Chemical Pollution - S&TC Riverfly Census monitoring and the WFD Watch List

A case study from the River Wensum, Norfolk

Key recommendations:

- Current regulatory procedures are failing to provide sufficient protection to freshwater ecosystems
- SPEAR should be officially integrated into existing WFD invertebrate monitoring
- Focus should be made on determining chronic and mixture effects in more invertebrate species
- Regulatory biological and chemical sampling should no longer be conducted in isolation of each other
- More effort should be put into in-river monitoring downstream of effluent discharges, particularly from a chemical perspective

Introduction

Rivers are net receivers of chemical stressors from anthropogenic origins. The composition of chemical inputs differs according to prevailing land uses around river catchments. Extensive agriculture, industrial activities and human conurbations all contribute different chemical mixtures to watercourses (Sabater *et al.*, 2016).

Chemical pollution is one of the main causes of degradation and biodiversity loss in aquatic ecosystems (Vörösmarty *et al.*, 2010). The direct measurement of stressors like chemicals is often resource demanding and point measurements are inadequate for assessing time-varying stressors. Macroinvertebrates have been used as bioindicators of river health for decades. Different invertebrate taxa have different ecological requirements (niches), so by knowing the habitat requirements of taxa, environmental conditions that lead to the observed community composition at given sites can be inferred (Schuwirth, Kattwinkel and Stamm, 2015)

Current monitoring of priority substance-based chemical status according to the Water Framework Directive (WFD) covers only a tiny fraction of toxic risks, extensively ignores mixture effects and lacks incentives and guidance for abatement. While European water bodies are contaminated with complex mixtures of ten thousands of chemicals, chemical status is defined on the basis of 45 substances with little insight into links between chemicals and ecosystem effects (Brack *et al.*, 2018). Effect-based biological indicators are a powerful tool for identifying pressure from contaminants. The invertebrate-based indicator SPEAR (SPEcies At Risk) uses trait information to identify chemical pressure and ecological effects in rivers (Knillmann *et al.*, 2018). SPEAR is the only method available at present that can link degradation of biology at a site to chemical exposure and give an indication of the level of contamination (Schriever *et al*. 2008).

Beketov *et al.*, 2009 defined WFD class boundaries for SPEAR, showing how the metric could contribute to the assessment of the ecological status of water bodies and integrate into existing WFD monitoring programmes. The existing SPEAR indicator is based on species-level data. Much of the macroinvertebrate data collected by the Environment Agency is at family level. However, a comparison of SPEAR indices based on species and family levels of taxonomic identification using data sets from other European regions revealed the family-level index is still effective (Beketov *et al*. 2008).

Recommendations have been made by the Environment Agency to validate the SPEAR approach in the UK through field investigations. SPEAR validation has been undertaken by scientists in a variety of countries already, including France and Finland (Schäfer *et al.*, 2007). This case study was created to demonstrate the value of using invertebrates to better understand chemical pressures on UK waters. SPEAR values derived from Salmon & Trout Conservation (S&TC) Riverfly Census species-level monitoring and chemical spot samples from WFD Watch List monitoring on the River Wensum are examined and recommendations to improve management and understanding of chemical pollution provided.

Method

Biological data (S&TC) -

Riverfly Census monitoring entailed three years of independently collected and analysed species-level invertebrate data (all sampling and analysis completed by Aquascience Consultancy Ltd). The Census launched in 2015 and initially covered 12 rivers across England, with 4-6 sample sites per river.

Invertebrates were collected in spring and autumn using the 3 minute kick-sweep sampling technique adhering to Environment Agency guidelines. Invertebrate samples were preserved in alcohol to be later identified to species-level under a microscope in a laboratory. The species found were inputted into a biometric calculator to obtain scores for various stress metrics for each sample site per season. To assess for chemical signatures on the invertebrate communities, the SPEAR biometric was calculated. SPEAR values were plotted and assessed using the WFD boundaries described by (Beketov *et al.*, 2009).

Chemical data (Watch List) -

Chemical data was obtained from the 2016 Water Framework Directive Chemical Watch List, via the Eionet website. The only river with substantial EU chemical data for comparative purposes out of the S&TC Riverfly Census rivers was the River Wensum, in Norfolk, England.

The chemical monitoring site used for Watch List monitoring on the River Wensum is called Sweetbriar Bridge. This site is directly downstream of all Riverfly Census sample points, but above the main urban input of Norwich. Therefore, it can be assumed that the Sweetbriar Bridge site will be representative of cumulative, mostly agricultural, chemical inputs occurring upstream (Fig. 1).

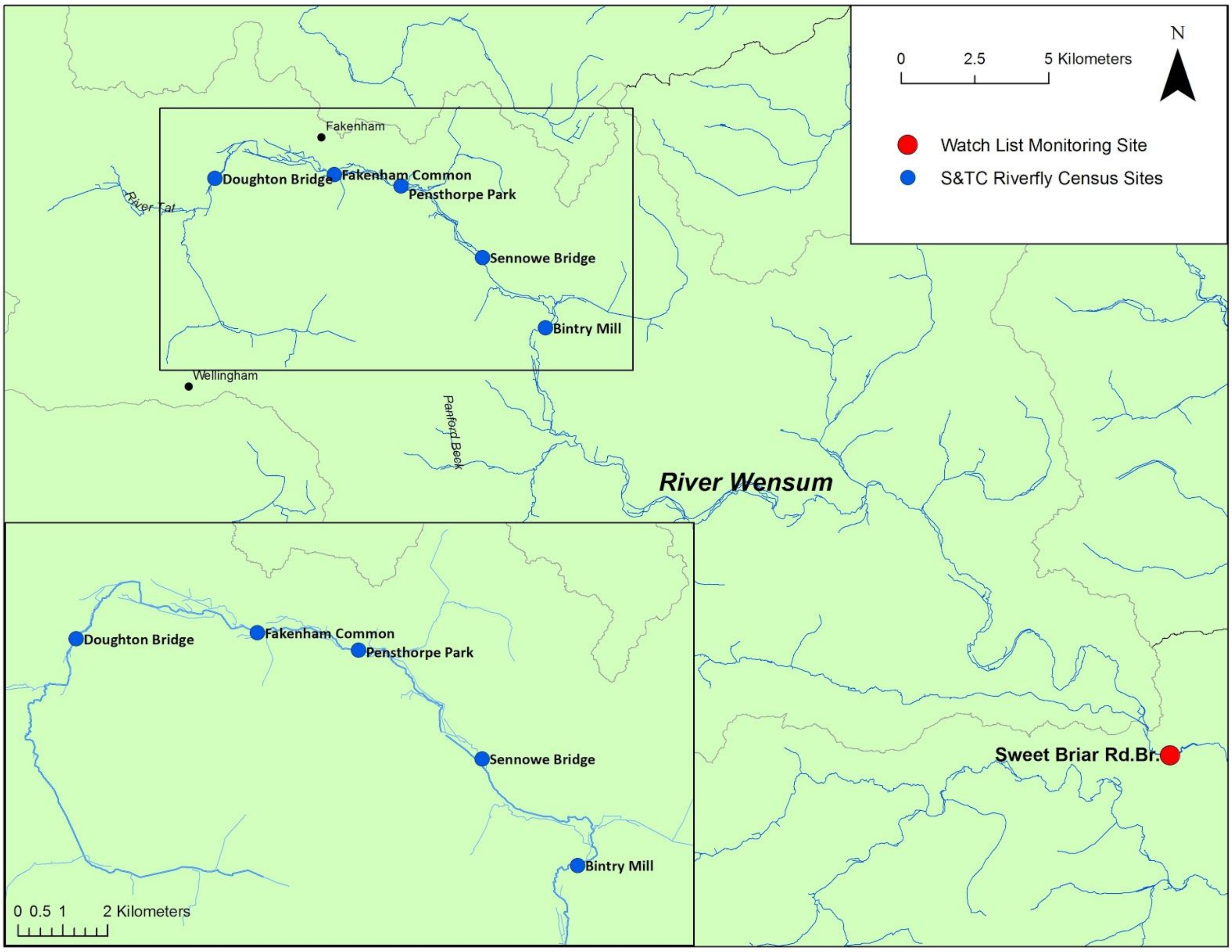


Fig. 1 - Location of S&TC Riverfly Census monitoring sites and Sweetbriar Bridge Watch List Chemical Monitoring Site on the River Wensum

Toxicant concentrations were plotted with boundary lines at the levels known to cause acute and chronic harm to river invertebrates. Where this was not possible Environmental Quality Standard (EQS [freshwater]) values were used.

Maps were created using ArcMap (Version 10.6.1) and graphs/statistics in RStudio (Version 1.1.383).

Results

SPEAR outputs:

Mean values of SPEAR from 2015-2017 on 12 rivers across England revealed that there was substantial failure across S&TC Riverfly Census sample sites in autumn (46%), when compared to the WFD standard recommended by Beketov *et al.*, 2009 (Fig. 2).

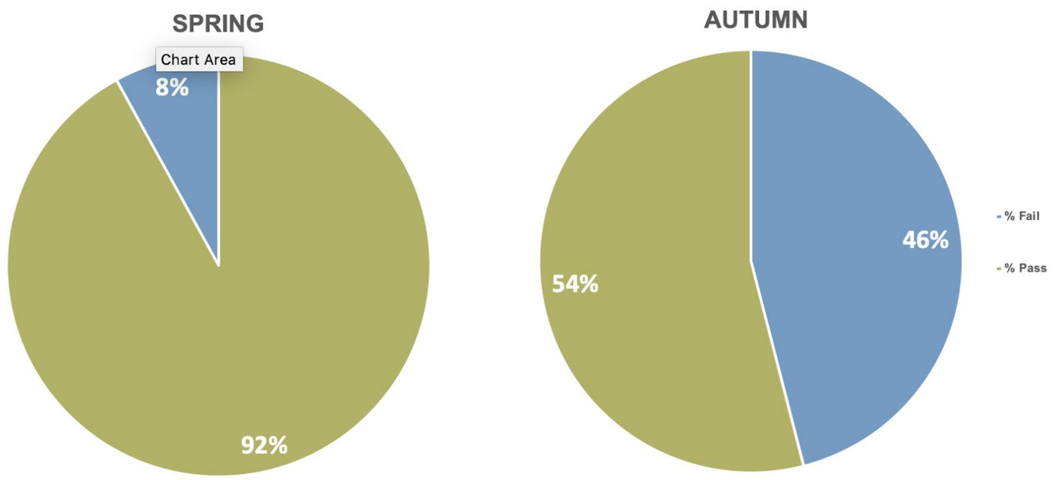


Fig. 2 - Pie charts demonstrating percentage SPEAR compliance in spring and autumn to proposed WFD pass standard across S&TC sample rivers (Mean SPEAR calculated per sample site, by season, from 12 rivers, 2015-2017)

Out of all the Riverfly Census monitoring sites, Pensthorpe Nature Park had the lowest SPEAR values and therefore exhibited the greatest chemical impact. At Pensthorpe, SPEAR values were lowest in spring 2015 and autumn 2016 (9.07 and 8.72 respectively)(Table 1).

Mean SPEAR values were calculated by season for each of the River Wensum monitoring sites, covering the sample period 2015-2017. Mean values ranged from 14.88 - 34.61 (spring) and 12.62 - 33.35 (autumn)(Table 1).

Only one site (Sennowe Bridge) passed the WFD standard in Autumn. Spring SPEAR scores were more variable than Autumn, the lowest spring SPEAR scores occurred at Pensthorpe Nature Park and Fakenham Common (9.07 and 15.70 respectively), which both failed WFD for two of the three years surveyed (Table 1 and Fig.3).

Table 1 - SPEAR values from S&TC Riverfly Census monitoring on the River Wensum 2015-2017 and three year mean values. Failure against proposed WFD standard highlighted in pink.

SPRING

	2015	2016	2017	Mean	95% CI
Bintry Mill	40.62	49.63	61.13	50.46	25.54
Sennowe Bridge	46.30	57.98	49.83	51.37	14.88
Pensthorpe Nature Park	9.07	25.06	36.83	23.65	34.61
Fakenham Common	22.47	42.14	15.70	26.77	34.12
Doughton Bridge	34.29	48.06	53.96	45.44	25.07

AUTUMN

	2015	2016	2017	Mean	95% CI
Bintry Mill	22.46	19.50	29.64	23.87	12.95
Sennowe Bridge	39.11	34.83	26.10	33.35	16.47
Pensthorpe Nature Park	16.55	8.72	12.59	12.62	9.73
Fakenham Common	23.63	25.54	23.17	24.11	3.12
Doughton Bridge	21.74	13.38	16.54	17.22	10.49

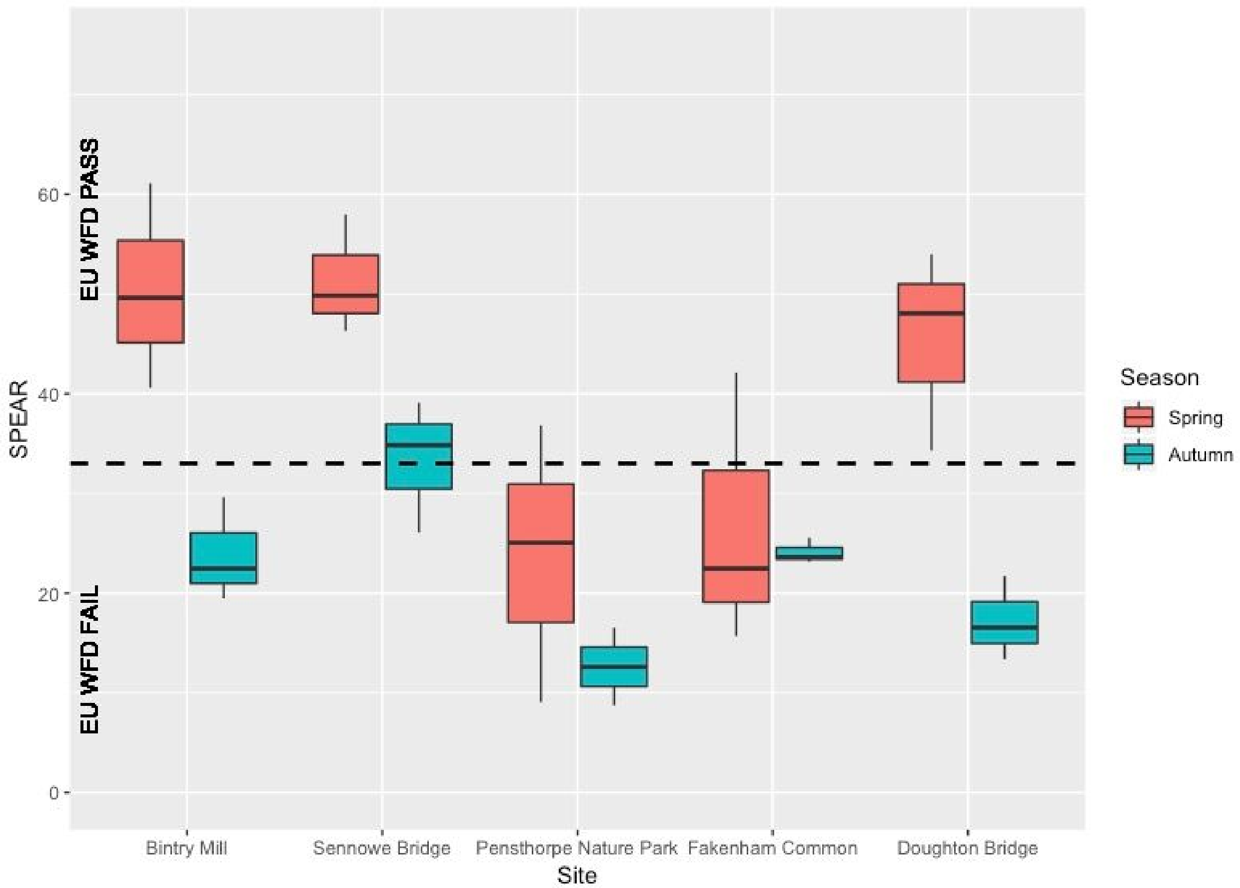


Fig. 3 - SPEAR compliance to proposed WFD standards at River Wensum S&TC Riverfly Census monitoring sites (2015-2017)

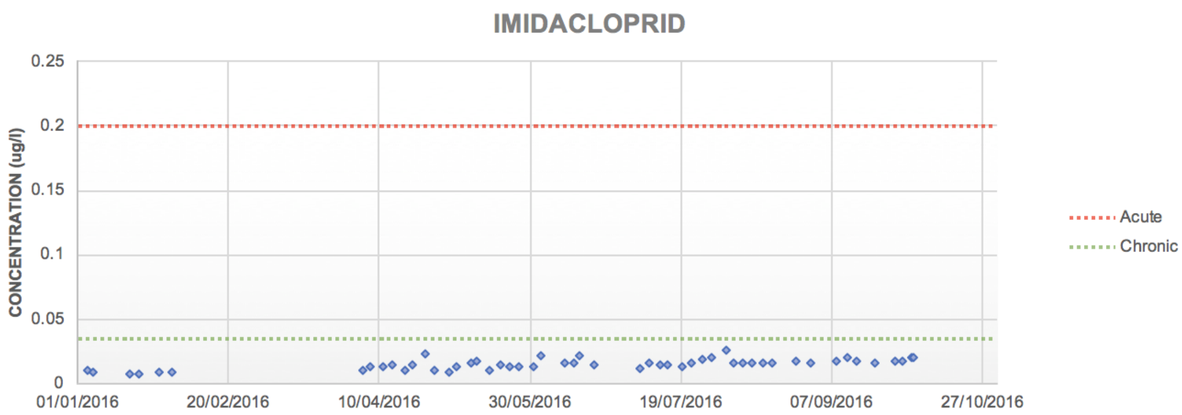
Watch List outputs:

Concentrations of toxicants were obtained from the River Wensum Watch List 2016 dataset, the chemicals evaluated included three neonicotinoids (imidacloprid, clothianidin and thiamethoxam), diclofenac (a nonsteroidal anti-inflammatory drug used as a painkiller) and clarithromycin (an antibiotic).

Neonicotinoids:

Concentration boundaries were plotted to represent recent recommendations by (Morrissey *et al.*, 2015). Neonicotinoid surface water concentrations of 0.2 µg/l (short-term acute) and 0.035 µg/l (long-term chronic) were proposed to avoid lasting effects on aquatic invertebrate communities.

None of the samples breached the acute, lethal boundary for neonicotinoids. Imidacloprid levels were the most stable out of the three neonicotinoids examined, with no large peaks present over the sample period. The highest imidacloprid concentration detected was 0.026 µg/l on 03/08/16 and the annual mean was 0.015 µg/l (±0.0012). All imidacloprid concentrations were below the chronic boundary line indicating minimal sublethal effects on the invertebrate community. In contrast, there was a much lower background concentration of thiamethoxam than imidacloprid, annual mean 0.0085 µg/l (±0.005). However, concentrations breaching the chronic boundary line were present from the end of May to early July, the highest concentration recorded was 0.065 µg/l on 15/06/16. Clothianidin had multiple peak concentration events during January, April and June. In January, clothianidin levels over double the chronic level recommended for mayflies were recorded (0.11 µg/l on 06/01/16) (Fig. 4).



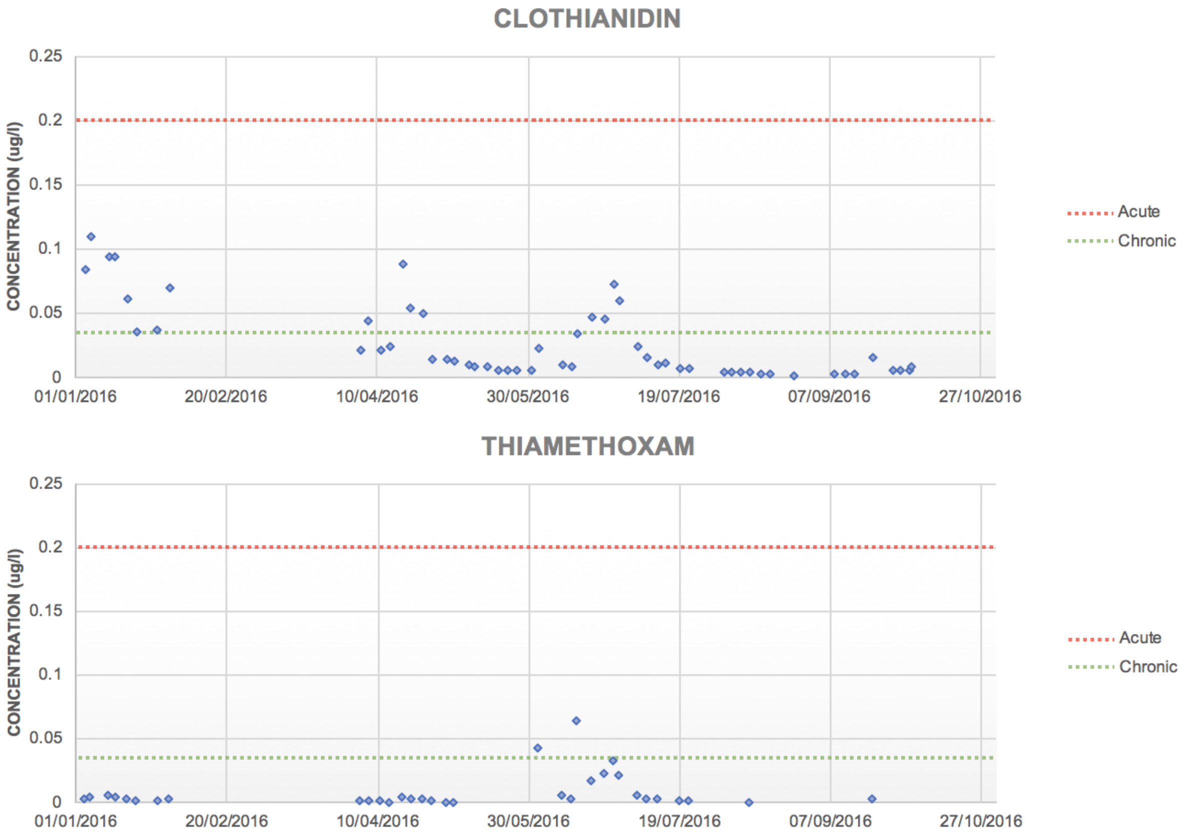


Fig. 4 - Concentrations of three neonicotinoids (imidacloprid, clothianidin and thiamethoxam) from 2016 Watch List chemical monitoring on the River Wensum at Sweetbriar Bridge

Diclofenac:

Diclofenac is an anti-inflammatory drug used in human and veterinary medicine. Chronic and acute toxicity values of diclofenac were not available for riverflies. The 48h EC50 for *Daphnia magna* was found to be 68 mg/l (Cleuvers, 2003). However, for some chemicals *D. magna* is remarkably insensitive, so may not be the best indicator of sublethal/chronic effects (Beketov and Liess, 2008). Diclofenac has an EQS [freshwater] value of 0.1 µg/l, so this concentration boundary was used for comparison (Fig. 5).

All diclofenac concentrations recorded were below the EQS value. Peaks of diclofenac occurred in April and May, the highest concentration detected was 0.076 µg/l on 03/05/16. The annual mean concentration was 0.013 µg/l (±0.004).

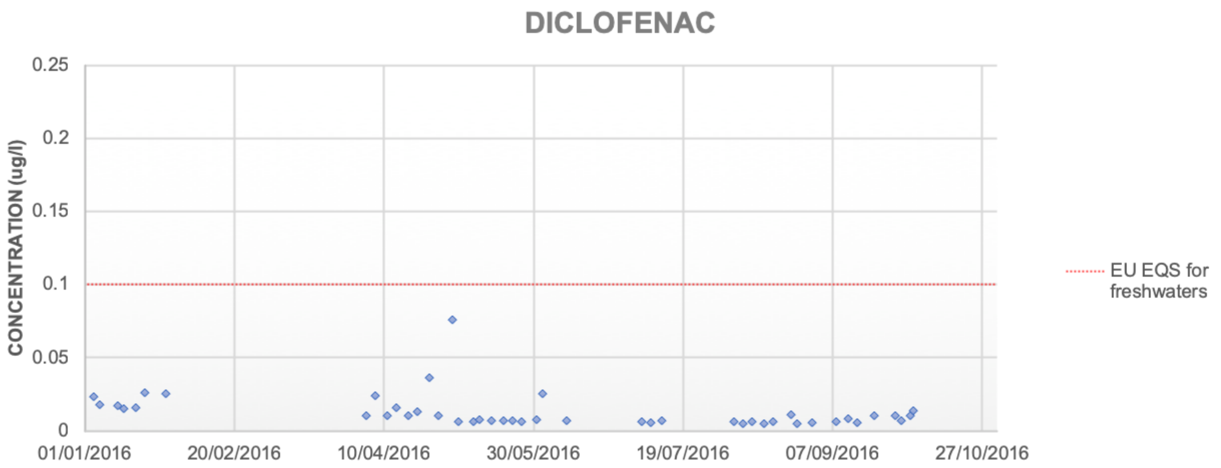


Fig. 5 - Concentrations of diclofenac from 2016 Watch List chemical monitoring on the River Wensum at Sweetbriar Bridge

Clarithromycin:

Clarithromycin is a human macrolide antibiotic. Up to 40% of consumed clarithromycin is excreted unchanged as the parent compound and about 60% is excreted metabolised and transferred to waterbodies through wastewater discharges (Baumann *et al.*, 2015). Very little information was available on chronic effects of clarithromycin on invertebrates. Currently the Annual Average Quality Standard for freshwaters (AA-QS [freshwater, eco]) is 0.13 µg/l, which was plotted for context (Fig. 6).

The annual mean concentration of clarithromycin during the sample period was 0.013 µg/l (± 0.001). No concentrations were detected above the AA-QS level, the highest concentration detected was 0.033 µg/l on 25/04/16.

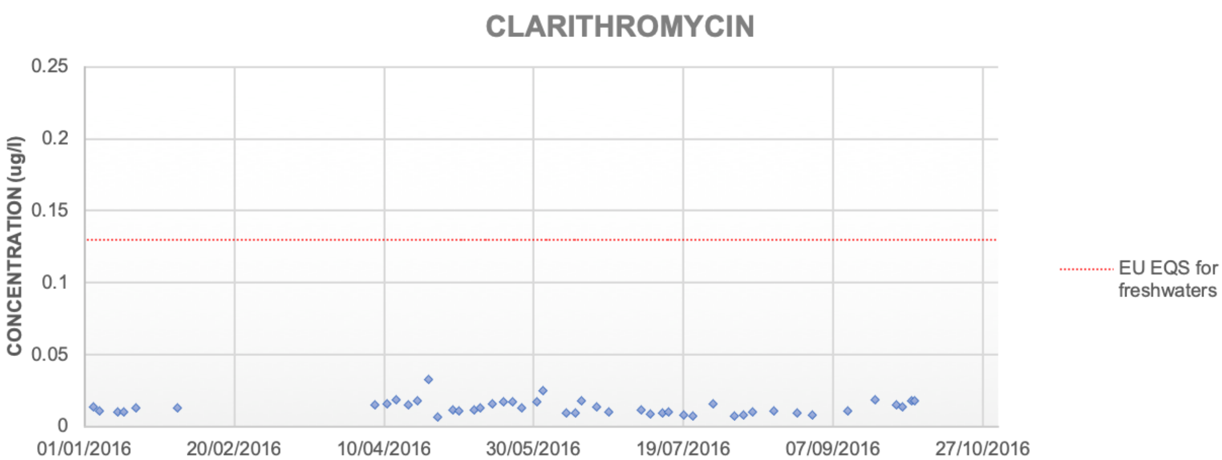


Fig. 6 - Concentrations of clarithromycin from 2016 Watch List chemical monitoring on the River Wensum at Sweetbriar Bridge

Discussion

In the European Commission draft guidance, pesticides are classified into sub-categories depending on when they are used. Imidacloprid is classified in the spring/summer category, whereas thiamethoxam and clothianidin are classified summer/autumn (Buglife, 2017). The peak of thiamethoxam in June-July 2016 reflects this, but clothianidin showed high concentration peaks in winter and spring as well as summer. The primary use of Clothianidin is on cereals and in 2016 there was still wide application across the British countryside. Cereal farming comprised 29% of farms in the catchment according to agricultural census data presented by Natural England (2015)(Fig. 7).

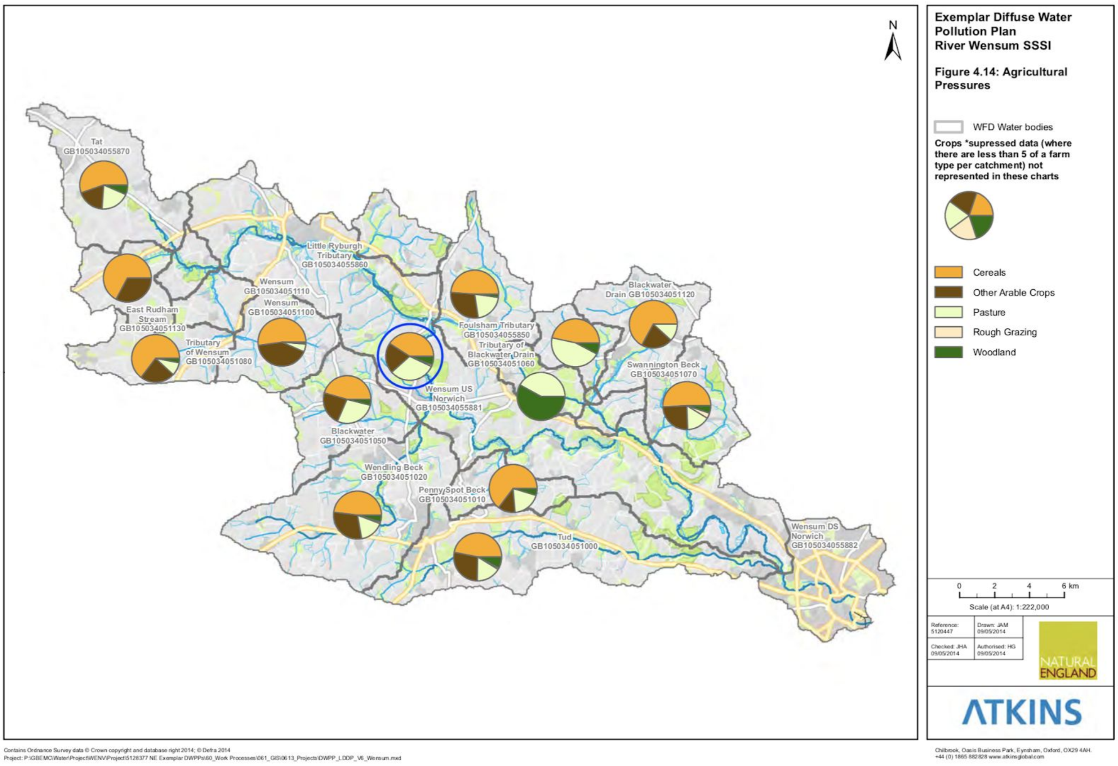


Fig. 7 - Agricultural pressures in the River Wensum catchment. Closest main river site to Sweetbriar Bridge WFD Watch List monitoring site highlighted in blue circle (Natural England, 2015)

Cereal farming dominated, especially in the upper catchment, but livestock farming was still prevalent particularly in the area surrounding the Sweetbriar Bridge chemical monitoring site (Fig. 7). Diclofenac and clarithromycin had spring concentration peaks during April/May 2016 which potentially could have been a result of livestock treatments. However, despite the upper Wensum being mainly agricultural, pharmaceutical loading from human wastewater cannot be completely excluded. According to Natural England (2015), 25% of the Wensum catchment population on private sewerage are found at the US Norwich site, just upstream of Sweetbriar Bridge (Table 2).

Table 2 - Estimate of population not connected to mains sewerage in the River Wensum catchment

Waterbody ID	Name	Properties not on mains sewerage	Population Equivalent	Population Equivalent %
GB105034051000	Tud	407	936	22%
GB105034051010	Penny Spot Beck	57	131	3%
GB105034051020	Wendling Beck	237	545	13%
GB105034051030	Blackwater Drain	0	0	0%
GB105034051040	Blackwater Drain	45	104	2%
GB105034051050	Blackwater	49	113	3%
GB105034051060	Tributary of Blackwater Drain	17	39	1%
GB105034051070	Swannington Beck	152	350	8%
GB105034051080	Tributary of Wensum	26	60	1%
GB105034051090	Tributary of Blackwater Drain	90	207	5%
GB105034051100	Wensum	45	104	2%
GB105034051110	Wensum	19	44	1%
GB105034051120	Blackwater Drain	70	161	4%
GB105034051130	East Rudham Stream	15	35	1%
GB105034051140	Tat	14	32	1%
GB105034055850	Foulsham Tributary	90	207	5%
GB105034055860	Little Ryburgh Tributary	28	64	2%
GB105034055870	Tat	30	69	2%
GB105034055881	Wensum US Norwich	472	1086	25%
GB105034055882	Wensum DS Norwich	0	0	0%
Total		**1863**	**4285**	**100%**

WFD Watch List monitoring has given much needed insight into the concentrations of specific chemicals in the River Wensum. However, as demonstrated by the Riverfly Census SPEAR results, despite described chemicals in this report being within their EQS standards in 2016, invertebrate communities experienced consistent chemical pressure in the upper catchment from 2015 to 2017 (Table 1). Failures against the proposed WFD standard were widespread in both spring and autumn (Fig. 3). Beyond the Wensum example, SPEAR results also revealed that invertebrate communities in rivers across the UK are experiencing deterioration from chemical pollution (Fig. 2).

Looking at chemicals using a one by one approach has its merits for reducing lethal concentrations of specific chemicals in waterbodies. However, it does not take into account existing burdens of chemicals in organisms and the enhanced detrimental consequences resulting from mixture effects. Cleuvers (2003) stated that for a range of stream organisms, acute (lethal) effects of single substances in the aquatic environment were very unlikely, but considerable combination effects could occur. Additionally, concentrations in the water may not be reflective of the concentrations built up in organisms from previous exposures. Particularly for diclofenac, in which bioaccumulative potential has been recognised as a risk that needs better understanding (Mehinto, 2009).

To grasp impacts of toxicants at ecosystem level, it is essential that better connections are made between chemical and biological sampling regimes. Currently in the UK no overlap exists between water quality and invertebrate monitoring. In order to achieve more informative and more intuitive monitoring, biological and chemical sampling should be completed together at the same locations. Relevant site selection is also critical to assessing chemical impacts. Borgmann *et al.* (2007) examined how a mixture of seven different common pharmaceuticals would impact multiple generations of the amphipod *Hyalella azteca.* They emphasised that although the substance combination in their study did not appear to be a major concern for *H. azteca* most Canadian fresh waters, significant impacts may be observed in areas closer to effluent discharges. Currently biological and chemical monitoring in-river downstream of discharges is sparse, even though data in these areas would be invaluable for understanding and managing chemical loading from a biological perspective.

Using SPEAR in combination with chemical sampling could also help fill in time gaps. Chemical monitoring is resource demanding and continuous measuring unrealistic. Invertebrate communities represent a much longer time period as they experience continuous exposure to the water. For example, in 2016 Watch List monitoring on the Wensum did not occur for earlier parts of the year (February/March) but obtaining SPEAR values from Spring 2016 would take into account chemical exposure during this missed time period.

This report has also highlighted the need for more toxicity data from chronic studies on invertebrates to assess the environmental risk of chemical residues. Other studies have also highlighted the need for better information on ecotoxicological effects of pharmaceuticals from the organism to the ecosystem level and from the individual to the population level to derive EQS values (Acuña *et al.*, 2015). For the chemicals examined in this report, invertebrate chronic levels outside of the standard toxicity test organism *D. magna* were only found for neonicotinoids (Morrissey *et al.*, 2015). Most EQS values are set based on information from lethal studies on select organisms. Different organisms can have markedly different tolerances to the same toxicant, therefore is essential to consider a broad range of organisms when setting concentration boundaries (Beketov and Liess, 2008). Many riverfly species are particularly sensitive to water quality disturbances, therefore using these organisms more in sublethal toxicity testing seems logical (Gerhardt, Bloor and Lloyd Mills, 2011; Firmiano *et al.*, 2017).

Report compiled by Lauren Mattingley, for science enquiries contact lauren@salmon-trout.org

References

Acuña, V. et al. (2015) “Balancing the health benefits and environmental risks of pharmaceuticals: Diclofenac as an example.,” Environment international, 85, pp. 327–333.
Baumann, M. et al. (2015) “Aquatic toxicity of the macrolide antibiotic clarithromycin and its metabolites,” Chemosphere, 120, pp. 192–198.
Beketov, M. A. et al. (2009) “SPEAR indicates pesticide effects in streams–comparative use of species-and family-level biomonitoring data,” Environmental Pollution, 157(6), pp. 1841–1848.
Beketov, M. A. and Liess, M. (2008) “Potential of 11 pesticides to initiate downstream drift of stream macroinvertebrates.,” Archives of environmental contamination and toxicology, 55(2), pp. 247–253.
Beketov, M. et al. (2008) “Freshwater Biological Indicators of Pesticide Contamination – An Adaptation of the SPEAR Approach for the UK. Science Report – SC030189/SR4”, Environment Agency, Bristol, UK
Borgmann, U. et al. (2007) “Effect of a mixture of seven pharmaceuticals on Hyalella azteca over multiple generations,” Chemosphere, 66(7), pp. 1278–1283.
Brack, W. et al. (2018) “Towards a holistic and solution-oriented monitoring of chemical status of European water bodies: how to support the EU strategy for a non-toxic environment?,” Environmental Sciences Europe, 30(33).
Buglife, Shardlow M. (2017) “Neonicotinoid Insecticides in British Freshwaters: 2016 Water Framework Directive Watch List Monitoring Results and Recommendations.”
Cleuvers, M. (2003) “Aquatic ecotoxicity of pharmaceuticals including the assessment of combination effects,” Toxicology letters, 142(3), pp. 185–194.
Firmiano, K. R. et al. (2017) “Mayfly bioindicator thresholds for several anthropogenic disturbances in neotropical savanna streams,” Ecological indicators, 74, pp. 276–284.
Gerhardt, A., Bloor, M. and Lloyd Mills, C. (2011) “Gammarus: important taxon in freshwater and marine changing environments,” International Journal of Zoology, 2011(524276).
Knillmann, S. et al. (2018) “Indication of pesticide effects and recolonization in streams,” 630, pp. 1619–1627.
Mehinto, AC. (2009) “Impacts of the human pharmaceutical diclofenac in the aquatic environment”, Doctor of Philosophy in Biological Sciences, University of Exeter, UK.
Morrissey, CA. et al. (2015) “Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review,” Environment international, 74, pp. 291–303.
Natural England (2015) “River Wensum SSSI - Exemplar Diffuse Water Pollution Plan and Action Plan. Improvement Programme for England’s Natura 2000 Sites (IPENS) – Planning for the Future.” IPENS001a.
Sabater, S. et al. (2016) “Shared effects of organic microcontaminants and environmental stressors on biofilms and invertebrates in impaired rivers.” Environmental pollution (Barking, Essex: 1987), 210, pp. 303–314.
Schäfer, R. et al. (2007) “Effects of pesticides on community structure and ecosystem functions in agricultural streams of three biogeographical regions in Europe,” Science of The Total Environment, 382(2–3), pp. 272–285.
Schriever, CA. et al. (2008) “Freshwater Biological Indicators of Pesticide Contamination.” Science Report. SC030189/SR3. Environment Agency, UK.
Schuwirth, N., Kattwinkel, M. and Stamm, C. (2015) “How stressor specific are trait-based ecological indices for ecosystem management?” 505, pp. 565–572.
Vörösmarty, C. J. et al. (2010) “Global threats to human water security and river biodiversity.” Nature, 467(7315), pp. 555–561.