12, there appears to be no clear relationship between oxygen saturation and nitrite concentration. However, between 0m and 520m downstream, both oxygen saturation and nitrite concentration generally track each. As oxygen saturation decreases, especially evident between 400m and 480m downstream, the nitrite concentration increases (figure 12). This suggests that there may be a negative relationship between the two variables. Despite this, after the dam the relationship is much less clear. In the water immediately following the dam, oxygen saturation and nitrite concentration increase simultaneously from 85.6% and 153 μgL^{-1} to 89.0% and 191 μgL^{-1}, respectively.

Regression analysis was further carried out to examine the relationship between oxygen saturation and nitrite concentration. It is clear from figure 13 that the regression analysis between the two variables for all 20 sites along the Malago is statistically significant at a 95% confidence level. Despite this negative relationship between oxygen saturation and nitrite concentration, there are many large residuals and hence, the R^2 value is relatively low at 0.27. This suggests that only 27% of the variation in nitrite concentration downstream may be explained by the oxygen saturation. Due to these large residuals, specifically 560m downstream (figure 13), along with observations of a potential change in the relationship between the two after the dam (figure 12), regression analysis was carried out disregarding sites downstream of the dam.

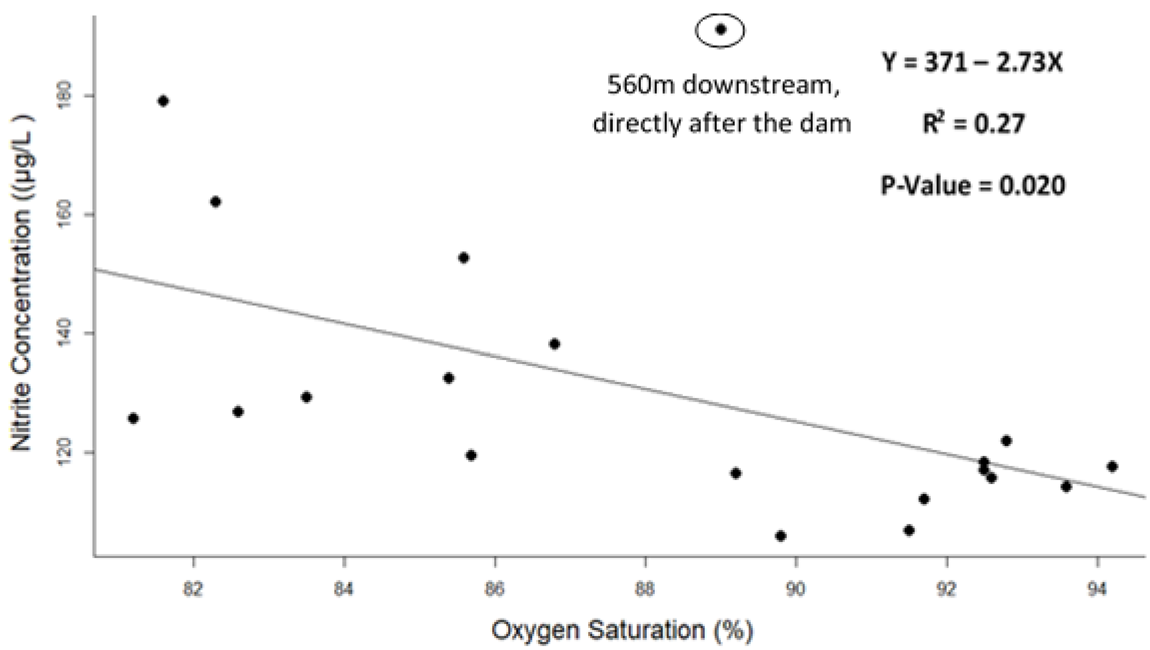

Figure 13: Regression analysis of Oxygen Saturation and Nitrite Concentration with an R^2 value of 0.27 and a p-value of 0.020, suggesting significance at a 95% confidence level.

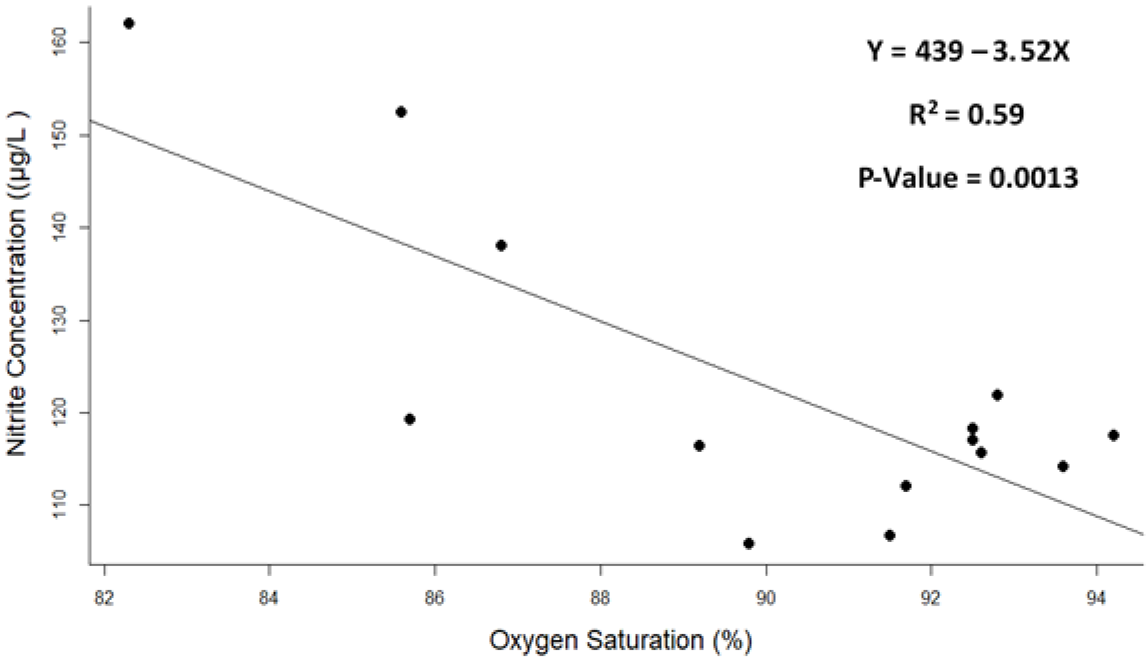

Figure 14: Regression analysis of Oxygen Saturation and Nitrite Concentration with the six sample sites after the dam removed. The regression analysis has an R^2 value of 0.59 and a p-value of 0.0013, suggesting significance at a 99% confidence level.

Upon removing all six sites downstream of the dam, the results of the regression analysis change. Many of the variables with large residuals have been removed and the R^2 value has hence increased to 0.59, suggesting that 59% of the variation in nitrite concentration may now be explained by oxygen saturation (figure 14). The p-value has also decreased to 0.0013, meaning that the model is now significant to a 99% confidence level instead of 95% (figure 14). This suggests that the relationship between nitrite concentration and oxygen saturation is more significant when values from the six sites downstream of the dam are removed.

3.4.3 Nitrite and Nitrate Concentration

The relationship between nitrite and nitrate concentration as a percentage of total oxidised nitrogen (TON) varies downstream along the Malago River. The proportion of nitrate concentration dominates throughout, ranging from 96.6% to 98.0%, with the proportion of nitrite hence ranging from 2.0% to 3.4%. The ratio appears to be relatively stable between 0 and approximately 400m downstream, but nitrite proportion begins to increase in the water preceding the dam (figure 15). Nitrite’s percentage of TON peaks at 560m downstream before reducing in the remaining stretch of river.

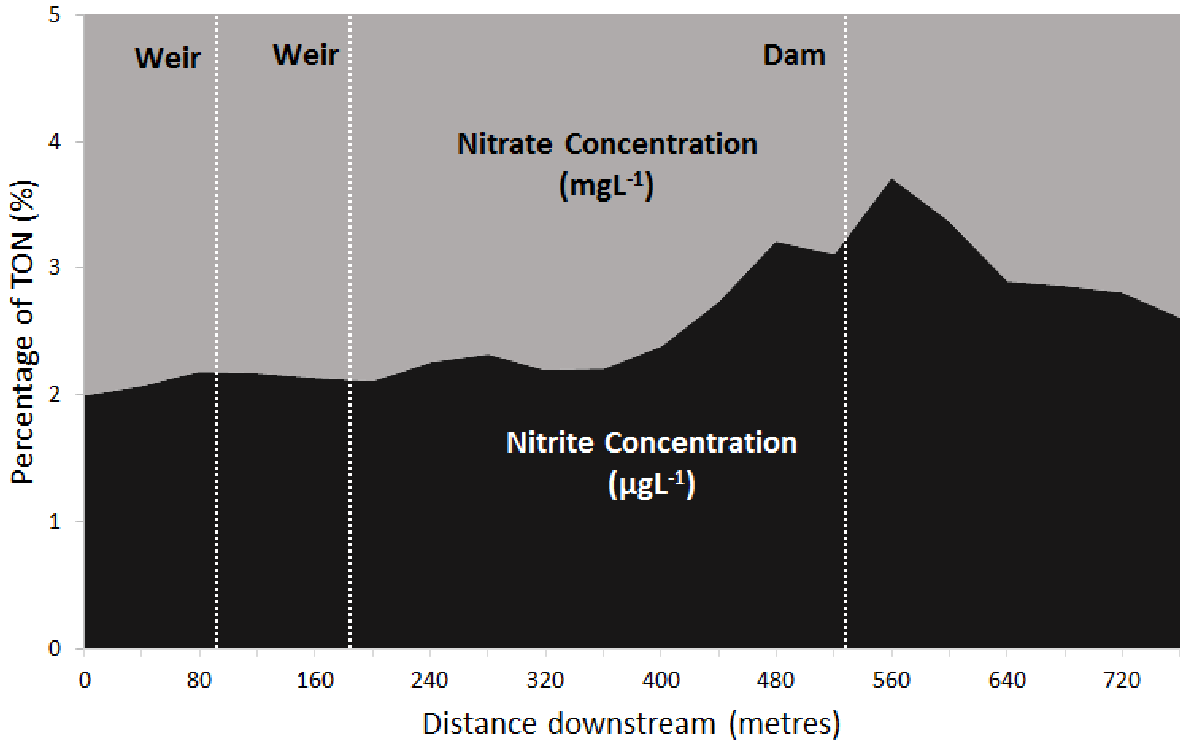

Figure 15: Nitrite and nitrate concentration as a percentage of total oxidised nitrogen (TON) downstream of the Malago River, with the inclusion of the locations of the weirs and dam.

4.0 Discussion

4.1 Hypothesis 1

H1: Ammonia, nitrite, nitrate and phosphate concentrations will fall within Environment Agency standards for high quality water.

The nutrient concentrations for the Malago River met the majority of the highest Environment Agency (2011) standards, showing that the Malago River's water quality is very good. However, the low recorded nutrient concentrations must be examined with caution. There had been no rainfall events at Colliters Brook gauging station, approximately 1.5 miles away from the Malago River, in the days prior to data collection (figure 16), and so as a result there was limited runoff from the surrounding land. An assumption must be made here that the Malago River responds to rainfall in a similar way to the river at Colliters Brook gauging station and that rainfall events are also similar due to their close proximity.

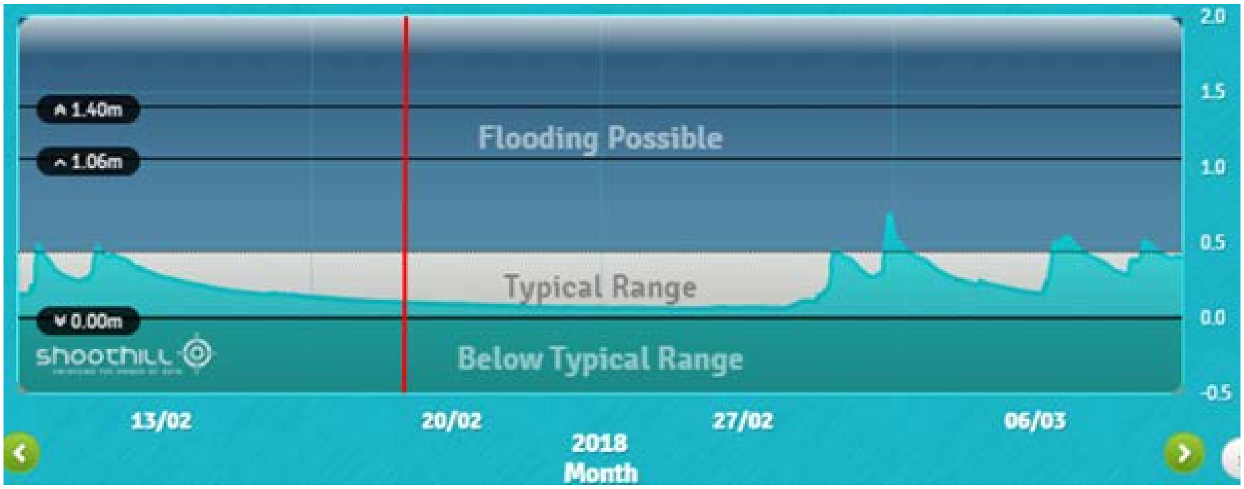

Figure 16: Colliters Brook gauging station, the nearest gauging station to the Malago, showing no significant rainfall inputs in the days preceding 19th February 2018 (Shoothill Gauge Map, 2018).

If there was a rainfall event much closer to data collection, one might expect the nutrient values to show very different results and so see a change in the water quality. Nutrients and pollutants from surrounding environments are flushed into rivers through runoff following rainfall events (Higashino and Stefan, 2014), and these fluxes are enhanced as rainfall intensity increases. Higashino and Stefan's conclusions (2014) therefore showed an almost proportional rise between river discharge and nitrate concentrations with little delay. Allotments are located in the North-West of Manor Woods Valley (figure 1b), where fertilizers are likely to be used containing nitrogen and phosphorous (Dadkhah et al., 2012). These nutrients will then reach the Malago River during periods of higher precipitation from surface runoff, interflow and infiltration (Higashino and Stefan, 2014). As aforementioned, the catchment area is urbanised with a large amount of concrete infrastructure, similarly the slopes either side of the river are relatively steep, particularly on the eastern side, hence the runoff in the area is likely to be rapid. This would most likely result in very short lag times between peak rainfall and peak river height. Therefore, although results for this investigation show the Malago River to be of high nutrient water quality, these standards may not be matched during or immediately following periods of higher precipitation.

Therefore, for this investigation hypothesis 1 can be accepted as the results collected proved consistent, yet caution must be taken in their applicability in different conditions. Ammonia, nitrate and phosphate levels all fell within the top 2 categories for good quality water. Nitrite also fell comfortably into the requirement for the supply of drinking water and so again proved consistent with the hypothesis. As a result, this stretch can be seen to be of high water quality and of good health, however, as research has shown this may be due to the limited rainfall prior to the collection. Combined with likely short lag times, the Malago River's water quality may decrease and vary significantly throughout the year depending on precipitation and runoff levels.

4.2 Hypothesis 2

H2: Microplastics build up in front of the dam on the River Malago, degrading the water quality.

Although recent literature suggests microplastics can accumulate behind dams (Zhang et al., 2015; Wang et al., 2017), microplastic concentrations found on the Malago cannot reliably be shown to be significantly affected by the either the dam or the smaller weirs upstream. The reasons for this may be two-fold. First, the dam studied by Zhang et al. (2015) is of a much larger scale (175m water depth) when compared to the 1.5m depth of the dam on the Malago. Since there have been no studies examining this effect at the smaller scale, it is possible the processes responsible for microplastic accumulation do not occur in small retention lakes like this one.

Second, the method for collecting microplastic data used, while highly effective at identifying microplastics too small for manta nets (<333µm), which made up a significant portion of the plastics found on the Malago, could be producing significantly elevated results as the method blank used yielded a count of 12200 L^{-1}. This is due to the almost complete use of plastic lab equipment in both the sampling process, and the analysis stage as well. A simple solution to mitigate this issue in future studies would be to use more glassware in place of disposable plastics. This high value for the blank may mean that all the sample counts are too high, however, without repeat method tests to evaluate this error, it is very difficult to ascertain the exact effect on the samples tested.

Because microplastics increase hugely along the Manor Woods section of the Malago, it is plausible that the majority, if not almost all the microplastic pollution on the Malago is derived from the large quantity of plastic litter left in or near the river rather than external sources upstream, however, considerably more detailed studies are necessary to quantify this. When compared to literature values (table 1) it is very clear that microplastic concentrations are much greater in the Malago than large scale rivers. This may be due to the differences in the sampling technique; the method used by Zhao et al. (2014) used a direct sampling method and filtered samples with a 32µm sieve, while the other studies used 333µm mesh nets for collecting plastics so there are huge discrepancies between the methods used. Results from a lab report (Mason et al., 2018) which uses the Maes et al. (2017) method are also shown, however this is not a peer reviewed article, so the results should be used with caution.

Author	**River**	**Mean microplastic concentration (counts L^{-1})**
This study	Malago, UK	19220
This study	[Method blank]	12200
Mason et al., 2018	[Study of bottled water]	325
Mani et al., 2015	Rhine, Germany	0.0056
Lechner et al., 2014	Danube, Austria	0.0004
Yonkos et al., 2014	Patapsco, USA	0.0030
Yonkos et al., 2014	Magothy, USA	0.0008
Yonkos et al., 2014	Rhode, USA	0.0004
Yonkos et al., 2014	Corsica, USA	0.0003

Zhao et al., 2014	Yangtze, China	4.14

Table 1: Studies on microplastic counts from this study, a study looking at microplastics in bottled water and various large scale rivers. Note the significant difference between the values found by this study, the study by Mason et al. (2018) and others, likely accounted for by differences in methods used.

4.3 Hypothesis 3

H3: Nitrite concentration increases in the sediment rich water before the dam, whilst oxygen saturation decreases.

It is evident from the results that the dam is having an impact on nitrite concentration (figure 12). It was hypothesised that the dam's possible control on nitrite concentration may be associated with oxygen supply due to higher suspended sediment loads (Kelso et al., 1997; McGee, 2008). However, since turbidity results showed no significant increase directly before the dam (figure 10), any conclusions derived from these results must be used with caution, despite evidence of significant silt accumulation since 1980 (figure 11 a & b). The potential silt accumulation in this investigation may be a control on the nitrification process (Philips et al., 2002). This is a possible explanation for the increase in nitrite concentration since ammonia is continuously decreasing downstream (figure 4). However, this does not explain why the nitrite concentration increases sharply directly before the dam, since the decrease in ammonia downstream is relatively constant. It is therefore likely that the oxidation of ammonia affects nitrite concentration but is not the primary control.

A more reasoned explanation for the increase in nitrite concentration is denitrification occurring in the water preceding the dam. It has been suggested that small scale dams result in denitrification in the water before them, whereby nitrate is converted to nitrite if oxygen supply is low (McGee, 2008). This also suggests that a possible explanation for figure 15 is that low oxygen saturation is increasing rates of denitrification and hence, more nitrate is being converted to nitrite. This would explain why nitrite's percentage of TON increases sharply before the dam, and therefore, why nitrate's percentage decreases. The regression analysis results for oxygen saturation and nitrite concentration (figures 13 & 14) suggest that denitrification is likely to be occurring in the water directly before the dam in the Malago River. Upon removing variables located after the dam between 560m and 760m downstream, the results from the regression analysis became significant at a 99% confidence level instead of 95%. This suggests that oxygen saturation is a significant control on nitrite concentration before the dam, and hence that low oxygen supply is creating an anaerobic environment (Kelso et al., 1997) whereby denitrification is occurring in the water preceding the dam.

The results from the regression analysis in figures 13 and 14 suggest that the data is consistent with the hypothesis. However, the higher significance level for the regression analysis with the removal of variables after the dam suggests that oxygen is less of a control on nitrite concentration proceeding the dam. A possible explanation for this is, by contrast, that oxygen is indeed a control, but it is in fact having the opposite effect; depleting nitrite concentration through nitrification in more oxygenated water (Philips et al., 2002). Turbulence after the dam at 560 m downstream caused mixing of the water (Hao, 2011), increasing the oxygen saturation to 89.0%.

Oxygen therefore becomes available to allow the nitrification of nitrite to nitrate to take over from denitrification, explaining the decrease in nitrite's percentage of TON after the dam (figure 15). An interesting observation is that nitrite concentration peaks after the dam (figure 12). This is likely due to a lag in both processes (Diab et al., 1993). Nitrite has accumulated in the water with lower oxygen saturation before the dam, resulting in high nitrite concentration directly after. Here, nitrification in the presence of oxygen is yet to have a significant effect on nitrite concentration. The evidence is first seen at the site 40m's downstream where nitrite concentration drops significantly (figure 12). These two processes of denitrification and nitrification occurring directly before and after the dam respectively, mean that the data is consistent with the hypothesis; the dam does appear to have a significant control on nitrite concentration.

5.0 Future Work

Taking into consideration the limitations of the investigation conducted on the Malago, there are several areas of research which should be explored in future to develop understanding of the Malago River system.

Whilst physical plastic litter is likely to contribute to the accumulation of microplastics downstream in the river, it will be useful to complete a more comprehensive study of microplastics in the area to identify more precisely where they come from. As Wagner et al. (2014) explains, there is a significant knowledge gap at present about the rates of microplastic inputs to small river catchments. In order to properly ascertain the true input of microplastics to the Malago, further tests using less plastic-contaminated equipment should be undertaken to ensure results are more representative of the studied site.

Taking water samples from the river further upstream and downstream of the reach will identify any other zones of microplastic accumulation or exhaustion. Similarly, including river sediment in the samples taken will provide understanding of the extent to which microplastics are entrained in the banks, and therefore how the microplastic counts will change with weather conditions and seasons, when more or less sediment is transported. Simultaneous measurements of turbidity could therefore also be carried out in different weather conditions to quantify this relationship with microplastic abundance. Measurements of microplastics, using the same method outlined in this report, from the rivers surrounding the Malago River would further inform whether microplastic sources are widespread, or more localised to the area. Understanding of specific sources would also be improved with counting of specific kinds of microplastics, as this study focused on only the total counts. This investigation does however provide sound evidence for the inclusion of the study of microplastics in river water quality assessments, particularly within small urban catchments, and the development of standards for microplastic sampling, to allow proper comparison between different locations and environments.

A significant limitation associated with the study is that it was undertaken in Winter, resulting in extremely unrepresentative measurements of biological activity through the variables BOD and chlorophyll. One aspect of the brief of this study was to investigate the effects of water quality on the life the river supports, therefore, due to the time of year, the results of this study cannot reliably assess the impact on the river's biology. Further research should therefore carry out this investigation at a different time of year in attempt to quantify the effects of the pollutants and nutrients measured.

In addition, the date on which fieldwork was undertaken does not provide information about the effects of recent rainfall on the river's water quality. Collecting data immediately after a rainfall event would provide the necessary information to assess the sources of pollutants, which will allow more informed decisions to be made regarding what actions, if any, should be taken to reduce pollution in the river. The results acquired at a different time of year in different conditions, combined with the results from this study, could conclude the hypothesis that the impact of pollutants on biological activity in the Malago River is non-uniform throughout different seasons and weather conditions.

In light of the limited spatial extent of the secondary data available on the Malago River regarding E-coli, a more detailed investigation should be conducted in which E-coli measurements are taken using a denser distribution of samples. This will enable a greater understanding of the sources of E-coli, and therefore help assess whether it exceeds water quality standards over the entire reach or only for certain regions. As a result, the client will be able to implement more appropriate measures in response.

6.0 Conclusions

6.1 Final Map

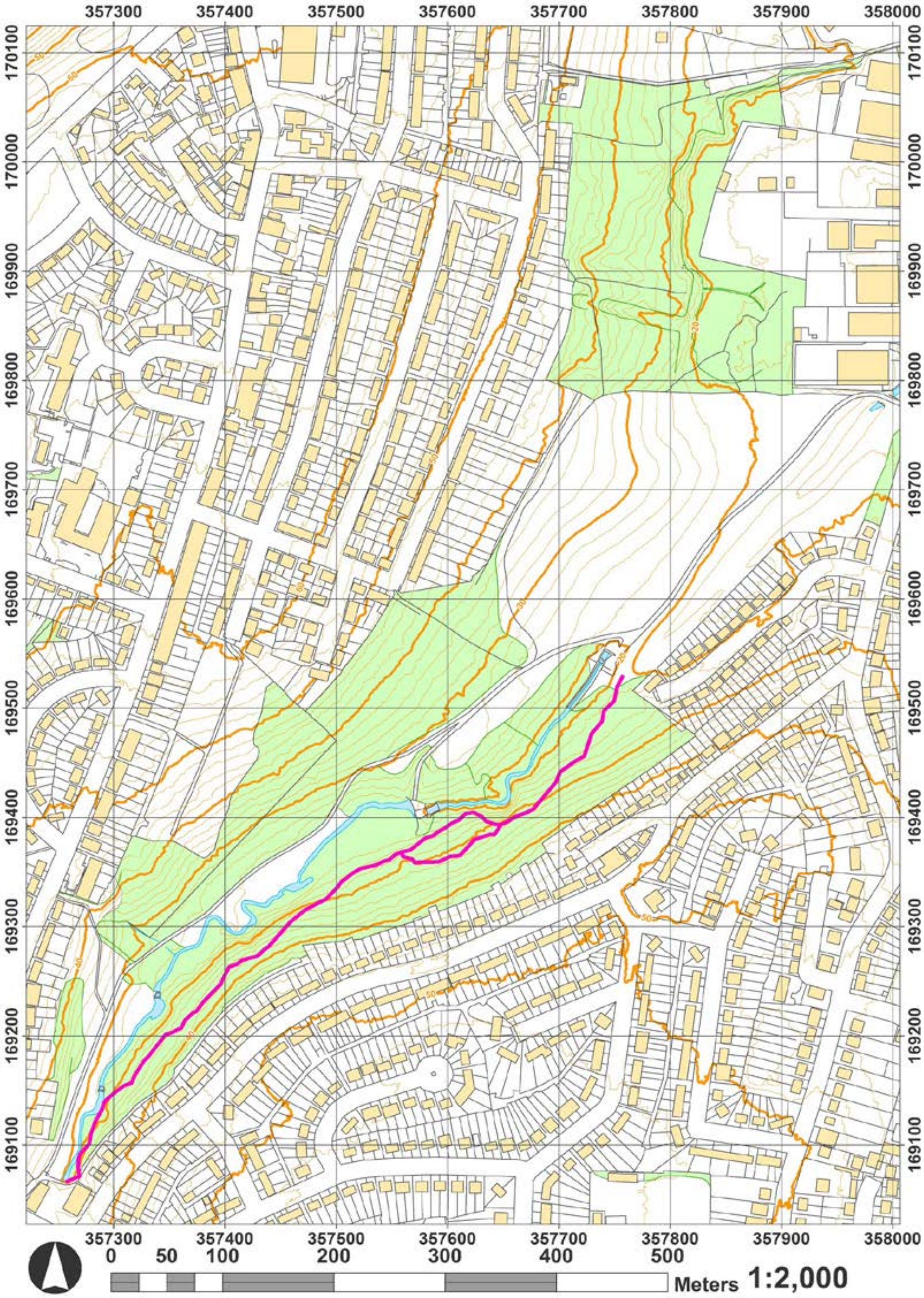

Figure 17: Final map of the Malago River and Manor Woods Valley, with LiDAR derived contours, GPS located footpath (shown in pink) and 100m gridlines for use in further surveys.

6.2 Conclusions from study

Results obtained in this report proved consistent with the first hypothesis; that values for ammonia, nitrite, nitrate and phosphate concentrations will fall within Environment Agency (2011) standards for high quality water. In many of these cases, particularly for nitrate and phosphate, the concentrations recorded were far below the standards given by the Environment Agency (2011). A key reason for this may be the lack of rainfall prior to the event and subsequently the lack of runoff (Higashino and Stefan, 2014) flowing into the river from the urbanised regions and the allotments. Surface runoff from the allotments may have, in particular, increased the concentration levels of nitrogen and phosphorous due to the strong presence of these nutrients found in fertilizers (Dadkhah et al., 2012). As a result, low concentrations were recorded which fell below the Environment Agency standards (2011) and so showing this stretch of the Malago River to be of good quality water. However, as a cautionary note, these concentrations may vary largely throughout the year depending on the precipitation and runoff rates.

Overall the data was not sufficiently consistent with the second hypothesis. Although there was accumulation of microplastics behind the two smaller weirs, this was not shown to occur by the bigger dam further downstream. The results were in fact very sporadic, and the blank used actually generated higher microplastic counts than some of the samples. On this basis, without more complete, reliable data we must accept the null hypothesis. In addition to the hypothesis, it was also noted that there was a significant increase in microplastics with distance downstream, the concentrations of microplastics were much higher than values found for inland rivers in the literature.

The results obtained in this report are consistent with the third hypothesis; that nitrite concentration increases in the sediment rich water before the dam in the presence of low oxygen supply. Whilst nitrification of ammonia to nitrite may be a contributing factor, the primary control is thought to be the process of denitrification occurring in an anaerobic environment (Kelso et al., 1997), converting nitrate to nitrite. The results of this study are consistent with this theory since nitrite and nitrate concentrations increase and decrease, respectively, as a percentage of TON. In addition, results from the regression analysis indicate that there is a negative relationship between oxygen saturation and nitrite concentration, which is more significant upstream of the dam. This analysis suggests that oxygen is a more important control on nitrite concentration before the dam. Furthermore, turbulence after the dam increases oxygen saturation (Hao, 2011), permitting the nitrification of nitrite to nitrate in an aerobic environment to take over from denitrification. This is further evidence to suggest that the dam on the Malago River indirectly affects nitrite concentration, through its influence on the water's oxygen saturation. The data therefore implies that the dam has an impact on the Malago's water quality in terms of nitrite and nitrate concentration, but its impact on water quality is negligible when compared to Environment Agency standards for water quality (2011).

Despite the conclusions this report is able to make, limitations, particularly associated with the time of year and scale of the study, implicate the applicability of the results. Additional studies conducted at different times of year, during different weather conditions, or on other similar sized catchments, will greatly develop understanding of the Malago River's changing water quality, and will test how well the conclusions reached in this study can be transferred to different spatial and temporal scales.

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8.0 Appendix

Metres Downstream	Temperature (O2)	Temperature (pH)	pH	Conductivity (µS)	O2 Saturation (%)	Turbidity (TU)	BOD Decrease (%)	Chlorophyll (mg/L)
0	10.3	9.2	7.9	760	89.8	2.6	-	0
40	10.8	9.4	7.9	770	89.2	2.2	13.47	0
80	10.4	9.4	7.9	770	85.7	2.2	16.5	0
120	10.5	9.4	7.92	770	91.7	2.1	20	0
160	10.6	9.4	7.91	770	91.5	2.1	13.5	0
200	10.6	9.4	7.93	770	94.2	2	7.8	0
240	10.7	9.5	7.88	770	92.8	3.9	10.7	0
280	11	9.5	7.9	770	92.5	2.9	-	0
320	10.7	9.5	7.91	780	93.6	2.1	-	0
360	10.7	9.6	7.87	780	92.5	3.1	10.3	0
400	10.6	9.6	7.9	790	92.6	2.8	17.1	0
440	10.9	9.5	7.85	800	86.8	3	-	0
480	10.5	9.4	7.88	820	82.3	2.4	3.1	0
520	10.9	9.2	7.88	830	85.6	2.3	11.7	0
560	10.3	9.1	7.86	840	89	2.1	4.1	0
600	10.3	9.1	7.85	850	81.6	3	7.9	0
640	10.2	9.1	7.84	840	82.6	1.8	14.8	0
680	10.8	9	8.04	850	85.4	1.7	8.71	0
720	10.7	9	7.89	860	83.5	1.8	-	0
760	10.2	9.1	7.83	840	81.2	2.5	14.9	0.008

Metres Downstream	Microplastics (counts / L)	Ammonia (mg/L)	Phosphate (mg/L)	Nitrite (µg/L)	Nitrate (mg/L)	TON (mg/L)	Nitrite % of TON	Nitrate % of TON
0	11600	0.431	0.064	105.868	5.203	5.309	1.994	98.006
40	7200	0.408	0.065	116.408	5.515	5.631	2.067	97.933
80	9600	0.398	0.063	119.300	5.357	5.477	2.178	97.822
120	19600	0.384	0.056	112.033	5.058	5.170	2.167	97.833
160	6000	0.354	0.055	106.680	4.882	4.989	2.138	97.862
200	20600	0.348	0.057	117.477	5.442	5.559	2.113	97.887
240	17600	0.352	0.071	121.888	5.283	5.405	2.255	97.745
280	14800	0.337	0.068	118.268	4.963	5.081	2.328	97.672
320	14400	0.332	0.054	114.094	5.086	5.200	2.194	97.806
360	24000	0.328	0.062	116.951	5.173	5.290	2.211	97.789
400	20200	0.329	0.069	115.599	4.736	4.851	2.383	97.617
440	20200	0.321	0.064	137.965	4.895	5.033	2.741	97.259
480	26000	0.304	0.064	161.999	4.878	5.040	3.214	96.786
520	23400	0.271	0.057	152.494	4.751	4.904	3.110	96.890
560	18800	0.263	0.061	190.993	4.956	5.147	3.711	96.289
600	31400	0.256	0.057	179.020	5.116	5.295	3.381	96.619
640	24800	0.234	0.058	126.743	4.245	4.372	2.899	97.101
680	24400	0.220	0.055	132.322	4.496	4.628	2.859	97.141
720	23600	0.218	0.058	129.095	4.460	4.589	2.813	97.187
760	26200	0.212	0.045	125.622	4.693	4.818	2.607	97.393

Table A1: Full tabulated dataset for the results of each variable at each of the 20 sites downstream of the Malago River.