Improvements in water quality by integrated constructed wetlands in the Moore Brook catchment

Sampling, analysis and report by Dr. Nathalie Gilbert, Thames21

DRAFT v1, December 2016

1.0 Introduction

Moore Brook is a tributary of the Pymmes Brook running through the London Borough of Enfield. Two integrated constructed wetlands were constructed in this catchment in 2014 at Firs Farm and Pymmes Park. They were designed to improve water quality as well as increase amenity and biodiversity value and alleviate flooding. Spot sampling was carried out monthly between January and December 2016 (n=12 samples) at both sites to monitor the performance of the newly completed wetland cells at improving water quality. This report presents the results. In summary, both wetlands demonstrated significant improvements in water quality in all measured nutrient parameters. These improvements included reclassification of WFD status in ammonia from moderate to high at both sites and BOD_5 (poor to moderate); and reclassification of faecal E. Coli (poor to good), between in the inflow and outflow of the treatment systems at Firs Farm.

1.1 Site Maps

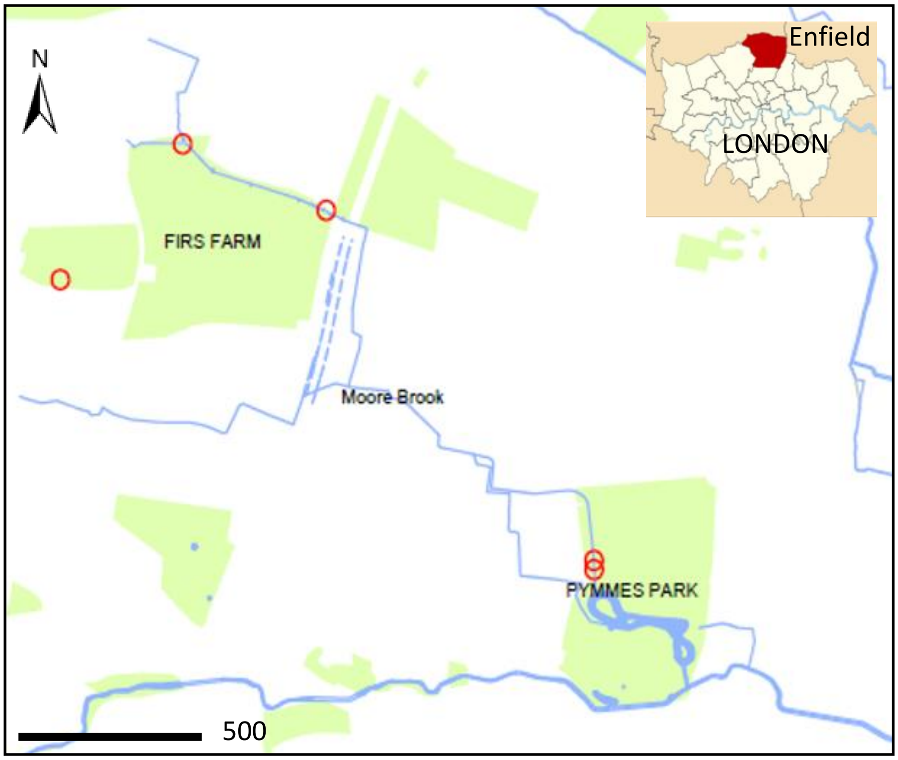

Figure 1: Integrated constructed wetlands sites and sampling locations (red circles) in the Moore Brook catchment, in the London Borough of Enfield.

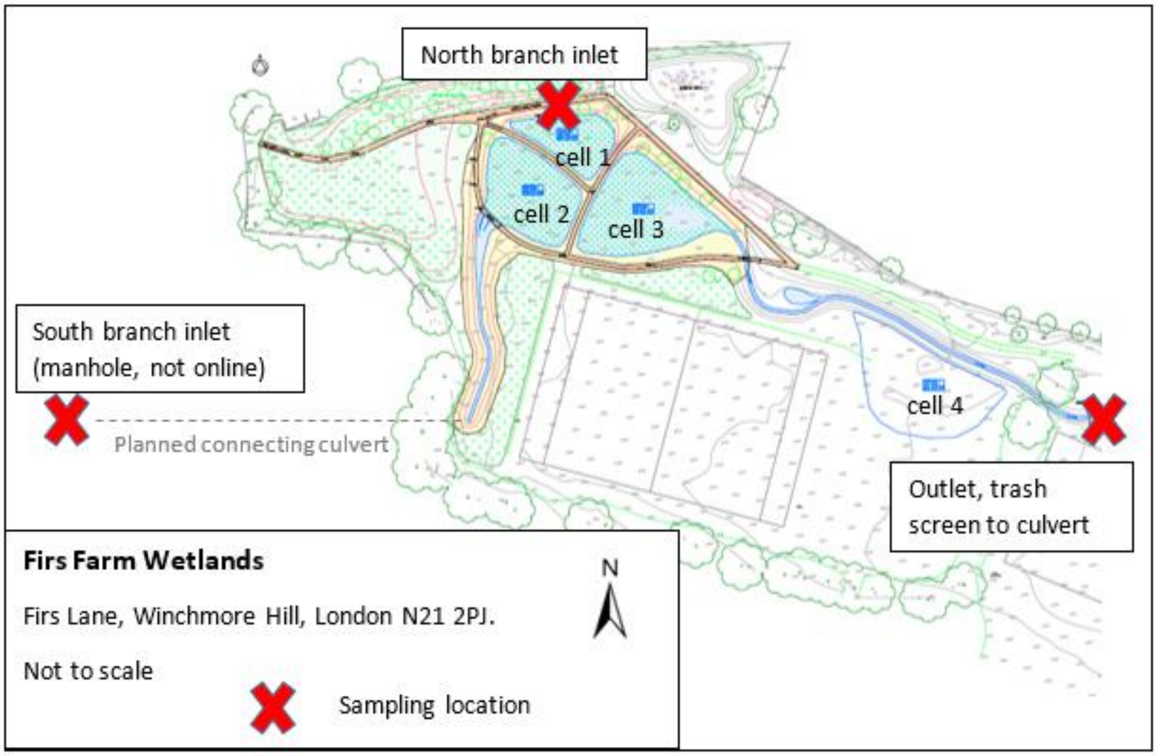

Figure 2: The three sampling locations, Firs Farm Wetlands. The South Branch inlet, located on Barrowell Green, was not online during the sampling period.

(Map adapted from the draft proposal, Enfield Council)

Figure 1 shows the location of the two sites within the Moore Brook catchment. Figure 2 shows the three water sampling locations in Firs Farm. Throughout the sampling period South Branch inlet was a culvert accessed via a manhole near Barrowell Green. Construction work to daylight this section and divert it into wetland cell 2 had not yet begun. Samples were also taken where the North Branch inlet entered cell 1 and where water exited the wetlands at the outlet trash screen. Figure 3 shows the sampling locations in Pymmes Park and consisted of a sample directly from the inflow to wetland cell 1 and where water exited the system into Pymmes Park lake at the end of the treatment system.

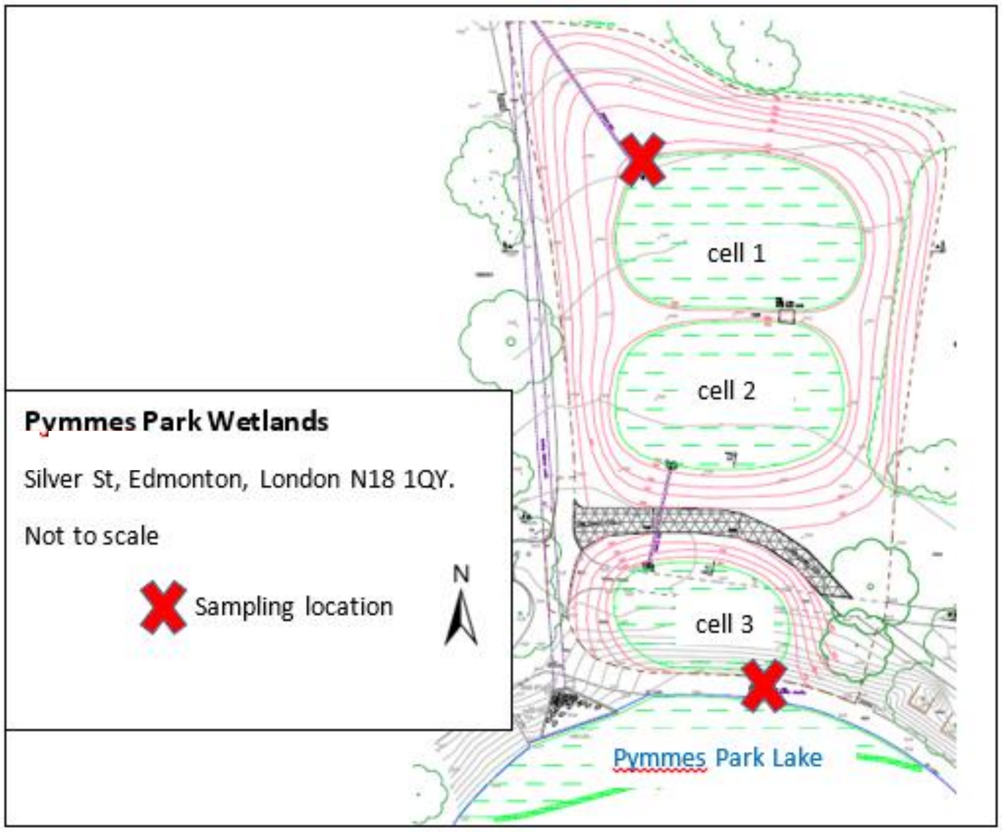

Figure 3: The two sampling locations, Pymmes Park Wetlands. The inflow to cell 1 and the outflow from the system into Pymmes Park Lake.

(Map adapted from the draft proposal, Enfield Council)

2.0 Methods

2.1 Water sampling

- Water samples were collected once per month between January and December 2016 (total 12 samples) and stored in a cool bag on ice blocks until analysis at the Thames21 laboratory, Bow Locks, later the same day.
- In addition to routine visits, two additional visits were made to Firs Farm wetland during August to monitor a pollution incident. Results for this are reported separately to the routine monitoring.
- Every visit pH, temperature and conductivity were measured on site at each sampling location using a Hanna HI98129 hand held probe. Turbidity (measured in Nephlometric Turbidity Units) was measured using a secchi tube.
- In order to calculate the pollution load entering the wetland, surface flow was measured as water flowed out from the North branch inlet pipe at Firs Farm (9 occasions). Passage of a float was timed

travelling a 1 m distance. Triplicate float measurements were averaged and approximate discharge was calculated by the velocity-area method. It was not possible to calculate pollution load into Pymmes Park wetland because of dense emergent vegetation growing across the inflow pipe.

- For every water sample, total nitrogen, ammonia, nitrate, phosphate and BOD_5 (Biological Oxygen Demand, incubated over 5 days) were analysed using ready to use reagent cuvette test kits produced by Hach Lange. Coliform bacteria analysis was by incubation of Biopaddles produced by La Motte. See Appendix 1 for descriptions of water quality parameters and appendix 2 for further details of laboratory methodologies.
- On two occasions (January and December 2016) heavy metals (copper, zinc, lead) were also analysed from each water sample. Cadmium was analysed on one occasion only (January 2016).
- Results are reported in a form that corresponds directly with the Water Framework Directive (WFD), for example nitrate-nitrogen (NO_3-N, the amount of nitrogen present as nitrate) is reported rather than nitrate (NO_3). Where possible, parameter concentrations are compared to water quality standards from the UK Water Framework Directive (WFD)[1,2,3] Table 1. The only standard available for interpretation of coliforms was the EU Bathing Water Directive[4], although this is not strictly applicable to wetland systems. The international European Nitrogen Assessment (ENA)[5] classification scale was used for total nitrogen and BOD_5 was assessed using the Environment Agency General Quality Assessment Scheme[6] (GQA).
- Results are in mg/L, except for coliform bacteria, which are presented as colony forming units (CFU) per 100ml of water.

Table 1: Water quality parameters and classification scales used by this report.
Parameters measured under the Water Framework Directed are indicated as WFD

Parameter	Classification Scale Nutrients:(mg/L), Coliforms: (CFU/100ml)				Source
Total Nitrogen		Good ≤ 0.5	Moderate 0.6 – 1.5	Poor > 1.5	1
Ammoniacal-nitrogen WFD	Very Good ≤ 0.6	Good 0.7 – 1.1	Moderate 1.1 – 2.5	Poor > 2.5	2
Nitrate-nitrogen WFD		Good ≤ 10	Moderate 11 – 20	Poor > 30	3
Orthophosphate WFD		Good ≤ 0.2	Moderate 0.3 – 0.8	Poor > 0.8	4
Total Coliforms		Good ≤ 500	Poor > 500		5

2.2 Statistical analysis

- Data from the South branch inlet of Firs Farm were excluded from statistical tests because this location was not yet connected into the wetland cells.
- Conductivity, BOD_5 (Firs Farm) and nitrate (Pymmes Park) displayed a normal distribution so paired T-tests were performed to compare mean differences between inflow and outflow water samples.
- Total nitrogen (Firs Farm) displayed a non-normal, symmetrical distribution so a Wilcoxon Signed Rank test was used.
- All other parameters had a non-normal, non-symmetrical distribution so exact sign tests were performed.
- Statistical analysis was carried out in R.

3.0 Summary of Results

3.1 Firs Farm

Table 2: Mean (min-max) values for pH and turbidity at Firs Farm wetlands.

	pH	Turbidity (NTU)
South branch	7.5 (7.0 – 8.3)	<12 (150 - 14)
North branch	7.5 (6.8 – 7.9)	<12 (50)
Outlet	7.7 (7.1 - 8.7)	<12 (12)

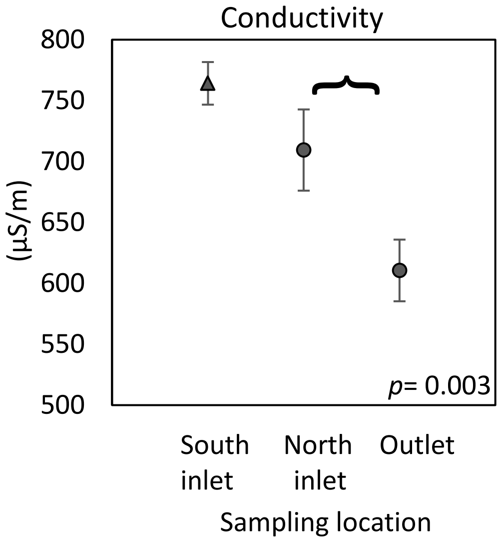

Figure 4: Mean (± SE) conductivity from Firs Farm wetlands. South inlet was not online so the statistical comparison refers to differences in mean concentrations between North inlet (inflow to cell 1) and the system outlet (at the trash screen), indicated with a bracket.

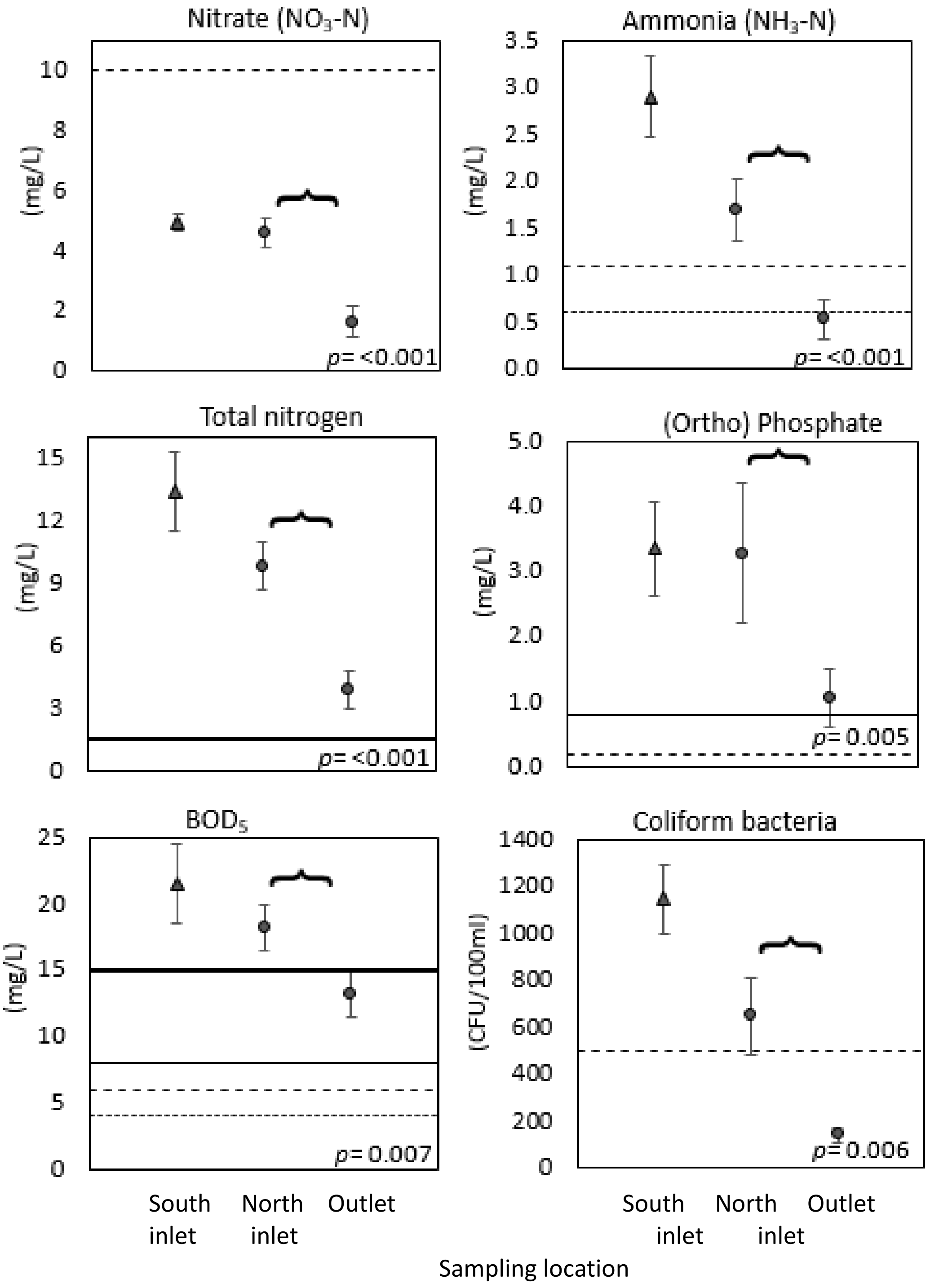

Figure 5: Mean (± SE) parameter concentrations from Firs Farm wetlands. South inlet was not online so statistical comparisons refer to differences in mean concentrations between North inlet (inflow to cell 1) and the system outlet (trash screen). These are indicated with brackets. Dashed lines represent threshold standards in water quality from the WFD or equivalent, simplified as poor (bold line), moderate (continuous line), good (dashed line), very good (dotted line). Excludes the pollution incident.

Table 3: Concentrations (mg/L) of dissolved heavy metals in Firs Fam wetlands.

	Copper (LoD: <0.1)	**Zinc** (LoD: <0.2	**Lead** (LoD: <0.1)	**Cadmium** (LoD: <0.1)
South branch	<0.1 , 0.143	<0.2 , <0.2	0.112 , 0.142	<0.2
North branch	<0.1 , 0.111	<0.2 , <0.2	0.139 , 0.112	<0.2
Outlet	<0.1 , 0.112	<0.2 , <0.2	0.143 , 0.107	<0.2

Cadmium was sampled once (January), other metals were sampled twice in January (first value) and December (second value). Limits of Detection (LoD) for each test are also indicated because most results were < LOD.

Physical parameters

- pH values were all classified as good (≥6 - ≤ 9), Table 2. Water was normally clear and reported no turbidity score (reported as <12 NTU). However, turbid water, indicating high loading of suspended particles, was recorded on 2 occasions in samples from South branch and 1 from North branch inlets.
- Pollution such as sewage increases conductivity due to the presence of nitrate and phosphate salts. Electrical conductivity decreases significantly between the North branch inlet and the outlet, Figure 4 (t(11)= 3.901, p= 0.003). This indicates that the concentration of dissolved salts and minerals in the water was decreased by transit through the wetland.

Nutrients

- There was a significant drop in mean concentrations of all parameters between the North branch inlet and the outflow. This resulted in a change in water quality classification status in three parameters (Figure 5):
  1- Ammonia, which is particularly harmful to aquatic life, improves from a WFD classification of “moderate” at the North branch inlet to “high” at the outflow (mean decrease: 68.7%, p= <0.001).
  2- BOD_5 (Biological Oxygen Demand) is a proxy of the degree of organic pollution in the water. BOD_5 improved significantly, resulting in reclassification from “poor” to “moderate” status (mean decrease: 28.0%, t(11)= 3.442, p= 0.007).
  3- Counts of faecal coliform bacteria include E.coli and other coliforms such as Salmonella spp., and Campylobacter spp that may cause diseases such as gastroenteritis and salmonellosis. According to EU bathing water standards (the only standards available for this parameter, but not applicable to non-designated bathing water areas such as these locations), classification improved from “poor” (imperative) at the inlet to “good” at the outlet, indicating a significant drop in the presence of potentially harmful bacteria in the water column (decrease: 78.0%, p=0.006).
- Phosphate, the key nutrient responsible for eutrophication, reduces in concentration from “poor” at the North branch inlet to “moderate” at the outlet (decrease: 67.9%, p= 0.005).

- Although demonstrating significant improvement (decrease 60.4%, $p= <0.001$) between the inlet and outlet, total nitrogen (nitrogen present as nitrate, nitrite and ammonia combined) remains classified at the outflow as “poor”. This means nitrogen remains present in the water column at levels that pose significant risk of eutrophication.

Heavy metals

- Lead was detected consistently in both water samples from each location (n=2, January and December). However, lead results must be interpreted with caution because we believe this test kit tends to amplify results when, as with these samples, concentrations are on the limits of detection.
- Zinc and cadmium were not present in detectable quantities.
- Copper was detected in all sites in December but not in January.

There is insufficient data to draw any conclusions about metal concentrations in these wetlands. Heavy metals are more often present bound to sediments, rather than dissolved in the water column, where they can remain resident for a considerable time before changes in conditions, (eg flood events) may cause them to be remobilised.

Pollution load

- Pollution loads indicate the total amount of a substance passing a particular point (in this case the North branch inlet pipe) in a specified amount of time. Pollutant load is not measured by the WFD but is informative for understanding the mass of nutrients entering the wetland treatment basins, rather than directly into the river system. Figure 6 represents a snapshot at the time of sampling. Sampling frequency was insufficient to calculate annual load estimates accurately.
- Flow was not calculated at the outlet, so estimates of nutrient mass removal by the wetlands were not calculated.

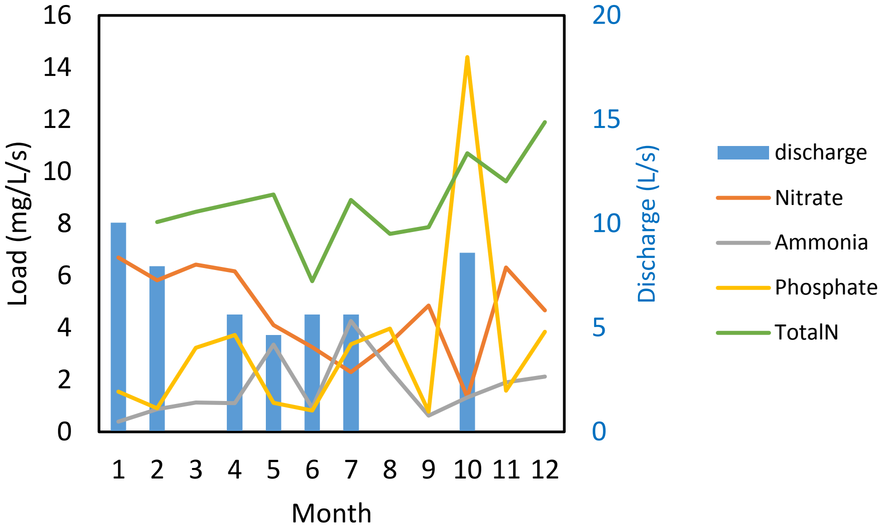

Figure 6: Pollution load estimates (Mg/L/second, lines) and estimated discharge (L/s, bars) entering North branch inlet, Firs Farm wetlands over 12 months (January, month 1, to December, month 12).

Pollution event, August 2016

Sampling was carried out on two additional occasions during August to monitor the significance of a persistent pollution event. Thames Water also responded to the event and their investigations tracked the source to a blocked sewer. The additional sampling locations are shown in Figure 7. Conductivity was sampled in all locations, nutrient parameters in location 2.

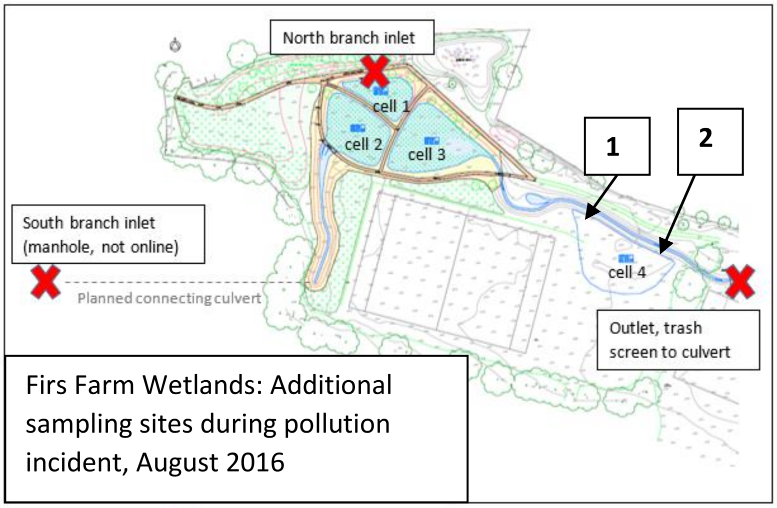

Figure 7: Location of additional sampling sites for investigating the pollution incident at Firs Farm.

Table 4: Parameter values reported during the pollution incident. At the regular sampling locations (north branch inlet, system outlet) values are compared to annual means (± SE) for the site. No additional data was available for the additional sampling sites (1 and 2). Location numbers correspond to the locations indicated in Figure 7. Parameters are measured in Mg/L, except for conductivity (µS/cm), turbidity (NFU) and coliform bacteria (CFU/100ml).

Location	Parameter	Annual Mean (± SE)	10-Aug	24-Aug
North branch inlet	Conductivity	709 ± 33.3	795	682
	Turbidity	<12	<12	12.0
	Nitrate	4.6 ± 0.5	2.08	2.9
	Ammonia	1.7 ± 0.3	1.2	0.3
	Total nitrogen	9.8 ± 1.1	6.24	9.8

Location	Parameter	Annual Mean (± SE)	10-Aug	24-Aug
North branch inlet *cont.*	Phosphate	3.3 ± 1.1	2.59	3.7
	BOD_5	18.2 ± 1.8	no data	26.1
	Coliforms	650	325	2250
1 – outflow at cell 4	Conductivity	no data	790	661.0
	Turbidity	no data	14	12
2 - Stream	Conductivity	no data	827	674
	Turbidity	no data	35	<12
	Nitrate	no data	no data, see text*	0.175
	Ammonia	no data	10.6	1.62
	Total nitrate	no data	14.6	5.28
	Phosphate	no data	4.45	1.77
	BOD_5	no data	no data	23.66
	Coliforms	no data	850	750
Outlet	Conductivity	611 ± 25.3	970	686
	Turbidity	<12	<12	12
	Nitrate	1.6 ± 0.5	0.247	0.175
	Ammonia	0.5 ± 0.2	6.96	0.707
	Total nitrate	3.9 ± 0.9	10.1	2.34
	Phosphate	1.1 ± 0.5	4.9	1.53
	BOD_5	13.1 ± 1.7	no data	10.01
	Coliforms	124 ± 32	350	75

- During the incident, there was a very strong smell of sewage, particularly in the lower half of the system beyond cell 3 and sewage fungus temporarily appeared in the stream beyond cell 4 indicating that the wetlands passed a significant amount of nutrients allowing the sewage fungus to form in the stream.
- Investigations were carried out some days after the incident was first reported. Consequently, concentrations derived from the North branch inlet are similar to annual means, with the exception of BOD_5 and coliforms bacteria (Table 4).
- The elevated conductivity measurements indicated the polluted water was passing through the treatment system and was, at the time of sampling, most concentrated in stream beside cell 4 and at the outlet. Ammonia and total nitrogen were also high compared to usual conditions.
- Nitrate was below detection limits in the stream on 10th August. This may be because the nitrogen fraction was present as ammonium and nitrite, rather than nitrate, but interference due to high Chemical Oxygen Demand (COD) cannot be ruled out.

3.2 Pymmes Park

Table 5: Mean (min-max) values for pH and turbidity at Pymmes Park wetlands.

	pH	Turbidity (NTU)
Inflow	7.4 (7.2 – 7.7)	<12 (13)
Outflow	7.4 (7.2 – 7.7)	<12 (<12)

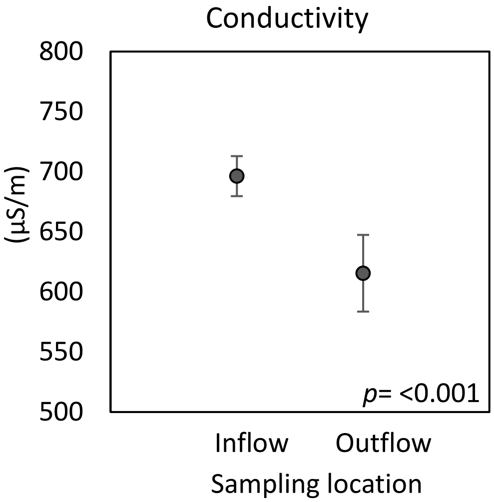

Figure 8: Mean (± SE) conductivity from Pymmes Park wetlands.

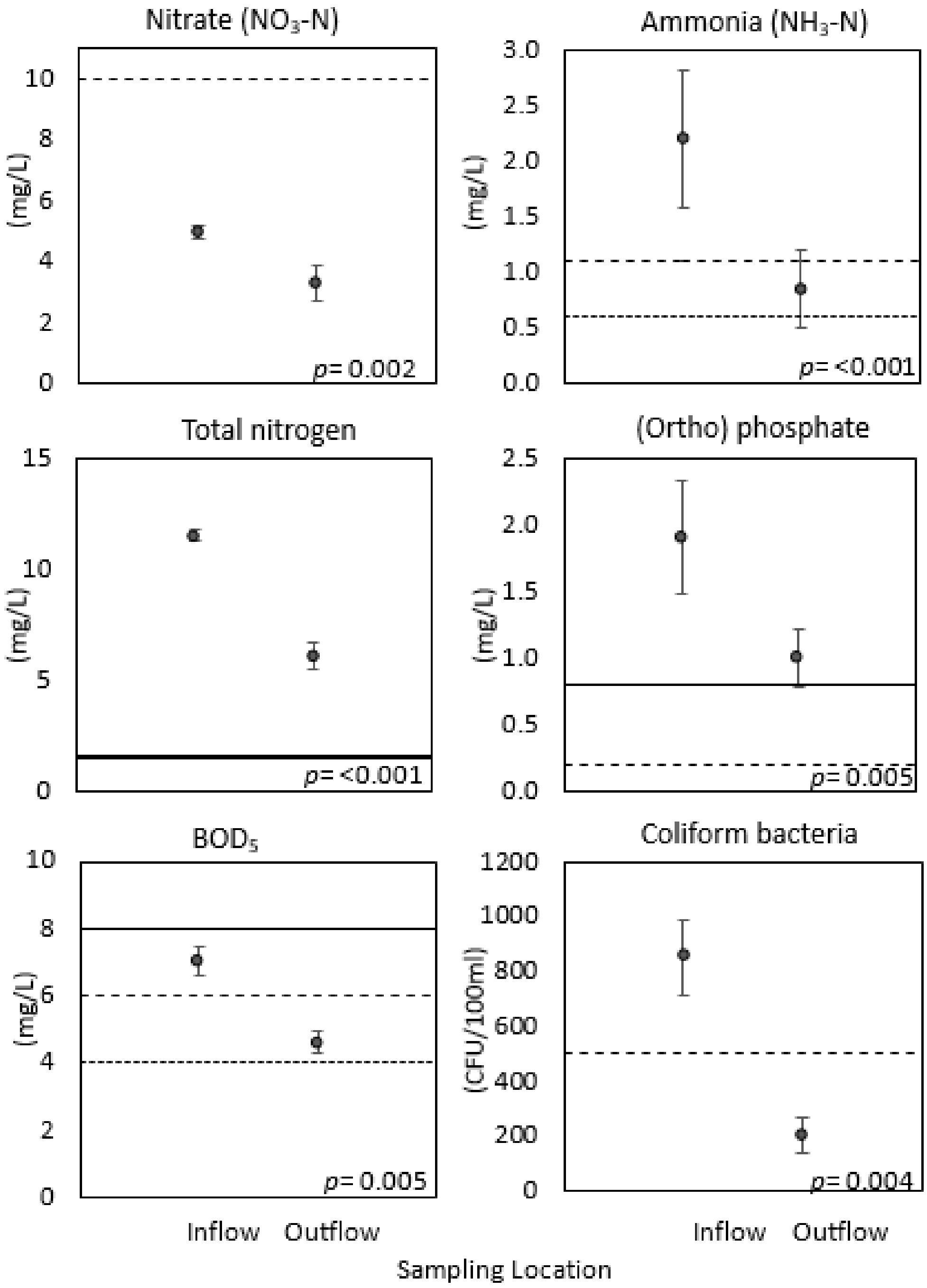

Figure 9: Mean (± SE) parameter concentrations from the inflow to cell 1 (inflow) and the outflow stream to Pymmes Park Lake (outflow) from Pymmes Park wetlands. Dashed lines represent threshold standards in water quality from the WFD or equivalent, simplified as poor (bold line), moderate (continuous line), good (dashed line), very good (dotted line).

Table 6: Concentrations (mg/L) of dissolved heavy metals in Pymmes Park wetlands.

	Copper (LoD: <0.1)	**Zinc** (LoD: <0.2	**Lead** (LoD: <0.1)	**Cadmium** (LoD: <0.1)
Inflow	<0.1 , 0.128	<0.2 , <0.2	0.105 , 0.115	<0.2
Outflow	<0.1 , 0.111	<0.2 , <0.2	0.128 , 0.128	<0.2

Cadmium was sampled once (January), other metals were sampled twice in January (first value) and December (second value). Limits of Detection (LoD) for each test are also indicated because most results were <LOD.

Physical parameters

- pH values were all classified as good (≥6 - ≤ 9), Table 5. At the inflow, water was clear on all occasions apart from one. No turbidity score was reported on any occasion at the outflow, indicating sediment -free water (reported as <12 NTU).
- Electrical conductivity decreases significantly between the inflow and outflow, Figure 7, p= <0.001). This indicates that the concentration of dissolved salts and minerals in the water was decreased by transit through the wetland.

Nutrients

- Between the inflow and outflow, there is a significant drop in mean concentrations of all parameters, Figure 9. As a result, BOD_5 (Biological Oxygen Demand), a proxy of the degree of organic pollution in the water, was reclassified from “moderate” to “good” status (decrease: 34.5%, p= 0.005).
- Ammonia, which is particularly harmful to aquatic life, improved from a WFD classification of “moderate” to “High” between the inflow and outflow (decrease 61.2%, p= <0.001).
- Although demonstrating significant improvement between the inflow and outflow (decrease 47.5%, p= <0.001), total nitrogen (ammonia, nitrite and nitrate combined) remains classified at the outflow as “poor”. This means nitrogen remains present in the water column at levels that pose significant risk of eutrophication.
- Phosphate, the other main nutrient responsible for eutrophication, reduces in concentration between the inflow and outflow, but remains classified as “poor” (decrease: 47.3%, p= 0.005).
- According to EU bathing water standards (the only standards available for this parameter, but not applicable to non-designated bathing water areas such as this area), classification of fecal coliform bacteria improved from “imperative” (poor) at the inflow to “good” at the outflow, indicating a significant drop in the presence of potentially harmful bacteria in the water column (decrease: 76.2%, p= 0.004).

Heavy metals

- Lead was detected consistently in both water samples from each location (n=2, January and December), Table 6. However, lead results must be interpreted with caution because we believe this test kit tends to amplify results when, as with these samples, concentrations are on the limits of detection.
- Zinc and cadmium were not present in detectable quantities at either sampling site.
- Copper was detected in all sites in December but not in January.

There is insufficient data to draw any conclusions about metal concentrations in these wetlands. Heavy metals are more often present bound to sediments, rather than dissolved in the water column, where they can remain resident for a considerable time before changes in conditions, (eg flood events) may cause them to be remobilised.

4.0 Recommendations

Continued water sampling as the wetlands mature

- This investigation took place shortly after the construction phase of the wetlands and before the South branch of Firs Farm came online. It is important to investigate the impact of the South branch on the wetland basins and on the overall ability of the wetlands to improve water quality.
- The Southern branch which is yet to be connected has consistently worse quality water than the Northern branch. There are a number of risks associated with this which aren't discussed in this report but will need to be considered in more detail.
- It is important to continue monitoring the constructed wetlands as they mature and beyond to assess their ongoing effectiveness when factors such as sediment deposition become important.
- Both wetlands have high potential as sites for other monitoring programmes, for example trends in benthic fauna.

Real-time monitoring of water chemistry

- A limitation of this report is that spot samples were only collected monthly. It was not possible to respond to rainfall events to capture first flush, or to estimate annual input loads into the treatment system.
- Real-time monitoring by probes deployed in the inflow and outfall of each wetland system would allow high resolution, detailed assessment of individual wetland performance over a range of flow conditions and temporal scales, for example performance during individual flood rainfall events, as well as informing assessment of individual constructed wetland performance.

5.0 References

[1] The Water Framework Directive (Standards and Classification) Directions (England and Wales) 2015 http://www.legislation.gov.uk/uksi/2015/1623/pdfs/uksiod_20151623_en.pdf accessed 17/10/2016

[2] Water Framework Directive 2000/60/EC

[3] UKTAG 2012 A revised approach for setting WFD phosphorus standards http://www.wfduk.org/sites/default/files/Media/Environmental%20standards/A%20revised%20approach%20for%20setting%20WFD%20phosphorus%20standards_101012.pdf accessed 05/12/2015

[4] EC Bathing Water Directive 76/160/EEC

[5] Sutton M.A., Howard C.M., Erisman J.W., Billen G., Bleeker A., Grennfelt P., van Grinsven H., Grizzetti B. (2011) The European Nitrogen Assessment: Sources, Effects and Policy Perspectives. *Cambridge University Press.*

Appendix 1: Description of water quality parameters

Physical parameters

pH

pH, which stands for the “power of hydrogen”, is a measure of the amount (molar concentration) of free hydrogen ions (H^+) in a water sample. In other words, it indicates the acidity (pH 0 - 6) or alkalinity (pH 8 - 14) of a water sample. pH 7, the measure of ‘pure’ water, is neutral. pH is a logarithmic scale meaning that as pH increases H^+ concentration will decrease by a power of 10.

Most aquatic organisms prefer pH between 6.5-9.0. pH outside of this range causes physiological stress and impacts hatch rates and mortality. Aquatic organisms, especially invertebrates, are particularly sensitive to changes (abrupt and gradual) in pH. A minor change in pH can increase the solubility of heavy metals and nutrients in water triggering chain reactions that can result in eutrophication.

Conductivity

Measured in microsiemens per centimetre, µS/cm, this is a measure the water’s capability to conduct electricity. Electrical conductivity indicates the concentration of dissolved salts and minerals in the water (higher conductivity = higher concentration of minerals, and the saltier the water).

Normal conductivity levels are derived from geological weathering but significant changes in conductivity may occur due to flooding, evaporation and pollution. Pollution such as sewage increases conductivity due to the presence of nitrate and phosphate salts. So, whilst conductivity itself is not a concern for aquatic health, it is easily measured and, if conductivity changes suddenly or is very different between two sampling sites, it can serve as an indicator of other water quality problems. Conductivity measurements may be used as a quick way to locate potential water quality problems when no other tests are available.

Turbidity

This is an indicator of the quantity of organic (eg plankton) and inorganic (eg sediment from roads) matter suspended within a water sample. It is determined by the visual transparency a water sample, measured in Nephlometric Turbidity Units (NTU) and is a proxy for the concentration of total suspended solids within water. Turbidity may indicate water quality issues such as the presence of contaminant particles (eg heavy metals), excessive growth of micro-organisms (algal blooms) and sediment run off from roads and arable land.

Phosphate

Phosphorus is an essential element for growth of photosynthesising plants and microorganisms. It is retained in soils so is usually scarce in water bodies and is therefore the growth limiting nutrient. Excess quantities of nutrients, especially phosphate, can cause eutrophication. In this process, nutrient excess stimulates overproduction of algae. After algal death, the abundance of organic matter and decomposing organisms depletes dissolved oxygen levels which deprives other aquatic life of oxygen. In anaerobic conditions, digestion of organics by bacteria promotes the conversion of sulphur into hydrogen sulphide, which has an eggy smell. Phosphorus may be present in freshwater environment in forms with different bioavailabilities. Orthophosphate, the readily available fraction dissolved in the water column, is measured by the Water Framework Directive.

In urban catchments, phosphates are present in laundry detergents and sewage and may enter waterways from sewage treatment systems and misconnected houses; also from fertilizer runoff from parks and gardens. In constructed wetlands, the main removal mechanisms for dissolved phosphate are uptake by plant roots, conversion to less bioavailable forms of phosphate and binding to soil sediments (Vymazal 2007).

Total nitrogen, ammonia and nitrate

Nitrogen is more water soluble than phosphate and is present in several forms as part of the nitrification cycle. In this process, ammonium (NH_{4+}) or ammonia (NH_3) is oxidized by bacteria first into nitrite (NO_{2-}) then into nitrate (NO_{3-}). Nitrate is the most stable form, therefore the most abundant. Total nitrogen (T_N), as the name implies, measures all three forms of nitrogen.

Similar to phosphate, nitrogen compounds cause excess nutrient availability and eutrophication. They derive from similar point source and diffuse pollution sources as phosphate and are also present in industrial and domestic cleaning products. Sewage treatment plants oxidise ammonia to nitrite then nitrate, so the presence of significant concentrations of ammonia in water samples may indicate the presence of raw sewage. Ammonia is toxic to aquatic species. The current Environmental Quality Standard for good status ammonia is 0.6 mg/l, however concentrations of >0.1 mg/L can cause eye and gill damage (hyperplasia) and impact hatching success in some fish (Salmonid) species. At higher concentrations, it is suspected to be a leading cause of fish deaths.

In constructed wetlands, the main removal mechanisms for nitrogen are conversion of the most toxic form (ammonia) into less harmful forms (nitrate) by the nitrification process, and the removal of nitrate by conversion into gaseous compounds of nitrogen by bacteria(denitrification). Denitrification occurs in sediments and decaying plant material.

Total coliform bacteria counts

Faecal coliforms enter the environment through contamination with faecal waste of animal or human origin. This may include poorly or untreated sewage plant effluent, leaky septic tanks, and agricultural waste. Faecal coliforms do not cause disease but indicate the presence of disease-causing bacterial pathogens in the aquatic environment. Faecal coliform tests assess the presence/absence of *Escherichia coli* (E. coli) colonies. The risk of infection is correlated with the degree of contamination in water, indicated by total coliform counts (TCC). This counts faecal E. coli and other coliform bacteria such as Salmonella spp., and Campylobacter spp that may cause diseases such as gastroenteritis, and salmonellosis. Total coliform counts are reported as colony forming units (CFU) per 100/ml of water, however it is not possible to verify that these faecal coliforms derive from humans without carrying out DNA tests.

Heavy Metals

Any relatively dense metallic element that is toxic at low concentrations is termed a heavy metal. Some heavy metals are essential trace elements for life (e.g. zinc, copper) but at higher concentrations they may cause poisoning. Heavy metals can become 'locked up' in bottom sediments where they remain for many years. Heavy metals do not biodegrade or break down into less harmful components in the environment. Instead they tend to bind strongly to organic material and bioaccumulate over time in living organisms. Individual metal toxicity in the environment depends on metal availability, which in turn depends on factors including temperature, pH, water hardness and the presence of other contaminants. Four heavy metals were selected for study:

- **Zinc**: Concentrations in waterways are naturally low, so high levels usually indicate contamination. It is present in urban surface water run-off from corrosion of rust-resistant coatings on iron and steel products (eg roof guttering) and from the wear of rubber in car tyres.
- **Copper:** Is an essential micro nutrient at low concentrations. At high levels is can be toxic to aquatic life, affecting fish, invertebrates and amphibian. Cooper normally occurs in water from flow through copper pipes and from additives intended to control algal growth in drinking water.
- **Lead:** Lead and lead compounds are not required by organisms, even in trace amounts. Lead is particularly dangerous because it is toxic in only very small doses and can accumulate in individuals, entire food chains and in sediments. Its presence is the environment is usually a consequence of anthropogenic activities and most lead in the aquatic system comes from road run-off (fuel combustion from cars). In acidic conditions, lead may also enter rivers through the corrosion of old lead pipes and leaded paint.
- **Cadmium:** Is is not required by organisms but is chemically similar to zinc, an essential micronutrient, so it is assimilated rapidly and excreted slowly by plants and animals. Consequently, it bioaccumulates in organisms quickly in comparison to other metals. Cadmium is present as an impurity in detergents and refined petroleum.

Appendix B - Hach Lange working procedures

All links accessed 20/11/2016

- **Total Nitrogen**

Method: Unfiltered sample. Koroleff Digestion (Peroxo-disulphate) and photometric detection with 2.6-Dimethylphenol
http://uk.hach.com/laton-total-nitrogen-cuvette-test-1-16-mg-l-tn-sub-b-sub/product?id=26370268941
http://uk.hach.com/laton-total-nitrogen-cuvette-test-5-40-mg-l-tn-sub-b-sub/product?id=26370269003&callback=qs

- **Ammonia**

Method: Filtered sample (0.45 µm membrane filter). Indophenol blue
http://uk.hach.com/ammonium-cuvette-test-2-0-47-0-mg-l-nh-sub-4-sub-n/product?id=26370269011&callback=qs
http://uk.hach.com/ammonium-cuvette-test-0-015-2-0-mg-l-nh-sub-4-sub-n/productdownloads?id=26370 269012

- **Nitrate**

Method: Filtered sample (0.45 µm membrane filter). 2.6-Dimethylphenol
http://uk.hach.com/nitrate-cuvette-test-0-23-13-5-mg-l-no-sub-3-sub-n/product?id=26370291438
http://uk.hach.com/nitrate-cuvette-test-5-35-mg-l-no-sub-3-subn/product?id=26370291439
&callback=qs

- **Phosphate**

Method: Filtered sample (0.45 µm membrane filter). Phosphomolybdenum Blue
http://uk.hach.com/phosphate-ortho-total-cuvette-test-0-05-1-5-mg-l-po-sub-4-sub-p/product?id=26370291448
http://uk.hach.com/phosphate-ortho-total-cuvette-test-2-0-20-0-mg-l-po-sub-4-sub-p/product?id=26370291449&callback=qs

- **BOD_5**

Method: Dilution method
http://uk.hach.com/bod-sub-5-sub-cuvette-test-4-1650-mg-l-o-sub-2-sub/product?id=26370291503&callback=qs

- **Metal digestion**

Method: Total metal content was determined for all heavy metals by heating in an acid environment in the presence of an oxidising agent (cracking) as a pre-treatment.
http://uk.hach.com/crack-set-reagent-set-for-metal-digestions/product-downloads?id=26370291742&callback=qs

- **Zinc**

Method: Unfiltered sample. Cracking then 4-(2-pyridylazo)- resorcin (PAR)
http://uk.hach.com/zinc-cuvette-test-0-2-6-0-mg-l-zn/product?id=26370291457

- **Copper**

Method: Unfiltered sample. Cracking then PAR
http://uk.hach.com/copper-cuvette-test-0-1-8-0-mg-l-cu/product?id=26370291428

- **Cadmium**

Method: Unfiltered sample. Cracking then Cadion
http://uk.hach.com/cadmium-cuvette-test-0-02-0-3-mg-l-cd/product?id=26370291404

- **Lead**

Method: Unfiltered sample. Cracking then PAR
http://uk.hach.com/lead-cuvette-test-0-1-2-0-mg-l-pb/product?id=26370291402&callback=qs