

Detecting river pollution using fluorescence spectrophotometry: case studies from the Ouseburn, NE England

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“Capsule”: *Fluorescence spectrophotometry can be used to detect sewage pollution in an urban river.*

Abstract

Recent advances in fluorescence spectrophotometry enable the analysis of river dissolved organic matter. We investigate the potential of detecting sewage pollution in a small, urbanised catchment. Downstream sampling highlighted a summer maximum in tryptophan fluorescence intensity during low flow. No correlation is observed between ammonia and tryptophan fluorescence intensity. In contrast, two sewage related point-pollution events had both high tryptophan fluorescence intensity and ammonia, suggesting that the summer tryptophan increase does not originate from foul sewage. Sewage inputs to the river were therefore monitored at summer baseflow. This demonstrated that >10% of the rivers' discharge is provided by sewerage inputs and that these inputs could be grouped by their fluorescence and ammonia properties: (1) 'clean' storm waters with low ammonia and tryptophan intensity (2) 'grey' waters with high tryptophan intensity and low ammonia concentration, and (3) 'foul' waters with high tryptophan intensity and ammonia concentration. All three types of sewerage input occurred irrespective of flow conditions, suggesting that sewerage cross connections are occurring.

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1. Introduction

Fluorescence spectrophotometry has the potential to discriminate between DOM fractions, in particular to differentiate the labile fraction into environmentally significant components. In addition, recent technological advances have led to rapid (~1 min) analysis of river water fluorescence in small (<5 ml) samples at concentrations of ~0.1 mg/l. The most significant advance in recent years has been the ability to simultaneously scan a wide range of both excitation and emission wavelengths to generate a fluorescence excitation-emission matrix or EEM. This has enabled different fluorescence centres to be easily visualized and measured. Fig. 1 presents a typical EEM, which shows the location in optical space of fluorescence centres that are

typically observed in river and waste waters (Coble, 1996; Newson et al., 2001; Baker, 2001, 2002a,b,c; Mounier et al., 1999; McKnight et al., 2001). The principal fluorophores are ascribed to aromatic and aliphatic groups in humic (H_{int}) and fulvic (F_{int}) substances and to aromatic proteins such as tryptophan (T_{int}) (Coble, 1996; Mayer et al., 1999; Mounier et al., 1999; McKnight et al., 2001).

The measurement of sewage waste water fluorescence has had a long history of investigation as a potential monitoring tool, with early research predating the use of fluorescence EEM technology. More recently, Ahmad and Reynolds (1995) suggested that synchronous scan fluorescence spectroscopy could be used in the analysis of wastewater and that it had utility in the process control of sewage treatment plants. Later research determined that sewage exhibited a maximum fluorescence at excitation wavelength of 280 nm and emission wavelength of 340 nm (Reynolds and Ahmad, 1997); note that this corresponds to the location of T_{int} in Fig. 1.

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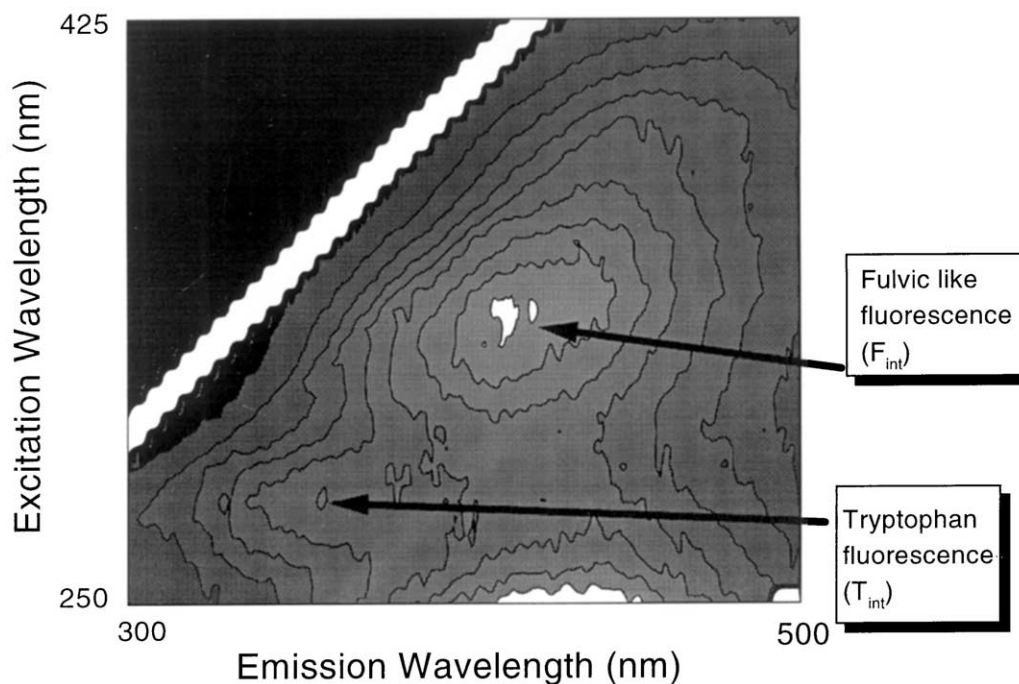


Fig. 1. Typical fluorescence excitation–emission matrix showing the locations of the fluorescence peaks analysed in this paper.

Fluorescence intensity at this location was observed to decrease with sewage treatment and a strong correlation was observed with biological oxygen demand. Galapate et al. (1998) used synchronous scan technology to identify a fluorescence fingerprint of sewage in a Japanese river, and observed a large fluorescence excitation peak at $\lambda = 274$ nm and $\Delta\lambda = 60$ nm. This synchronous scan would therefore pass through the T_{int} centre shown in Fig. 1. Most recently fluorescence EEMs have been used to identify sewage related DOM in river water (Baker, 2001). Some sewage impacted rivers in NE England were characterised by high fulvic-like (F_{int}) and even higher tryptophan (T_{int}) fluorescence intensity (Baker, 2001), and it was demonstrated that fluorescence quenching by metal ions was not important, due to the high concentration of organic matter in the wastewater. The high T_{int} observed in wastewater and sewage impacted rivers can be explained by the difference in DOM quality between sewage and natural water. For example, Ma et al. (2001) extract DOM fractions from both natural and wastewater effluent using reverse osmosis and ion exchange. They demonstrated that natural water DOC comprised 54–68% fulvic-acid fraction, 13–29% humic-acid fraction and 9–30% hydrophilic fraction, whereas wastewater comprised equal amounts of fulvic-acid and hydrophilic fractions with no humic acids. Such differences are likely to explain the difference in fluorescence properties between wastewater and natural water.

Therefore recent advances in fluorescence spectrophotometry have started to differentiate potential sew-

erage-related river pollutants from natural water sources. However, research to date has focused on laboratory experimentation or simplistic fluvial systems, for example, reaches up and downstream of sewerage inputs. As well as the distinctive sewage fluorescence fingerprint, other potentially polluting waste products also fluoresce. Farm wastes (sheep barn waste, silage liquor, pig and cattle slurry) and pulp mill effluents also have distinctive fluorescence properties (Baker, 2002a,b) that might also impact on river fluorescence properties in agricultural catchments. Research is therefore necessary to investigate whether fluorescence spectrophotometry can be utilised to detect pollution events in the more complex system of a small catchment that potentially has a wider variety of DOM sources. In this paper we focus on the detection of sewerage related pollution, which in the UK is frequently the most important factor affecting water quality. Sewage effluent affects 34% of the river length in Scotland and urban drainage (which can contain misconnected sewage effluent) a further 11% (Marsden and Mackay, 2001). Future trends in the expansion of urban areas suggest an increase in the relative importance of diffuse source pollution (from cross connected sewers) as point source discharges (such as combined sewage overflows or CSOs) are decreased due to the Urban Waste Water Treatment Directive (91/271/EEC) (Marsden and Mackay, 2001). In this study we investigate the potential of detecting sewerage related river pollution using fluorescence spectrophotometry in a small, urbanised catchment in NE England

2. Description of study catchment

The catchment chosen for our research is the Ouseburn, NE England, which is 55 km² in area. Fig. 2 shows the catchment together with locations for water samples that were collected between June 2000 and January 2002; these follow that of Turnball and Bevan (1994) and also incorporate the UK Environment Agency chemical water quality sample sites on the river. Mean river discharge over the study period measured at the Environment Agency gauging station at Crag Hall (site 23) was 0.39 m³/s (15 min sampling frequency; median 0.17 m³/s, max. 17.0, min. 0.025). The lower catchment (downstream of site 13) is heavily urbanised as it flows through the city of Newcastle-upon-Tyne, with housing and a dense road network comprising the main land-uses. The sewerage of the urban area is a combination of older combined sewerage systems that intermittently drain into the river through CSOs, as well as separate sewerage with storm drains draining to the river from more recent housing builds. Predominantly arable farms (upstream of site 13) and the city international airport (runoff draining into sites 6 and 8) dominate the upper catchment.

The catchment has a previous history of research. Integrated water quality monitoring (chemical, bacterial and biological) on the river in the early 1990s found it was adversely affected by combined sewer overflows,

cross connected sewers and airport deicer (Turnball and Bevan, 1994, 1995). The authors showed that the intermittent nature of the pollution events on the river prevented chemical water quality monitoring from being an effective detection technique. The findings of Turnball and Bevan (1994) suggest that the Ouseburn is typical of UK urban rivers. In these cases, non-point source pollution is often the most serious threat to water quality (Faulkner et al., 2000), especially at low flow due to sewerage misconnections and failing CSOs, together with point source pollution from first foul flushes from CSOs at high flow.

As well as previous research data, basic chemical and biological water quality data are available for the catchment for the sampling period. Environment Agency chemical water quality data collected monthly over the period June 2000–January 2002 permits the Environment Agency to assign the chemical water quality of the river as Good to Very Good (Environment Agency, unpublished data). River water had a mean biological oxygen demand, ammonia and dissolved oxygen of 3.2 mg/l, 0.15 mg/l and 94.7%, respectively at site 23; 2.3 mg/l, 0.14 mg/l and 92.9% at site 16; 5.4 mg/l, 0.88 mg/l and 82.5% at site 10, and 1.7 mg/l, 0.12 mg/l and 84.1% at site 3. Chemical water quality data contrast with biological water quality monitoring at the same sample sites. Biological quality measured using RIVPACS (Wright et al., 1998) in terms

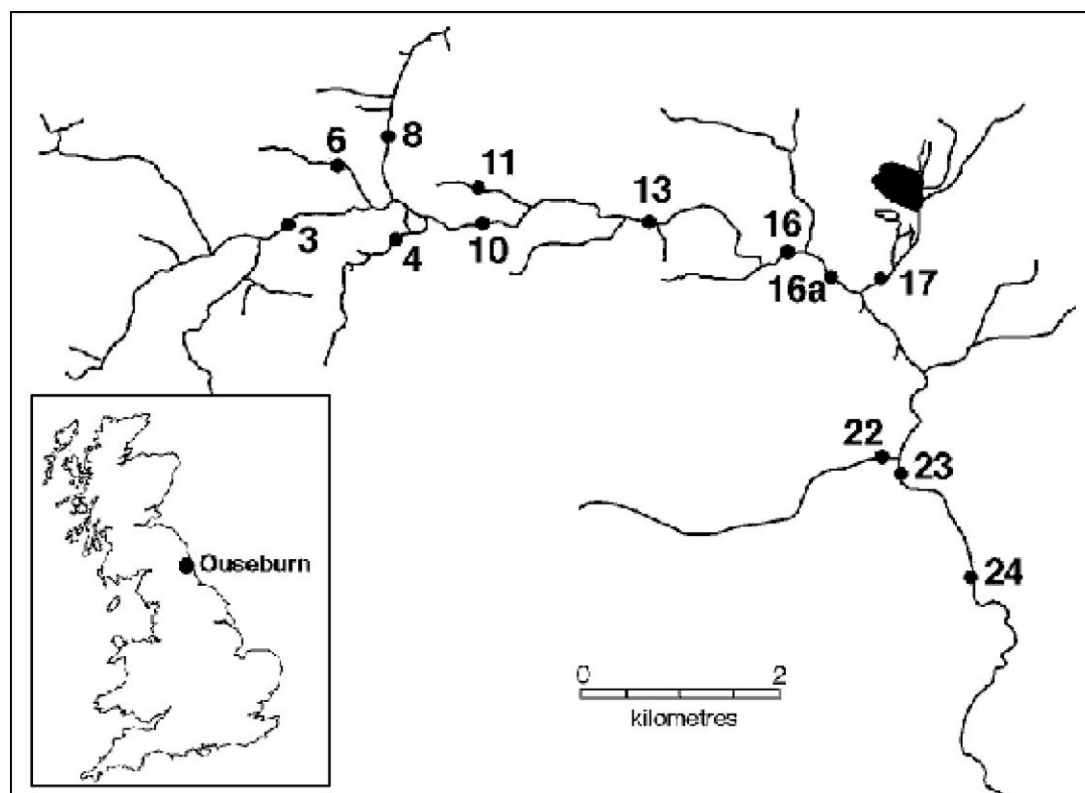


Fig. 2. The Ouseburn catchment, Newcastle-upon-Tyne, NE England (55° 0' N, 1° 35' W), showing sampling locations used during programs 1 and 2.

of the number of taxa observed/expected (NTAXA) and average score per taxa (ASPT) observed/expected has a strong downstream trend. NTAXA and ASPT are 0.72 and 0.73 at site 3; 0.43 and 0.64 at site 10; 0.43 and 0.64 at site 16 and 0.44 and 0.70 at site 23; grading the river as fair at site 3 and poor elsewhere. Such a discrepancy between biological and chemical monitoring results is also typical of urban rivers (Faulkner et al., 2000), suggesting that the Ouseburn is today as impacted by urban pollution as it was in the 1990s by Turnball and Bevan (1994).

3. Materials and methods

Water samples were collected on the Ouseburn during three integrated sampling programs:

1. The first was a reconnaissance survey to sample the Ouseburn near its downstream limit at high temporal frequency in order to determine whether fluorescence spectrophotometry could identify catchment scale fluorescence trends from upstream pollution sources. Recognizing that pollution in the catchment is likely to be from both point and diffuse sources, ideally continuous and automated sampling is ideally required. However, this was not practicable (due to a lack of secure auto-sampling locations), and instead grab samples were taken at the downstream site 24 at approximately 6-day intervals (105 samples over the 20-month study period).
2. The second program was a monthly sampling regime on all accessible major tributaries (seven sites: 3, 4, 6, 8, 11, 17, 22), together with intermediate main stream samples (five sites: 10, 13, 16, 16a, 23). Fig. 2 shows the water sampling locations. This program was primarily to investigate if spectrophotometric techniques such as fluorescence spectrophotometry can be used to discriminate dissolved organic matter between tributaries (Baker, 2002c). However, on two occasions sewerage related pollution events were detected: these are detailed here.
3. After consideration of the results of the first reconnaissance sampling program, a third water sampling regime was undertaken towards the end of the study period. This third program took place at low flow conditions during the summer of 2001 along a 500 m reach of the river (adjacent to and downstream of site 16) in order to investigate if diffuse source pollution from cross connected sewerage could be detected by fluorescence. Twelve accessible sewerage sources (10 storm drains from a separate sewerage sys-

tem, one storm drain in a combined sewerage system with two up-system CSOs and one CSO) were monitored and water sampled when active over a 6-week period in July and August 2001. Fig. 3 shows the sampling locations and sewerage connections.

Water samples were collected in 30-ml polypropylene bottles which had been precleaned in 10% HCl and distilled water. Samples were refrigerated upon return from the field, and analysed within 24 h. The samples were filtered (Whatman GF/C preashed glass microfibre filter papers). Fluorescence measurements were undertaken using a Perkin-Elmer LS-50B luminescence spectrometer as described elsewhere (Baker, 2001; Baker and Lamont-Black, 2001). The Raman peak of water at 348 nm was used as a test for machine stability and to permit inter-laboratory comparison and results were adjusted to a Raman peak intensity of 20.0 units. Absorption at 254 and 340 nm was undertaken using a WPA Lightwave UV-vis spectrometer in order to check for any possible inner-filtering effects (Mobed et al., 1996; Ohno, 2002). No correction to the fluorescence EEMs was necessary as absorption was typically $<0.3 \text{ cm}^{-1}$, and maxima of $0.3\text{--}0.5 \text{ cm}^{-1}$ at 254 and 340 nm decreased tryptophan and fulvic-like fluorescence intensities by $<10\%$. In order to compare fluorescence data with a conventional water quality determinand, ammoniacal nitrogen was also measured using a Hanna Instruments Ion Selective Meter, which uses an adapted Nessler method and measures ammoniacal nitrogen to $\pm 0.05 \text{ mg l}^{-1}$. Finally, TOC was also determined using a Shimadzu 5000 TOC analyser; all samples were analysed in duplicate or triplicate and the mean value used.

4. Results

4.1. Catchment scale fluorescence trends

Fig. 4 shows data for the fluorescence spectrophotometric properties T_{int} and F_{int} , for which previous research has suggested that they may provide information about the DOM fraction in river water (Baker, 2001, 2002a,b). In addition, ammonia is presented; this was measured both by the author and by the Environment Agency as part of their Chemical Water Quality sampling scheme. Discharge data from the $\sim 1.6 \text{ km}$ upstream of Crag Hall gauging station at site 23 are also shown. The results from the Ouseburn sampled at ~ 5 day resolution since June 2000 show that the fluorescence is clearly seen to be dominated by higher levels of T_{int} in summer. A clear seasonal cycle in tryptophan fluorescence intensity is visible that weakly negatively correlates with discharge (T_{int} vs. Q ;

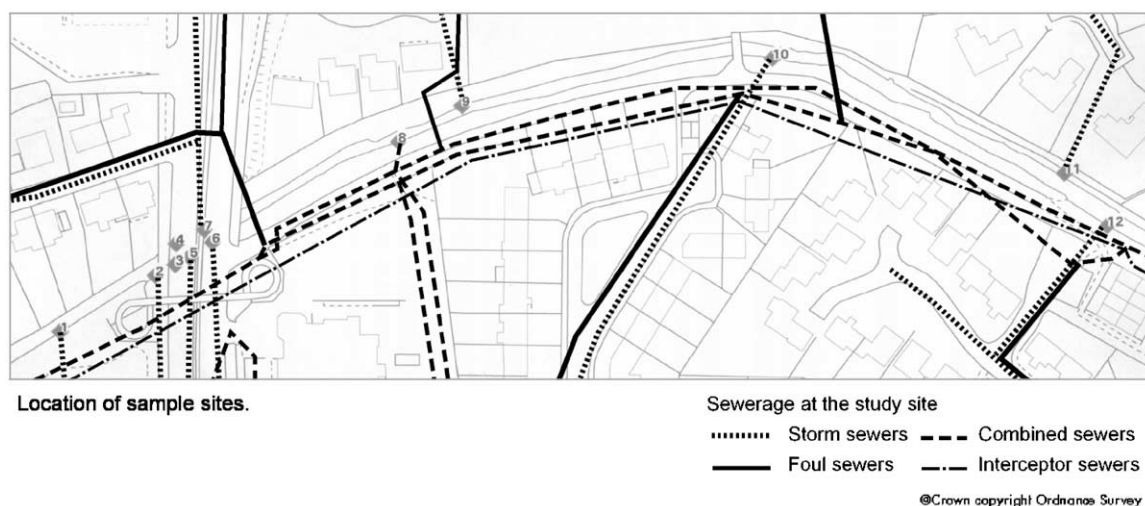


Fig. 3. Locations of sewerage inputs sampled in program 3. The sampling location is adjacent to and downstream of site 16 in Fig. 2; in this figure site 16 is a river grab sample taken between S8 and S9.

$r = -0.27$, 95% confidence range of r from -0.08 to -0.46). One possible cause of a weak and inverse T_{int} -discharge correlation is a combination of T_{int} sources that have different relationships with discharge. For example, diffuse source inputs would be diluted at high flow, giving an inverse relationship between T_{int} and discharge if the inputs had high T_{int} . In contrast, high T_{int} pollution pulses from CSOs at times of high flow and from CCSs at variable flow conditions could confound such a relationship. The third sampling program investigates the possible source(s) of this summer increase in T_{int} . In contrast to the T_{int} , there is no correlation between F_{int} and discharge ($r = -0.08$, with a 95% confidence interval from -0.30 to 0.15). Similar to the discharge- T_{int} relationship, F_{int} has a variety of possible relationships with discharge, including an increase in autumn during the start of winter recharge due to the mobilisation of soluble fulvic-like substances from the soil, as well as possible decreases with increasing discharge at high flow due to dilution effects.

Ammonia is used as a chemical water quality determinand by the Environment Agency as it is environmentally hazardous both because of its toxicity to fish and because of its ease of oxidation, enabling it to deplete dissolved oxygen rapidly. It is the initial product of the decay of nitrogenous organic wastes, and the breakdown of animal and vegetable wastes. Sewerage effluent is one source of ammonia in water. Given its use as a well understood pollution indicator, we also measured river ammonia concentrations alongside fluorescence. When ammonia data is compared to the fluorescence results, no correlation is observed (ammonia vs. T_{int} ; $r = 0.08$, 95% confidence range of $-0.35 < r < 0.21$). This result is unexpected given the possible correlation between both of these parameters and pos-

sible sewage pollution. Ammonia also shows a seasonal cycle; peaks occur during the late winters of 2000–2001 and 2001–2002 and during periods of preceding frost and/or snow cover, suggesting a non sewerage source. The Environment Agency ammonia data, with a lower sampling frequency, fails to show this trend and instead has a noisy signal with occasional ammonia peaks at times of high river discharge (e.g. on the 12/10/01 when discharge was $> 5 \text{ m}^3/\text{s}$). The combination of the two datasets demonstrates that ammoniacal nitrogen maxima can occur both in winter as well as during high discharge events, the latter probably due to failing or consented CSO discharges.

Frequent downstream sampling of the Ouseburn highlights:

1. Seasonal trends in the fluorescence spectrophotometric parameters T_{int} and F_{int}
2. A T_{int} maximum in summer during low flow and an inverse relationship with discharge.
3. A seasonal trend in ammoniacal nitrogen, with a maximum at times of winter frost and snow, together with extremes in ammoniacal nitrogen during some high discharge events. The seasonality in ammoniacal nitrogen when sampled at ~ 5 day frequency is not visible in the monthly Environment Agency dataset
4. No correlation is observed between ammoniacal nitrogen and T_{int} , despite the fact that both could be water quality indicators of sewage pollution. This is due to Ouseburn winter water quality during periods of cold and frost having high ammonia, low T_{int} , and summer water quality having low ammonia and high T_{int} . The source of the latter water is in the discussion of the third sampling program.

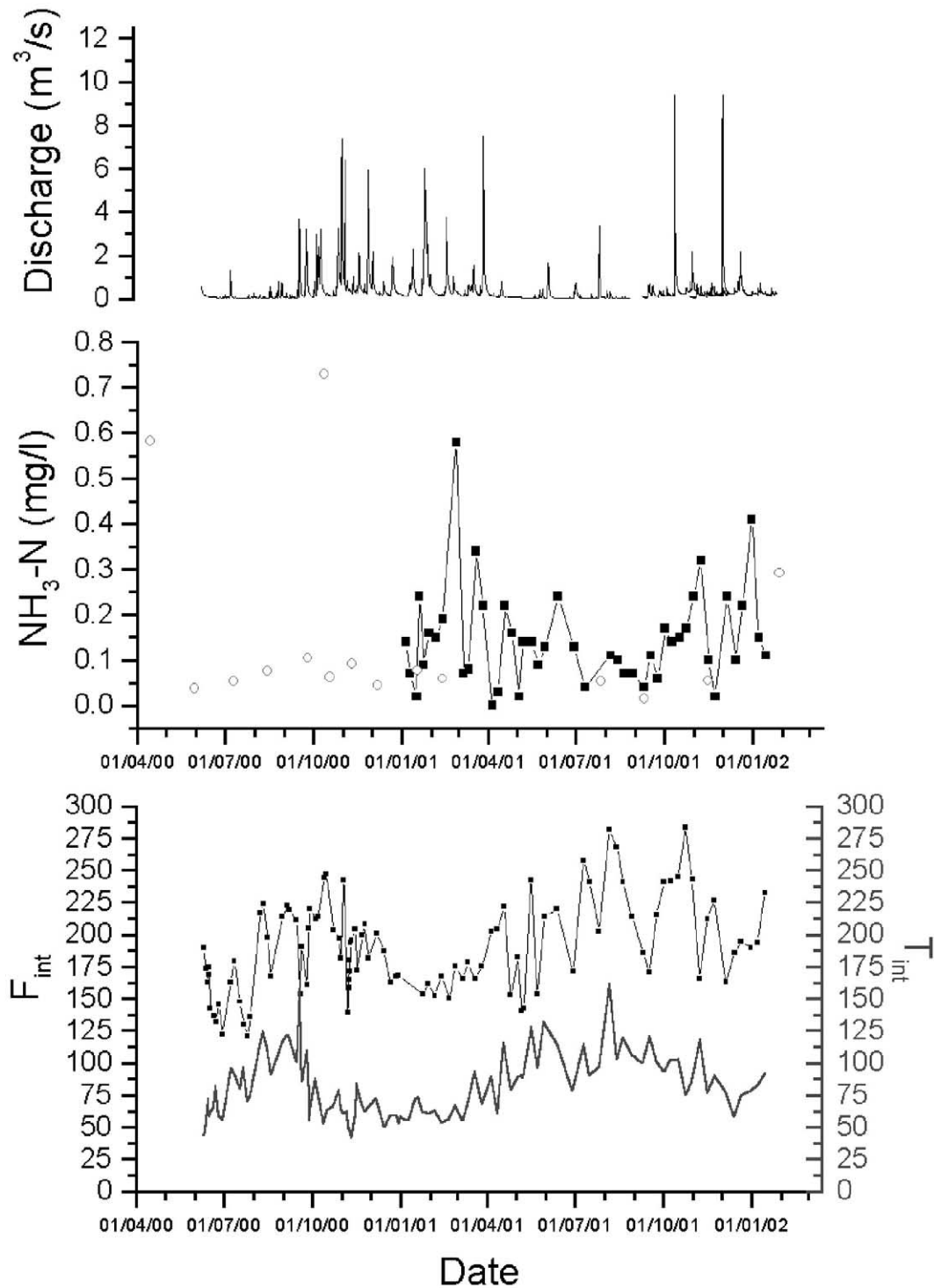


Fig. 4. (Top) discharge data (15-min intervals from Crag Hall gauging station). (Middle) ammonia. Open circles is data collected by the Environment Agency as part of UK national water quality monitoring. Solid squares is ~ 5 day frequency sampling by the authors. (Base) fluorescence properties T_{int} (solid line) and F_{int} (line and symbol).

4.2. 30 August 2001 and 2 November 2001 pollution events

Fig. 5 presents T_{int} data from the monthly sampling program in 2000–2002 for each of the mainstream and tributary samples. Two high T_{int} events

at sites 3 and 4 stand out from the rest of the sampling program as statistical extremes ($\times 3$ the interquartile range of the data). Table 1 presents the fluorescence data for all samples sites on the 2 days where high T_{int} waters were sampled, together with other water quality and basic geochemistry data

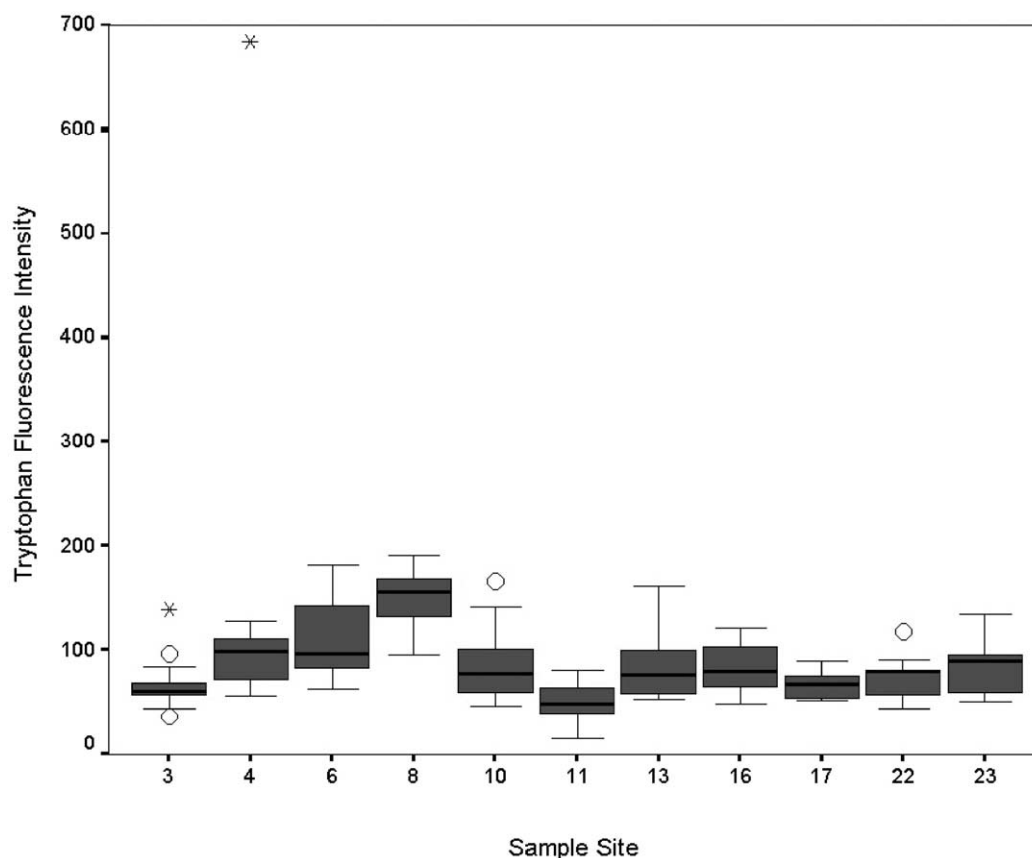


Fig. 5. Boxplot of T_{int} data collected in sampling program 2. ○ and * represent outliers (cases with values between 1.5 and 3 box lengths from the upper or lower edge of the box) and extremes (cases with values greater than 3 box lengths from the upper or lower edge of the box), respectively.

(TOC, pH, electrical conductivity, ammonia and absorbance).

The event at sample site 4 was sampled on the 30 August 2001. Routine sampling noted a high T_{int} and F_{int} and ammonia concentration, with a downstream dilution trend noted (Table 1). Subsequent investigation by the Environment Agency traced the pollution to a sewerage source, a collapse of a manhole into the sewerage system upstream of site 4. This led to untreated sewage overflowing and entering the nearby river. The event at sample site 3 on the 2 November 2001 was similar, with the water samples having a high T_{int} and ammonia concentration. Subsequent investigation by the Environment Agency located the pollution source to a upstream blocked sewer, which had led to an unconsented discharge into river via a former CSO.

In both events we observe a good correlation between ammonia and T_{int} . Fig. 6 shows both this relationship as well as the correlation between ammonia and $T_{\text{int}}/F_{\text{int}}$ (as used in Baker, 2001). Correlation coefficients are 0.96 (95% confidence interval from 0.82 to 0.99) for ammonia vs. T_{int} and 0.89 (95% confidence interval from 0.92 to 0.99) for ammonia vs. $T_{\text{int}}/F_{\text{int}}$. Subtle differences are observed between the two events. On the 30 August 2001, T_{int} , F_{int} , ammonia and TOC all increased, whereas on the 2 November 2001 only T_{int}

and ammonia increased. These differences are due to differences in both sewage quality and quantity, but shows that fluorescence, and in particular T_{int} , can detect the pollution irrespective of these differences. It is also interesting to note that in both pollution incidents there were no obvious signs of sewage pollution (odour, colour, sewage litter or solids) and that neither event was reported by members of the public, suggesting that fluorescence can detect subtle but environmentally significant pollution events.

Analysis of these two sewage related point-pollution events has demonstrated that both events are characterized by high tryptophan fluorescence intensity, and that T_{int} and $T_{\text{int}}/F_{\text{int}}$ have statistically significant correlations with ammonia. Neither event was sampled at the downstream site 24 as part of the first sampling program as the point-pollution events occurred in-between the 6 day frequency sampling. This observation suggests that automatic sampling is necessary in order to detect point source pollution events: the strong correlation between ammonia and T_{int} and $T_{\text{int}}/F_{\text{int}}$ suggest that automatic monitoring of these variables would provide useful water quality data. In particular the correlation between $T_{\text{int}}/F_{\text{int}}$ and ammonia explains 85% of the variability between the variables, suggesting that good a predictive capability is possible for ammonia

Table 1
Chemical and spectrophotometric water quality data for the 30 August and 2 November pollution events

Date	Site	pH	Electrical conductivity (micro-S)	Ammonia (mg/l)	Carbon analyses			Absorption		Tryptophan fluorescence T_{int}	Fulvic-like fluorescence F_{int}	$T_{\text{int}}/F_{\text{int}}$
					TC (mg l ⁻¹)	IC (mg l ⁻¹)	TOC (mg l ⁻¹)	A_{254} (cm ⁻¹)	A_{340} (cm ⁻¹)			
02-November-2001	3	7.89	789	2.91	37.09	31.76	5.33	0.123	0.034	140	126	1.11
02-November-2001	13	7.80	652	1.61	48.36	40.8	7.56	0.139	0.041	82	139	0.59
02-November-2001	16	7.70	674	1.41	48.43	41.39	7.04	0.110	0.030	79	137	0.58
02-November-2001	23	7.70	720	0.83	49.75	41.97	7.78	0.141	0.040	77	149	0.52
02-November-2001	4	7.34	714	0.21	48.35	41.13	7.22	0.154	0.041	80	171	0.47
02-November-2001	6	7.71	1065	0.13	62.9	54.19	8.71	0.154	0.056	96	219	0.44
02-November-2001	22	7.92	1062	0.11	83.98	79.64	4.32	0.124	0.031	80	174	0.46
30-August-2001	3	7.05	909	0.06	52.13	48.15	3.98	0.065	0.013	61	101	0.60
30-August-2001	10	6.39	823	4.21	50.07	42.64	7.43	0.149	0.035	166	183	0.90
30-August-2001	13	7.08	885	4.98	61.76	53.04	8.72	0.162	0.037	162	201	0.80
30-August-2001	16	6.94	944	1.49	55.08	48.65	6.43	0.125	0.030	111	168	0.66
30-August-2001	16a	6.07	960	0.87	54.21	48.12	6.09	0.128	0.027	113	167	0.68
30-August-2001	23	7.13	966	0.46	56.24	49.74	6.50	0.129	0.029	115	168	0.69
30-August-2001	4	6.92	896	19.50	80.22	58.18	22.04	0.467	0.116	684	418	1.64
30-August-2001	6	6.67	1454	0.11	59.47	50.35	9.12	0.213	0.046	178	270	0.66
30-August-2001	8	6.39	823	0.39	62.21	50.03	12.18	0.326	0.078	173	360	0.48
30-August-2001	11	6.62	951	0.05	72.91	71.02	1.89	0.037	0.008	49	73	0.66
30-August-2001	17	6.91	501	0.09	36.13	24.07	12.06	0.349	0.091	89	119	0.75
30-August-2001	22	7.63	1190	0.08	80.51	75.79	4.72	0.097	0.018	81	170	0.48

Samples sites are as shown in Fig. 2 and are arranged firstly upstream–downstream in the main river and then by tributary in upstream–downstream order. Polluted waters are emboldened.

by measuring $T_{\text{int}}/F_{\text{int}}$ fluorescence. The implications of this for water quality monitoring is discussed further in the conclusions.

4.3. Sewerage inputs at summer baseflow

After the observation of high tryptophan fluorescence intensity in summer and a weak but statistically significant inverse correlation with discharge, a third sampling program was initiated in the summer of 2001. One possible explanation of the T_{int} –discharge relationship is a diffuse T_{int} source that is diluted in winter at high river discharges. One possible diffuse source is storm water inputs into the river from the sewerage system. Within sampling program two we observed many active storm water discharges into the river at summer low flow conditions, when storm sewers should be dry and inactive. This indicates the existence of cross-connected sewerage (CCS) inputs that could provide an obvious source of diffuse pollution. CCSs can input both foul (toilet connections) and grey (bath, laundry and dishwasher connection) waste waters to the river. Downstream observations at site 24, where no correlation between T_{int} and ammonia is observed, suggest that if sewerage inputs are a significant source of the high T_{int} observed in the river in summer, then no significant foul (sewage) water should be present in the majority of CCS inputs. The fluorescence properties of grey wastewaters have not been investigated but could be a possible source of high T_{int} , low ammonia inputs to the river, with grey wastewater characterized by low ammonia

concentrations (with typically 0.01–0.10 mg/l NH_4 per mg/l TOC) and high TOC (typically 10–1000 mg/l) (Eriksson et al., 2002).

In order to investigate if CCS inputs could be a source of the high tryptophan fluorescence intensity at summer baseflow, a 500 m length of the Ouseburn was sampled over a six week period. Initially we sought to sample the whole of the catchment between sites 16 and 24 (a length of ~ 6.6 km), but a reconnaissance survey demonstrated so many active sewerage inputs that that for logistical reasons we restricted our survey to a short 500 m length downstream of site 16 where 12 sewerage inputs were monitored and sampled. Fig. 7 and Table 2 present the time of sampling with respect to river flow and the summary statistics for each of the sewerage inputs. Four samples were taken at summer baseflow prior to two storm events on the 4 and 8 August 2001; no storm sewerage inputs on these dates should have occurred due to the dry antecedent conditions. Four samples were taken after this storm event, when we might expect the storm sewers still to be active.

Eleven of the twelve sampled inputs were active at least once during our sampling period. Of these, six (50%; site numbers S1, S5, S8–11) were continuously discharging irrespective of the flow conditions. Of these sites, S1 and S8 form part of a combined sewerage systems whereas S5, S9–S11 are storm sewers in a separate sewer system. Five inputs were discontinuous discharges. Some of these were active after the rain events on the 4 and 8 August (S2, S4, S6, S7; all storm sewers), whereas one was active under either wet and/or dry flow conditions (storm

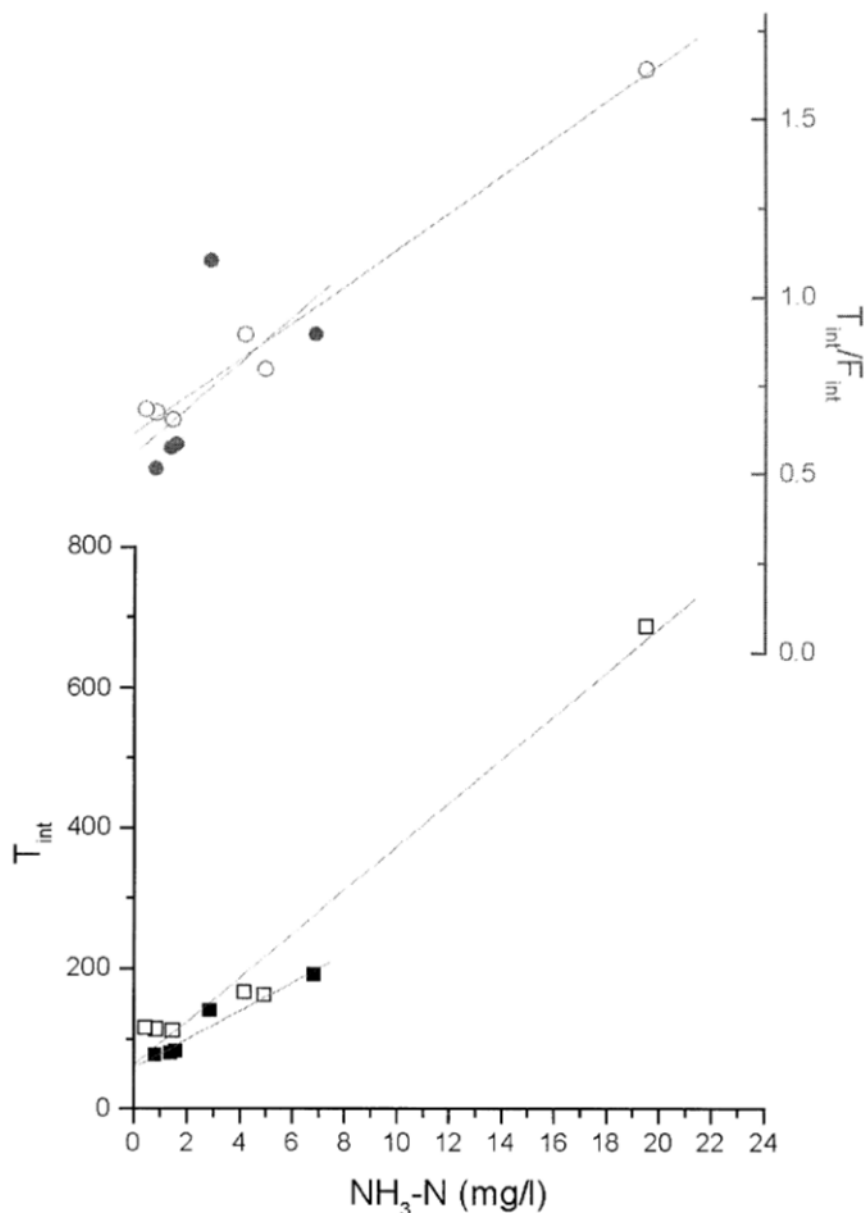


Fig. 6. Ammonia vs. $T_{\text{int}}/F_{\text{int}}$ (top) and T_{int} (base) for the two pollution events sampled in program 2.

sewer S12). Discharge of the sewerage inputs ranged from continuous slow seeps (~ 3 ml/s at site S11) to continuous and significant flows (constant 2 l/s at S1; given the summer base flow of the Ouseburn of ~ 0.025 m³/s, this one site comprises 10% of the flow of the river).

Fluorescence properties of the discharges are presented in Fig. 8a and b, together with ammonia (Fig. 8c). Only sites S10 (a storm sewer) and S8 (a newly improved CSO where the water is probably groundwater seepage) have continuously good water quality. All other storm sewerage inputs (S1-7, S9, S11, S12) have variable and occasionally occasional high levels of ammonia, F_{int} and/or T_{int} . Given this variability, the water quality of the sewerage inputs is classified using principal components analysis and the results shown in

Fig. 9a. Fig. 9a demonstrates that 55% of the variability in the data can be explained by two sets of components. The first component correlates strongly with variables that reflect the concentration of organic matter in the water (TOC and absorbance) and explains 31% of the variability. The second component explains a further 24% of the data and correlates with variables that reflect the quality of the sewerage related organic matter (high $T_{\text{int}}/F_{\text{int}}$ and/or high ammonia). Two sets of water samples are of interest in Fig. 9a. One group has high scores in PC1 and PC2 and is therefore both high in concentration and high in sewerage related parameters. These are from inputs S1, 9, 11, and 12, and they occur both before and after the 4 and 8 August storm events, suggesting that these samples reflect sewage cross

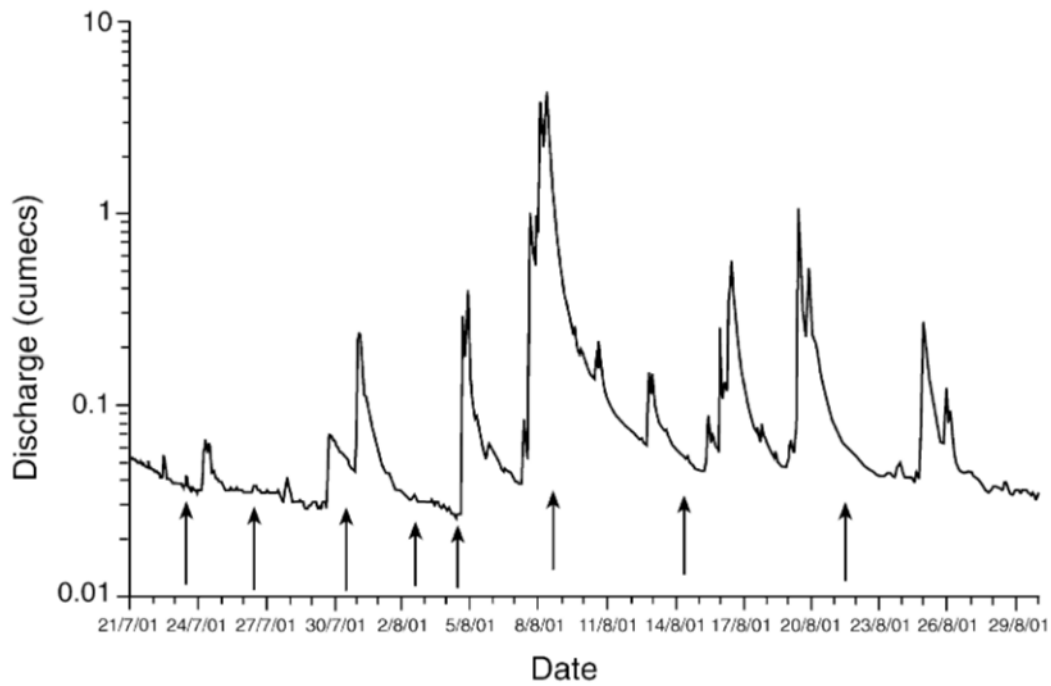


Fig. 7. Sampling dates for research program 3. River discharge is also shown, data taken from the Crag Hall gauging station.

Table 2
Spectrophotometric and chemical water quality measurements for the sewerage inputs sampled in the summer 2001

Site Northumbrian Water ID	pH	Electrical conductivity ($\mu\text{S cm}^{-1}$)	Ammonia (mg l^{-1})	Total carbon (mg l^{-1})	Inorganic carbon (mg l^{-1})	Organic carbon (mg l^{-1})	Absorbance		T_{int} (units)	F_{int} (units)
							254 nm cm^{-1}	340 nm cm^{-1}		
SI	Mean 7.79	10.11	1.17	43.0	33.4	9.6	0.142	0.035	138	148
2512 (storm with 2 upsystem CSOs)	S.D. 1.11	292	1.82	17.8	19.6	4.7	0.085	0.036	54	47
S2	Mean 7.14	1571	0.04	45.0	40.0	5.0	0.130	0.025	104	171
2511 (storm)	S.D.									
S3	Mean 8.09	649	0.23	34.3	22.0	12.7	0.328	0.074	121	251
road drain	S.D. 0.59	523	0.32	11.6	16.1	12.4	0.350	0.083	92	227
S4	Mean 7.28	867	0.08	56.7	53.0	3.3	0.080	0.013	69	115
road drain	S.D. 0.57	16	0.07	3.5	4.0	0.6	0.028	0.006	11	5
S5	Mean 7.51	1957	0.16	33.9	25.5	8.5	0.197	0.030	108	224
2518 (storm)	S.D. 0.61	791	0.26	9.1	13.4	9.3	0.196	0.035	52	181
S6	Mean 7.11	1011	0.46	49.5	33.0	16.0	0.505	0.150	170	341
2515 (storm)	S.D.									
S7	Mean 6.44	201	0.41	14.0	5.1	9.1	0.132	0.018	191	190
2516 (storm)	S.D.									
S8	Mean 7.37	1794	0.03	66.9	63.4	3.4	0.072	0.011	50	94
2500 (CSO)	S.D. 0.43	32	0.02	10.4	10.4	0.8	0.027	0.007	6	3
S9	Mean 7.61	1380	0.62	67.5	52.3	15.1	0.196	0.044	202	211
3509 (storm)	S.D. 0.48	504	0.63	26.2	20.2	9.9	0.064	0.028	145	68
S10	Mean 7.70	721	0.14	44.8	38.3	6.5	0.129	0.031	79	136
4506 (storm)	S.D. 0.40	118	0.23	9.2	9.6	4.9	0.155	0.045	28	104
S11	Mean 7.73	958	0.22	58.6	45.1	13.4	0.141	0.034	153	201
5608 (storm)	S.D. 0.47	392	0.23	30.8	23.4	15.3	0.056	0.016	109	115
S12	Mean 7.56	422	5.85	77.0	15.9	61.0	0.201	0.067	388	289
5567 (storm)	S.D. 0.71	331	6.87	59.2	22.2	64.0	0.162	0.023	266	67

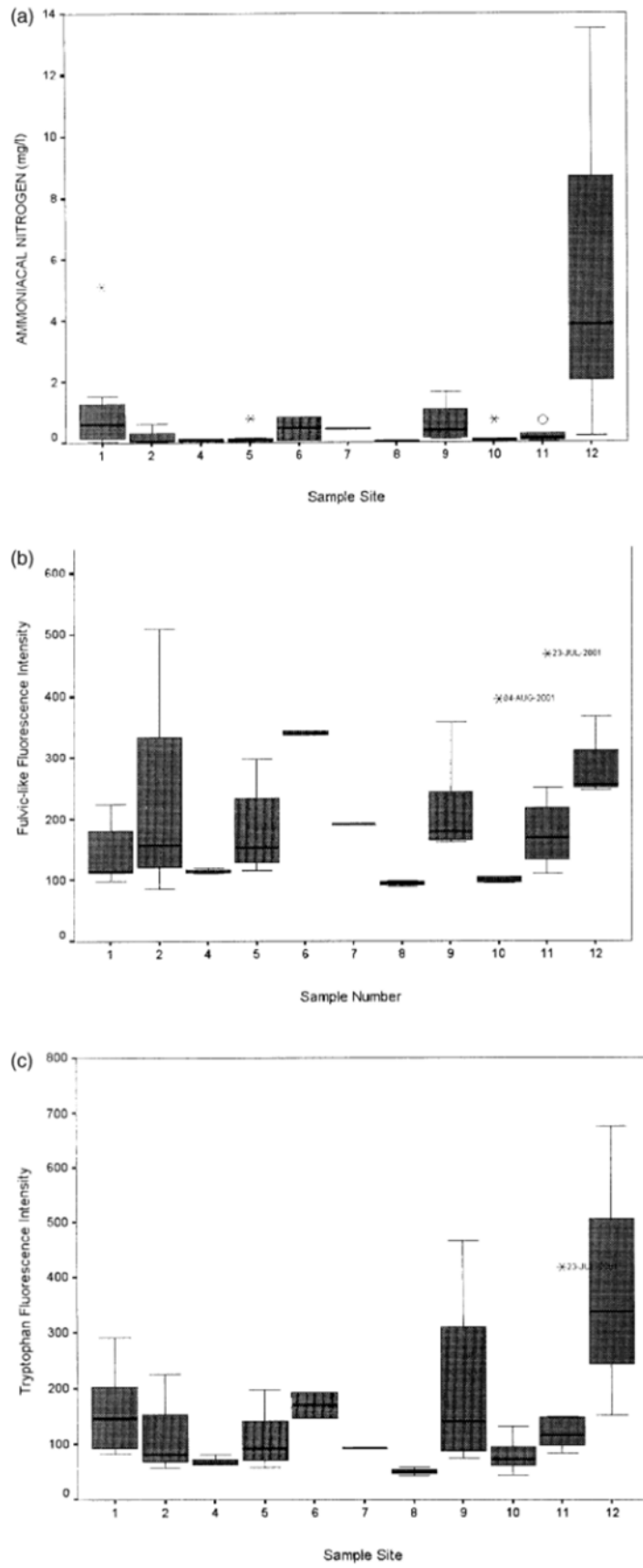


Fig. 8. Ammoniacal nitrogen (a), T_{int} (b) and F_{int} (c) for the sewerage inputs. The dates of the outlying ammonia samples are omitted for clarity and occur on 30 July (S1), 8 August (S5), 4 August (S10) and 30 July (S11).

probably deriving from misconnections with foul inputs (toilets) or up system CSO failures. These samples follow a similar trend of high ammonia, high T_{int} to the sewage pollution events observed in the second sampling programme.

Another potential source is from eroded organic deposits within the sewerage system (Ahyerre, 2001; Ahyerre et al., 2001), which have been demonstrated elsewhere to be the main source of organic matter in wet weather flows (Gromaire-Mertz, 2000) and thus also in dry weather cross-connected flows. Further research is needed to identify which source is predominant. However laboratory analysis of grey water fluorescence demonstrates that it is characterised by T_{int} between 50 and 600 intensity units and ammonia <1.0 mg/l for sink, laundry, bath and shower waters (Fig. 9b; $n=12$; unpublished data). Therefore the fluorescence properties of the sewerage inputs in Fig. 9b could be simply explained by mixing relative proportions of grey, storm and foul waters. It is informative to note that the grey water samples follow a similar trend to the high T_{int} , low ammonia waters observed at summer baseflow in the first sampling programme.

The monitoring of sewerage inputs at summer baseflow has demonstrated that:

1. In just this 500 m stretch of river, at summer baseflow at least 10% of the discharge is provided by sewerage inputs.
2. Principal Components Analysis demonstrates that the second principle component correlates with high ammonia and/or high $T_{\text{int}}/F_{\text{int}}$. Samples with high PC2 scores occur irrespective of flow conditions and together with the high ammonia and/or high $T_{\text{int}}/F_{\text{int}}$ suggests that sewerage cross connections and CSO failures are occurring.
3. Only two sewerage inputs have both high T_{int} and ammonia (S1 and occasionally S12). The former has up-system CSO which may be failing and discharging foul water, whereas S12 is a short length of sewerage with a probably foul cross connection. Most inputs however (S2, S9, S11 and occasionally S1) have low ammonia and high T_{int} , which could derive from grey wastewater. Given the potentially large number of additional sewerage inputs throughout the rest of the catchment, this provides one possible explanation of the inverse relationship between T_{int} and discharge in the Ouseburn with high T_{int} observed in summer at site 24.

5. Conclusions

Data for the fluorescence parameters T_{int} and F_{int} , as well as ammonia, sampled in the Ouseburn at ~ 6 day

resolution at site 24 show that the river is clearly dominated by T_{int} in summer. Research on sewerage inputs into the river near site 16 in this study suggest that the source of this high T_{int} possibly arises from low ammonia water from cross connected sewers (CCSs) which occur in the catchment. The Ouseburn is recognised by the Environment Agency as having significant problems with continuously discharging storm sewers which appear to be cross-connected and release water of poor quality into the river. The results raise an interesting question in relation to the use of the use of ammonia as a chemical water quality determinant in an urban river context, given the difference between the ammonia and T_{int} . Ammonia is highest in winter during periods of frost and snow cover, suggesting a non-sewerage source, yet this procedure is failing to detect summer sewerage inputs due to the latter having a largely low nitrogen source.

Two sewage pollution events observed on the Ouseburn, NE England agree with previous research in the region that a high T_{int} and $T_{\text{int}}/F_{\text{int}}$ can fingerprint sewage. Individual sewage pollution events have differences in T_{int} , F_{int} and TOC due to variations in wastewater quality. In this study, we further demonstrate that there is strong ammonia– T_{int} relationship within the pollution events where 85% of the variation in ammonia can be explained by measuring $T_{\text{int}}/F_{\text{int}}$. This is important given the potential to use fluorescence spectrophotometry, together with fibre-optic technology, as an on-line water quality tool. The potential for the use of optodes for water quality monitoring is increasing (Buffle and Horvai, 2000; Glud et al., 2000), and the simplest automatic monitoring would be permanent or mobile fluorescence spectrophotometers with a fibre optic extension that could collect fluorescence EEM data automatically. Further research is necessary, especially given that at the catchment scale we have also demonstrated the presence of high T_{int} –low ammonia inputs from the sewerage system. However, monitoring of fluorescence intensity of the T_{int} and F_{int} centres and calibration against ammonia for known point source sewerage related (CSO, STW) pollutants could permit real-time monitoring of this variable.

Faulkner et al. (2000) demonstrate that evidence gleaned from chemical sampling in an urban catchment affected by diffuse pollution is affected by the choice of sample site and timing of sampling. Our results provide further evidence of the difficulties in limitations of using chemical water quality determinants in an urban catchment. However, regular sampling of river fluorescence properties has provided useful information as to the water quality of our study river. Further research is undoubtedly needed, including automatic monitoring, to compare the relationship between observed fluorescence properties and other chemical water quality determinants such as dissolved oxygen and BOD in rivers and chemical analyses of waste waters, and to

replicate our study in both similarly impacted and contrasting river systems. This is the focus of current research. On a practical level, our results suggests that best management practice, such as source control (soakaways), housekeeping practices (correct connections) and treatment controls (retention ponds), as incorporated within the concept of sustainable urban drainage (D'Arcy and Frost, 2001), could be beneficial.

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