



Neonicotinoid Insecticides in British Freshwaters

2016 Water Framework Directive Watch List Monitoring Results and Recommendations

14th December 2017 Matt Shardlow

Saving the small things that run the planet

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Summary

- 1. Aquatic invertebrate populations represent an important part of the UK's biodiversity, they provide valuable ecosystem services, recycling organic matter and keeping rivers clean. In addition they provide essential food for fish and birds.
- 2. Neonicotinoids are widely used insecticides with three main applications in the UK, firstly as a seed coating for field crops, secondly as sprays for crops and domestic gardens, and thirdly as an externally applied arthropod parasite treatment for pets.
- 3. Neonicotinoids are water soluble, mobile and can persist for months or years; as a result they have been found polluting waterbodies around the world.
- 4. Mayflies, caddisflies, flies and beetles tend to be most sensitive to neonicotinoid pollution. In laboratory tests half of mayflies and caddisflies died when exposed to concentrations in the range 0.1–0.3 μg/L; at just 0.03 μg/L 10% of mayflies died. Sub-lethal effects on invertebrates have also been detected, including, changes in feeding rates, mobility, predation rates, reduced growth and reduced emergence at levels between 0.3 and 1.5 μg/L.
- 5. In field studies a reduced abundance of aquatic insects is apparent when Imidacloprid concentrations in water are above 1 or 2 μ g/L, and large scale surveys in the Netherlands revealed sharp declines in aquatic invertebrate abundance between 0.013 and 0.067 μ g/L, while 0.02 μ g/L led to a 30% fall in bird numbers over ten years.
- 6. The recommended ecological thresholds for neonicotinoid water concentrations are 0.2 μg/L - short-term acute - and 0.035 μg/L - long-term chronic; above these levels aquatic ecology can be expected to be significantly damaged.
- 7. Under the EU Water Framework Directive substances on a Watch List are being monitored, the list includes five neonicotinoid insecticides.
- 8. Twenty-three sites were sampled in 2016 in the UK 16 in England, four in Scotland, three in Wales and three in Northern Ireland by the Environment Agency, SEPA, NRW and NIEA. Sites were selected to provide a range of catchment scenarios, including some reference sites that should have been free of pollution. The Northern Ireland data has yet to be released to the public. Data was accessed via the Eionet website in November 2017.
- 9. 74% of sites monitored were contaminated with neonicotinoids, eight rivers exceeded the chronic pollution limit and two exceeded the acute pollution limit. The rivers exceeding their limits were all in England with a cluster in Eastern England. More Clothianidin was detected than any other neonicotinoid.
- 10. The River Waveney was the most heavily polluted river in this sample, exceeding the average annual chronic pollution limit, it also exceeded the acute pollution level for over a month, peaking at 1.03 μg/L. This would undoubtedly have impacted significantly on the insect life of the river. Worryingly the Waveney and another chronically polluted river, the Wensum, supply water to the Norfolk Broads, an internationally important wetland that supports many endangered aquatic species. The high Thiamethoxam readings indicate that the probable source of pollution in these rivers was Sugar beet fields.

- 11. Fairly low levels of Thiamethoxam were detected in the River Ouse in Bedfordshire, higher levels would have been predicted due to common use in the catchment of the insecticide on Oilseed rape prior to the partial ban in 2013. This gives hope that after neonicotinoids are banned the recovery of chemical quality status might happen within a few years.
- 12. The River Tame recorded the greatest exceedances of pollution limits, 12.7 times higher than the chronic pollution level, however there were only two sample dates. There is no arable farming in the catchment. This would appear to be the result of a pollution event involving Clothianidin (and/or Thiamethoxam?) in September.
- 13. Imidacloprid was detected in a number of arable catchments despite it having very little use on arable fields in 2016 or the preceding few years. However, Imidacloprid was recorded at surprising levels on a number of urban rivers where it was responsible for three the Tame, Wyke and Somerhill Stream exceeding their chronic pollution limits. While potted plants maybe a factor, veterinary pour-ons and flea collars are implicated as the most likely source of pollution.
- 14. Imidacloprid was detected in the Allt an Dubh Loch, a remote stream in the Cairngorms, above Loch Muick, as a reference site none of the 'Watch List' substances were supposed to occur there. Imidacloprid was detected on one of the two dates monitored. There is no upstream agriculture or forestry so the most likely source of this pollution is a dog or other treated animal entering the stream.
- 15. Contamination levels of Acetamiprid and Thiacloprid were reassuringly low, however neither of these latter neonicotinoids insecticides have been as widely used as Clothianidin or Thiamethoxam, and the waterbodies selected do not represent areas where they are most commonly used.
- 16. The Water Framework Directive Watch List monitoring has been very successful in relation to neonicotinoids in the UK. In England particularly, where more sites were included and more sample dates undertaken, the monitoring has presented an informative snap-shot of the pattern of neonicotinoid pollution.
- 17. It is clear from the data that neonicotinoid pollution is a significant problem in Britain and that unacceptable harm to the environment has doubtlessly been done. Unless measures are put in place this harm is likely to continue and potentially worsen.

18. Six recommendations are made -

- Monitoring of these five neonicotinoids should be continued, regardless
 of their future Watch List status, and the number of sites and sample
 dates expanded. In particular more rivers should be included that are a)
 at risk of, or in probability are already, being impacted by arable
 insecticides and veterinary medicines, and b) representative of areas
 with greenhouses, extensive orchards, soft fruit production and
 commercial forestry.
- 2. A comprehensive EU wide ban on the agricultural use of Imidacloprid, Clothianidin and Thiamethoxam should be introduced due to the unacceptable harm they are causing to the aquatic environment; this

- ban should include greenhouse uses. There is no obvious alternative way to reduce or mitigate their impact on aquatic life.
- 3. Urgent action is required to reduce Imidacloprid pollution in water bodies and return them to a good chemical condition:
 - a) The use of Imidacloprid as an externally applied veterinary medicine should be suspended in the UK - this is the measure most likely to rapidly reduce chronic pollution levels.
 - b) A thorough review of the use of ectoparasite treatments, including a full risk assessment in relation to the aquatic environment, must be urgently undertaken. The report should make recommendations that address all risks of environmental harm. Currently ectoparasite medicines do not even come with a warning to pet owners indicating that they should keep treated animals out of streams, rivers, ponds and lakes.
 - c) If it becomes apparent that chronic pollution of aquatic habitats by ectoparasite treatments is originating via storm drains and/or waste water treatment works outflows then mitigation measures may not be feasible and permanent bans may be required.
- 4. The Environment Agency should develop a clear regulatory approach to responding to neonicotinoid pollution This should include:
 - Adopting and applying formal EQS standards based on a rational assessment of risk, considering the wealth of evidence relating to Imidacloprid and the likely comparable toxicity of the other neonicotinoids.
 - b) A clearly communicated approach to investigating and resolving neonicotinoid pollution events identified by monitoring.
- 5. The apparent pollution incident on the River Tame should be investigated and potential sources examined. Monitoring on this river should be stepped up to become at least fortnightly so that any future incidents can be detected.
- 6. Defra should establish an initiative to transform insecticide environmental risk management so as to ensure future generations have a better protected environment, in line with the Defra Chief Scientist's recent call for improved "pesticidovigilance". This should include:
 - a) Formal engagement between the Environment Agency, SEPA, NRW, Chemicals Regulation Directorate and Veterinary Medicines Directorate on a joint project.
 - b) The development of a new, independent, transparent and open approach that uses a more ecologically comprehensive evidence base in approving insecticide uses, monitoring environmental prevalence, researching environmental impacts, and reviewing post-approval use.

Introduction

The Watch List

The Water Framework Directive 2000 (WFD) is an EU legislative instrument that has the following key aims:

- expanding the scope of water protection to all waters, surface waters and groundwater
- achieving "good status" for all waters by a set deadline
- water management based on river basins
- "combined approach" of emission limit values and quality standards
- getting the prices right
- · getting the citizen involved more closely
- streamlining legislation

The Directive sets a general requirement for ecological protection, and a general minimum chemical standard, on all surface waters (although in practice only large waterbodies and rivers are covered). These are the two elements "good ecological status" and "good chemical status".

The WFD establishes via the 2008 Environmental Quality Standards Directive a list of 35 hazardous chemicals (priority substances) for which "Environmental Quality Standards" (EQSs) are set. The EQS is the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment. To be in good condition water bodies must not exceed the EQSs. The setting of EQSs is tailored to the risks associated with individual chemicals, and follows guidance established by the European Commission (2011). As a general rule data on the lethality of chemicals (LC50s) and the concentrations at which there is no observable effect to a range of organisms are considered and safety factors applied to account for uncertainties, unforeseen sub-lethal effects and the variability in susceptibility likely to occur in untested organisms. For freshwater EQSs a factor of 10 safety margin is usually applied for substances where there is good evidence establishing the no observable effect concentration.

In addition to the priority substances the above legislation also allows for the designation of 10 additional chemicals (or groups of chemicals) as Watch List substances. These are substances that could be hazardous and about which there is environmental concern. A list of 17 chemicals was established as the first Watch List in March 2015. To understand if the selected chemicals pose a risk each Member State must monitor at least once annually at a minimum number of monitoring sites. Substances can only be on the list for four years, after which they are either dropped or prioritised for inclusion as a priority substance.

The first Watch List contains neonicotinoids as a category substance, with all five commonly used neonicotinoids listed to be monitored – Imidacloprid, Clothianidin, Thiamethoxam, Acetamiprid and Thiacloprid.

Monitoring for the first year of the Watch List substances was due to commence six months after the list was established (i.e. 20th September 2015), and completed within one year (i.e. before 20th September 2016).

Results from the UK were reported to the Commission by 20th December 2016, fulfilling the UK's legal obligations.

Use of Neonicotinoids in Britain

Neonicotinoids are used as insecticides. There are three main applications, firstly as a seed coating for field crops, secondly as a spray for crops and domestic gardens, and thirdly as an externally applied arthropod parasite treatment for animals.

Seed treatments

Imidacloprid was the first neonicotinoid used as a seed treatment. In 2006 it was used on 718,509 ha of crops (16.5% of arable land), but from 2006 was replaced by two newer neonicotinoids Clothianidin and Thiamethoxam. In 2014 these two treatments were used on 1,421,408 ha of crops (33.4% of arable land). Confirmed high risks from neonicotinoid seed treatments to honeybees and wild bees (EFSA 2013a, b and c) resulted in the European Commission introducing a partial ban that prevented the use of neonicotinoid seed treatments on flowering crops and spring sown crops. In the UK the most significant effect of the partial ban on use was on Oilseed rape, which had previously been almost entirely treated, hence between 2014 and 2016 there was a drop in the area of crops treated with both Clothianidin and Thiamethoxam, however Clothianidin is commonly used on cereals so in 2016 was still widely applied in the British countryside. On the other hand, Thiamethoxam was a much less commonly applied seed treatment than in the preceding years and was used on 29,645 ha of Sugar beet and 2,197 ha of Oilseed rape (OSR) – planted under a derogation to the EU ban permitted by the UK Government. It should be noted that the area of Sugar beet treated with neonicotinoids reported in the Fera PUSSTATS (Garthwaite et al. 2003-2017) is thought to be an underestimate as it is routinely stated that the whole UK crop is treated with neonicotinoid seed treatments; the 2015/16 report of the British Beet Research Organisation indicated that over 98.5% of the crop was treated (BBRO 2016). The discrepancy is likely to be due to farmers being unaware what the seeds were treated with when planted by contractors.

Seed treatments are also used on outdoor vegetable crops, 12 ha with Imidacloprid (lettuces) and 1,497 with Thiamethoxam (lettuces, swedes and turnips) in 2015 (Garthwaite et al. 2016a).

Sprays

Acetamiprid and Thiacloprid are used as sprays on a range of crops, particularly vegetables and fruit crops, they are also widely sold in hand held spray bottles for domestic use. On outdoor vegetable crops in 2015 3,166 ha were sprayed with Acetamiprid and 28,114 with Thiacloprid (brassicas, peas and beans and carrots, parsnips and celery) (Garthwaite et al. 2016a). Thiacloprid was the most commonly used insecticide spray on orchards in 2016 - 15,007 ha, Acetamiprid was used on 1,800 ha (Garthwaite et al. 2017b). Thiacloprid was sprayed on 5,586 ha of soft fruit in 2014, and an amateur licenced Imidacloprid spray was also used for spot treatment on a small area, the product was withdrawn by the following year (Garthwaite et al 2015). Thiacloprid was used on 297 ha of protected greenhouse food crops in 2015, and Acetamiprid was used on 187 ha (Garthwaite et al. 2016b). Thiamethoxam is used as a spray on potatoes and fruit crops, but not very commonly, 2,200 ha on potatoes in 2016. There is no data on prevalence of garden use.

Figure 1 - Thiamethoxam arable crop use in UK in 2016 Fera PUSSTATS data

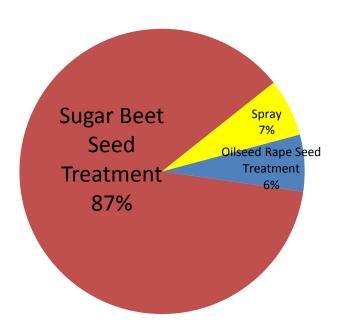
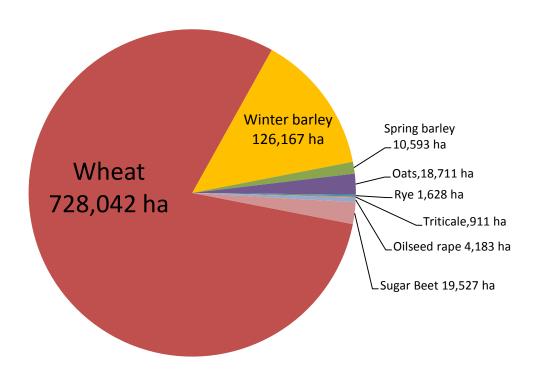


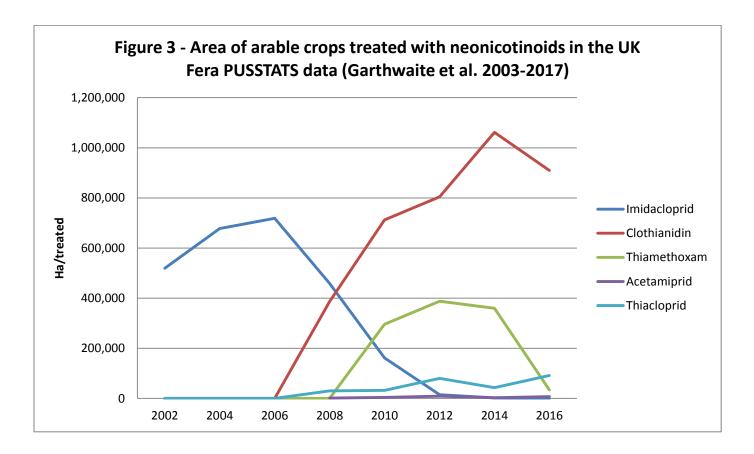
Figure 2 - Clothianidin use on UK arable crops in 2016 Fera PUSSTATS data



Imidacloprid is used as a spray on ornamental plants in greenhouses, data on prevalence of use is not collected, but a recent survey found that 70% of potted plants on sale in

garden centres in the UK were contaminated with neonicotinoids (Lentola et al 2017). While the study found Thiamethoxam, Clothianidin and Imidacloprid in the plants, some of the plants may have originated outside the UK.

Neonicotinoid sprays are also used in forestry, Acetamiprid is used outdoors, but Imidacloprid is only authorised for use in greenhouses.



Animal treatments

Imidacloprid is applied to animals to kill arthropod parasites; there are 68 registered veterinary products covering domestic pets; dogs, cats, rabbits and ferrets (Veterinary Medicines Directorate 2017). The usual form of application is a pour on solution, but impregnated collars are also available. There are two other groups of chemicals commonly used as animal applied insecticides (pyrethroids and Fipronil) and a range of other chemicals available; there is no data on the prevalence of Imidacloprid pet treatments.

Routes for Neonicotinoids to Enter Waterbodies

Neonicotinoids are water soluble and comparatively persistent, particularly in soils and sediments, hence they occur outside their application area. Persistence is generally calculated in terms of the DT50 – the time it takes for 50% of the chemical to dissipate.

Table 1. Leaching properties of various systemic insecticides (PPDB 2012) (from Bonmatin et al 2015)

Neonicotinoid	Solubility in water at 20 °C at pH 7 (mg/L)	GUS leaching potential index	Aqueous photolysis DT50 (days) at pH 7	Water-sediment DT50 (days)
Imidacloprid	610 (high)	3.76 (high)	0.2 (fast)	129 (slow)
Clothianidin	340 (moderate)	4.91 (very high)	0.1 (fast)– Stable ^a	56.4 (moderately fast)
Thiamethoxam	4,100 (high)	3.82 (high)	2.7 (moderately fast)	40 (moderately fast)
Acetamiprid	2,950 (high)	0.94 (very low)	34 (stable)	_
Thiacloprid	184 (moderate)	1.44 (low)	Stable	28 (fast)

^a USEPA (2010)

While the figures in Table 1 suggest that there are large differences between the chemicals, e.g. some stable in water and some persisting for months, it should be noted that there is limited data available on aquatic persistence and data from studies of persistence in soil suggest that a wide range of time periods may be involved depending on specific circumstances (see Table 2).

Table 2. Estimated dissipation times (DT₅₀), the time in days for neonicotinoids in soil to half breakdown, summarised from different studies (from Goulson 2013)

Imidacloprid 1250, 990–1230, 455–518, 233–366, 36–46, 34–45, 28–44.

Clothianidin 6931, 1386, 1155, 990, 693, 578, 533, 533, 495, 365, 315, 277, 239,

148, Negligible dissipation in 25 months.

Thiamethoxam 294-353, 46-301, 34-233, 7-109.

Acetamiprid 450, 388, Mean 31.

Thiacloprid >1000, 74, 3.4–27.

It should also be noted that the decay products of these insecticides can also be toxic to insect life, indeed Thiamethoxam usually first decays into Clothianidin.

When used as a seed treatment between 80-98.4% of the neonicotinoid is washed from the seed into the soil (Sur and Stork 2003) where it can accumulate and leach through soil and into water courses (Bonmatin et al. 2015).

When the treated seeds are planted the process produces a cloud of dust that which can travel for well over 100 metres (Krupke et al. 2017 and Gabriel-Forero et al.2017) contaminating more distant soil, vegetation and water bodies.

Leaching of neonicotinoids from greenhouses is a particular concern and has been associated with the highest levels of water contamination in studies in Canada (Struger et al 2017), Sweden (Kreuger et al. 2010) and the Netherlands (Tamis et al. 2016 and related sources). Pollution from greenhouses is also capable of causing groundwater contamination (Gonzalez-Pradas 2002). The flooding of greenhouses and their subsequent emptying into surface water may result in severe contamination (Blom et al. 2008).

Both runoff and soil transmission of neonicotinoids increase with precipitation levels (Kattwinkel et al. 2011). Conversely in the drier periods, lower flow in rivers has the potential to increase pesticide concentration and accumulation in sediments (Masiá et al. 2013).

In the only study on drainage from treated sugar beet fields, water immediately draining from the field contained 2.8 μ g/L of Thiamethoxam and 1.2 μ g/L of Imidacloprid (Balmer et al. 2016).

Imidacloprid applied to pets will wash off in a variety of circumstances: in rain onto whatever habitat the animal is on, which may result in the pollution of storm drains and water courses; when the animal or its bedding is washed (Jacobs et. al 2001), which may result in the pollution entering the sewage systems and storm drains and thereby watercourses; or direct pollution of a watercourse, lake or pond if the animal is allowed to swim in the waterbody. In addition some Imidacloprid is likely to be excreted by the animals in urine and faeces after absorption through the skin (Craig et. al. 2005 and Wang et al. 2017). Packaging generally recommends re-application every four weeks, but it is likely that, if not washed off, Imidacloprid would be active for a longer period (Hassen et al. 1999).

In addition to the standard pathways from uses, neonicotinoids can also be involved in pollution incidents from washing farm machinery, inappropriate disposal of insecticides (including domestic and veterinary), disposal of potted plants, flooding, industrial chemical manufacture incidents, transportation incidents, and seed treatment incidents.

Toxicity of Neonicotinoids in Water

Neonicotinoids work by binding to the nicotinic acetylcholine receptors (nAChR) in neurons, creating a continuous nerve signal and eventually destroying the nerve. As damage accumulates the organism functions less effectively until it reaches the point of death. Variability in the ability of animals to detoxify explains the different toxicity to different species, but because neurons do not readily regenerate, damage is cumulative (Rondeau et al. 2014).

The standard test organism used in the pesticide authorisation process, the water flea *Daphnia magna*, turns out to be remarkably insensitive to neonicotinoids (Beketov and Liess 2008). An acute LC50 (the concentration at which half the animals die in 48 or 96 hrs) of around 7,000 µg/L is several orders of magnitude above the levels that are similarly toxic for a number of aquatic insect groups. However, the initial assessment of the aquatic risk from neonicotinoids was therefore more optimistic than has subsequently become apparent. Another issue with assessing risk to aquatic life is that most of the studies have been done using Imidacloprid, and while the basic mode of action of the neonicotinoids is the same (blocking nerve receptors) this has allowed uncertainty in relation to the aquatic toxicity of the other four neonicotinoids considered here to hinder action.

It is now clear that neonicotinoids are very highly toxic to aquatic insects at low concentrations. The chronic LC50 for the midge *Chironomus tentans* is just 0.91 μ g/L Imidacloprid (Stoughton et al.2008). Roessink et al. (2013) examined acute and chronic toxicity of Imidacloprid to a wide range of aquatic insects and other crustaceans and found that mayflies (Ephemeroptera) and caddisflies (Trichoptera) were the most sensitive species in both acute and chronic tests, with LC50 and EC50 values in the range of 0.1 to 0.3 μ g/L. At an environmental concentration of just 0.03 μ g/L 10% of mayflies died. Even hardy water fleas can be vulnerable to Imidacloprid when exposed also to the adjuvant that is used alongside the insecticide when sprayed; Chen et al. (2010) recorded a 19% reduction in *Ceriodaphnia dubia* population at 0.3 μ g/L Imidacloprid in such conditions.



Picture 1 - Mayfly Baetis sp. © Ben Hamers

However, sublethal effects caused by neonicotinoids have become the major issue to consider for wild pollinators (for example Whitehorn et al. 2012 and Sandrock et al. 2014). It matters little if an organism can survive for 96 hrs in a laboratory, if it is then unable to successfully feed, overwinter, resist disease or reproduce. In assessing environmental harm it is necessary to consider the bigger picture of sublethal effects and their influence on population survival.

Mayflies of the genera *Baetis* and *Epeorus* showed a reduction in reproductive success when exposed to concentrations of Imidacloprid, applied as a formulated pesticide (Admire), at concentrations as low as 0.1 μ g/L and in addition there were reductions in head length in *Baetis* and thorax length in *Epeorus*, indeed no male *Epeorus* emerged at 0.25 μ g/L after 20-day exposure (Alexander, Heard & Culp 2008).

Short (24-h) pulses of Imidacloprid at 0.1 µg/L caused subsequent feeding inhibition for several days in the mayfly *Epeorus longimanus* (Alexander et al 2007)

Concentrations of Thiacloprid between 0.75 μ g/L and 1 μ g/L affected the behaviour of *Gammarus* shrimps and mayflies, resulting in the mayflies being more vulnerable to predation (Englert et al. 2012).

There was a reduction in growth and emergence rates in the midge *Chironomus riparius* when exposed to sublethal concentrations of 1.2 μ g/L Imidacloprid and a significant delay in time-to-emergence when larvae were exposed to 0.4 μ g/L and to high levels of predation cue (Pestana et al. 2009).

Cavallaro et al. (2016) is the only study that has compared the aquatic toxicity effects of Imidacloprid, Clothianidin, and Thiamethoxam. Using the midge *Chironomus dilutus* the effects of Imidacloprid and Clothianidin were similar, while Thiamethoxam was less toxic, but note again that Thiamethoxam decays into Clothianidin (see Table 3).

Table 3 - Chronic toxicity in *Chironomus dilutus* (Cavallaro et al. 2016)

	Concentration at which 50% died after 14 days /µg/L	Concentration at which 50% failed to emerge after 40 days /µg/L
Imidacloprid	1.52	0.39
Clothianidin	2.41	0.28
Thiamethoxam	23.60	4.13

Miles et al (2017) investigated the toxicity of Clothianidin to several wetland species; the most sensitive species was the water beetle *Graphoderus fascicollis* (Coleoptera) with a LC50 value of 2 μ g/L.

Considering the range of toxicological information, species sensitivity data and ecological evidence available the Netherlands has set a reference value for Imidacloprid - 0.0083 µg/L for chronic long-term exposure (AA EQS) and 0.2 µg/L for short-term acute exposure (MAC EQS) (Smit et al. 2015).

While a number of Predicted No Effect Concentration (PNEC) values have been put forward for other neonicotinoids, they vary on the basis of how much research has been undertaken examining their impacts on insects, hence the PNEC for little studied Acetamiprid is 60 times higher than the PNEC for Imidacloprid and even Clothianidin is 16 times higher (Loos et al. 2017). The differences in levels appear to be directly related to the basis of evidence, for instance Carvalho et al. (2015) used a single non–Daphnia magna invertebrate data point to determine PNEC values for both Acetamiprid and Clothianidin, but set a much lower PNEC for Imidacloprid on the basis of 13 non–Daphnia magna invertebrate data points. Since then new evidence on Imidacloprid toxicity has further reduced the PNEC, but no such information has become available for Acetamiprid or Clothianidin (Loos et al. 2017).

In light of evidence of harm to aquatic insects a comprehensive review by Morrissey et al. (2015) concluded that due to the similar toxicity action of the neonicotinoids, the likelihood that they will act in a linearly synergistic manner and the data bias towards Imidacloprid the best approach is to set limits for neonicotinoids as a pollutant group. They used an analysis of species sensitivity distributions (SSD) and impacts on aquatic communities and ecosystems, mesocosm and field studies, to propose environmental thresholds, stating "we recommend here that ecological thresholds for neonicotinoid water concentrations need to be below 0.2 μg/L (short-term acute) or 0.035 μg/L (longterm chronic) to avoid lasting effects on aquatic invertebrate communities".



Picture 2 – Water beetle *Graphoderus* zonatus © Roger Key

Evidence of Aquatic Pollution and Harm from Neonicotinoids

Widespread and frequent contamination of surface water with neonicotinoids has been reported in every country where neonicoitnoids are widely used in agriculture and there has been any systematic monitoring; including the Netherlands (Van Dijk et al. 2013), California (Starner and Goh 2012, Hoyle and Code 2016), mid-western USA (Hladik et al (2014), Canada (Main et al. 2014), Hungary (Székács etal. 2015) and Sweden (Kreuger et al. 2010).

In field studies a reduced abundance in aquatic insects is apparent when concentrations of Imidacloprid in water are above 1 or 2 μ g/L (Sánchez-Bayo and Goka 2006, Pestana et al. 2009, Colombo et al. 2013).

There have been two studies of ecological impacts of neonicotinoid pollution of freshwaters at a national level, both in the Netherlands.

Van Dijk et al. (2013) found that the macrofauna abundance in Dutch surface waters dropped sharply between 0.013 and 0.067 μ g/L of Imidacloprid. There were significant negative relationships between pollution and the abundance of shrimps (Amphipoda), pond snails (Basommatophora), flies (Diptera), mayflies (Ephemeroptera) and hoglice (Isopoda).

Hallmann et al. (2014) undertook a sophisticated analysis of neonicotinoid water pollution and bird populations, using time series to create a proxy control and factoring in a wide range of landscape variables. They found that water pollution levels of just 0.02 μ g/L of Imidacloprid led to a 30% fall in bird numbers over ten years.

Contamination of freshwaters has been reviewed by Sánchez-Bayo et al. (2016) who concluded that:

"Negative impacts of neonicotinoids in aquatic environments are a reality. Initial assessments that considered these insecticides harmless to aquatic organisms may have led to a relaxation of monitoring efforts, resulting in the worldwide contamination of many aquatic ecosystems with neonicotinoids.

The decline of many populations of invertebrates, due mostly to the widespread presence of waterborne residues and the extreme chronic toxicity of neonicotinoids, is affecting the structure and function of aquatic ecosystems. Consequently, vertebrates that depend on insects and other aquatic invertebrates as their sole or main food resource are being affected. Declines of insectivore bird species are quite evident so far, but many other terrestrial and amphibian species may be at risk."

Methodology

Sampling of the watch list chemicals was undertaken by the Environment Agency in England, NRW in Wales, SEPA in Scotland and the NIEA in Northern Ireland. Twenty-three sites were sampled, 16 in England, four in Scotland, three in Wales and three in Northern Ireland. Sites were selected to provide a range of catchment scenarios, including some reference sites that should have been free of pollution sources.

An additional site, the Lugg was selected in England, but no data appears to have been collected in 2016. The Northern Ireland data has yet to be released to the public.

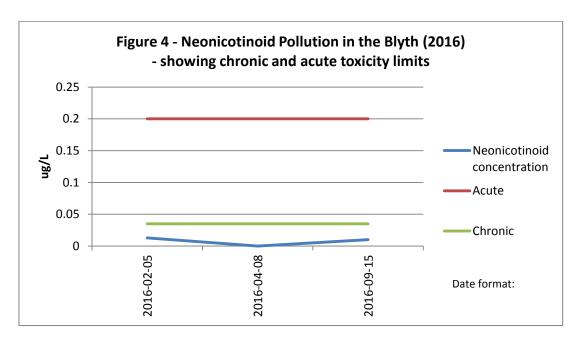
All available details on the methodology used are set out in Appendix 1, which formed part of the UK submission to the European Commission.

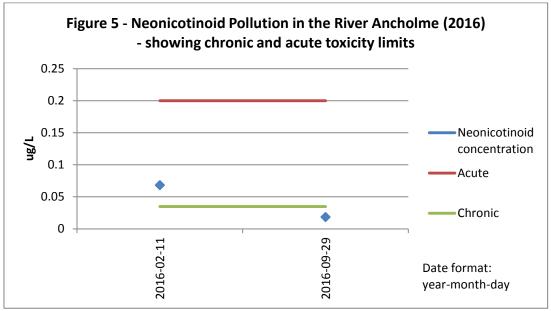
Data was accessed via the **Eionet website** in November 2017.

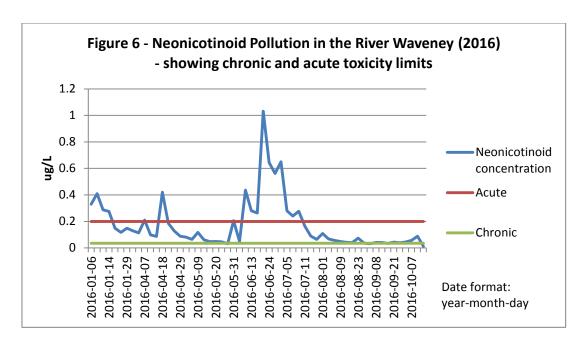
Results

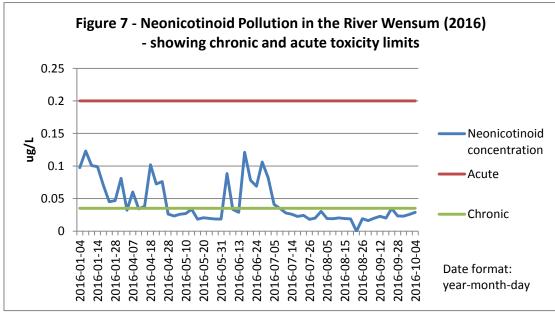
The monitoring results for waterbodies in England, Scotland and Wales where Neonicotinoids were detected are presented in Figures 4 to 19. The graphs display the acute and chronic environmental limits recommended by Morrisey et al. 2015.

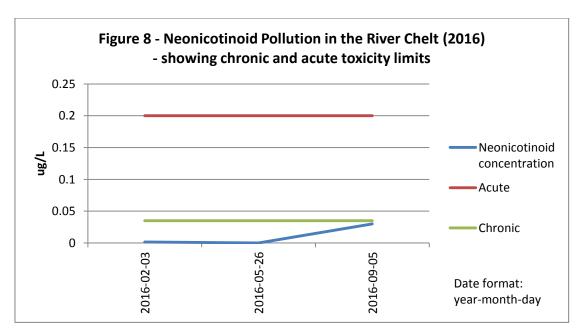
No neonicotinoids were recorded from Windermere and the River Eden in England, the Rivers Ugie and Ythan in Scotland and the rivers Mawddach and Towy in Wales.

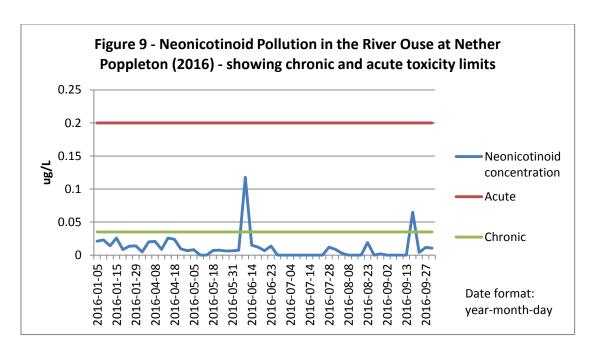


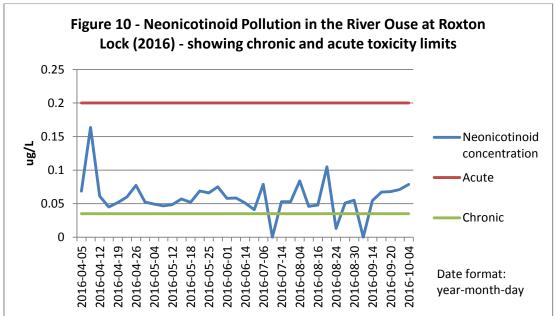


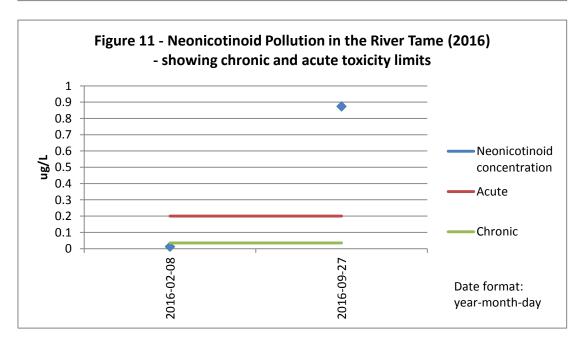


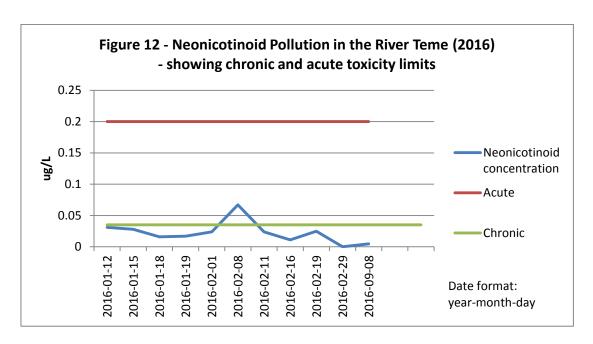


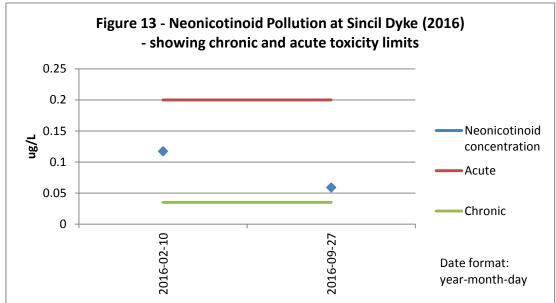


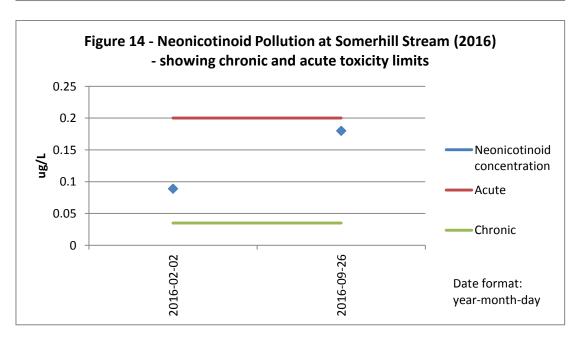


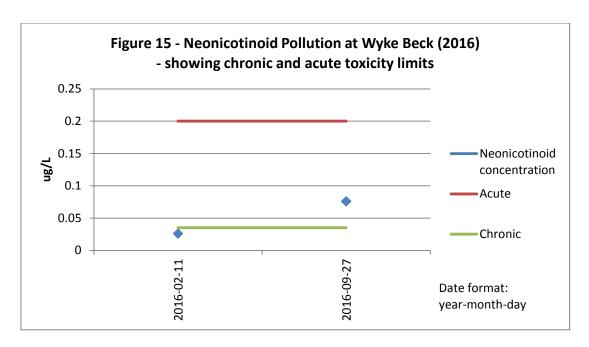


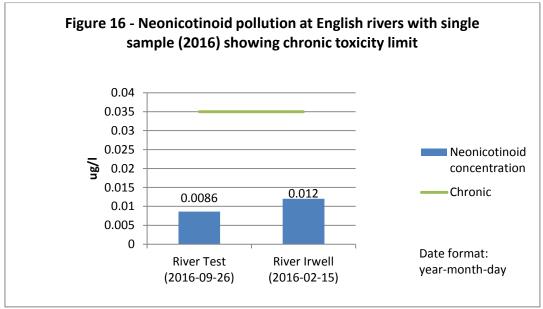


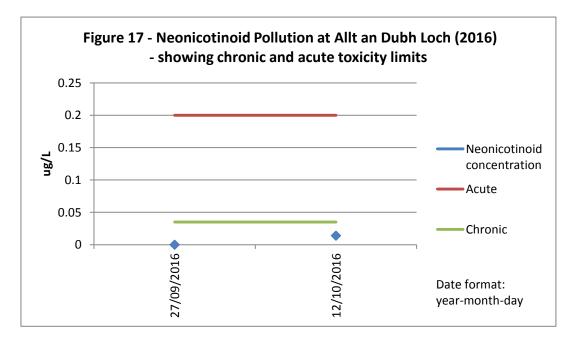


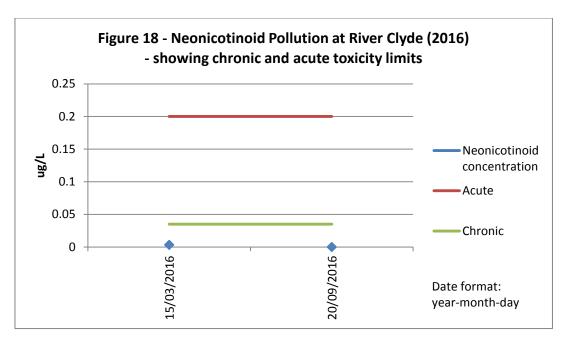


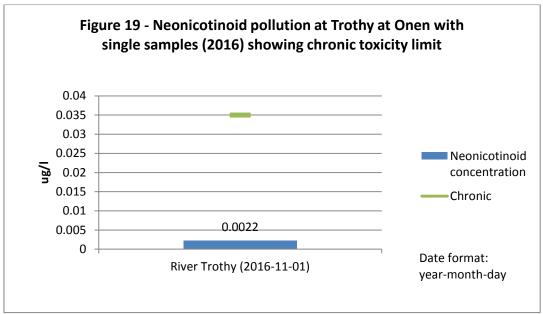










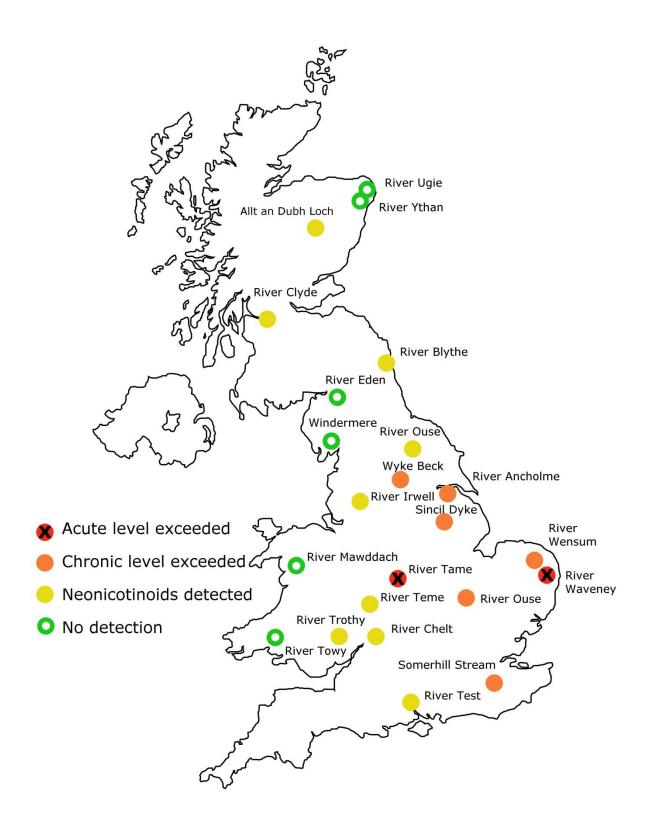


^{*}Observations below the limit of quantification (LOQ) excluded from graphs.

Table 4 – Overview of occurrence of neonicotinoids in 2016 watch list monitoring in England, Scotland and Wales

	No. sites monitored	No. sites recording neonicotinoids	No. sites above chronic toxicity level	No. sites exceeding acute level	No. sites with annual average >50% of acute level	No. measurement events	No. detections	% detections	No. measurements above acute level	% above acute level
England	16	14	8	2	3	239	214	89.5	17	7.1
Scotland	4	2	0	0	0	6	2	33.3	0	0.0
Wales	3	1	0	0	0	3	1	33.3	0	0.0
Britain	23	17	8	2	3	248	217	87.5	17	6.9

Figure 20 - Location of British Watch List monitoring sites and neonicotinoid status.



The data is summarised by country in Table 4 and is displayed by location in Figure 20. Only four upland waterbodies and the two Aberdeenshire rivers were free from neonicotinoid pollution. The worst pollution was found in Eastern England where seven rivers exceeded their chronic pollution limits, and the River Ouse in Yorkshire was the only river with a significant arable catchment that was under the limit. The River Tame was an unusual case and is discussed below.

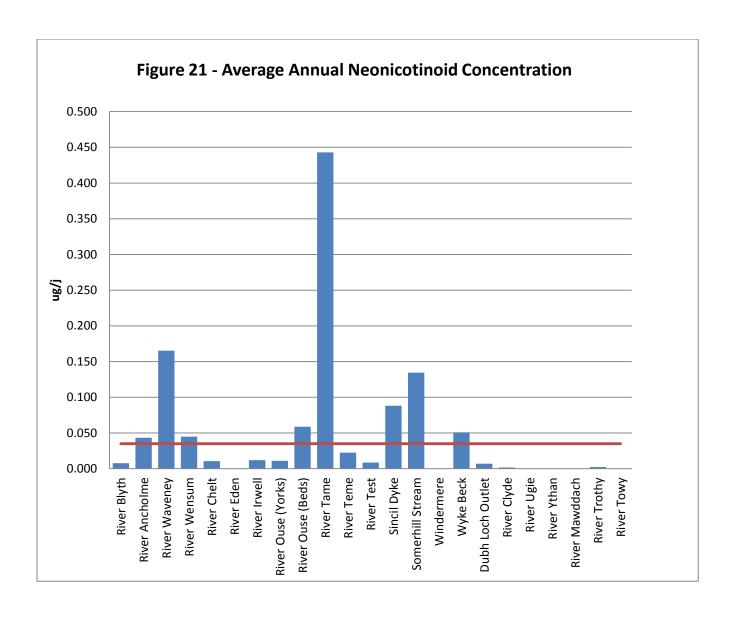


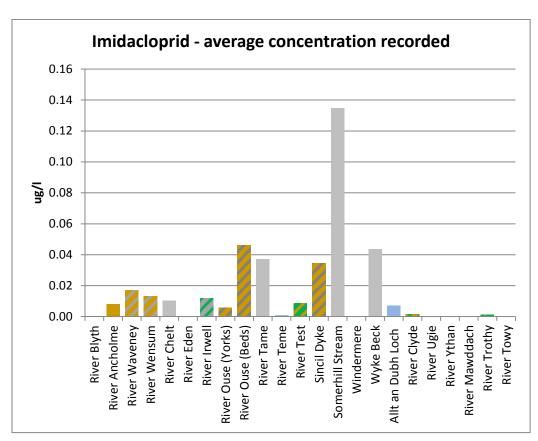
Table 5 - Occurrence of neonicotinoids in water bodies in England, Scotland and Wales

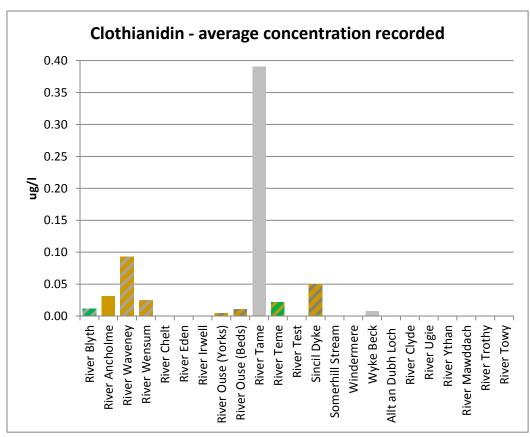
Site	Average Neonicoti noid Concentr ation µg/L	Ratio to Chronic Limit	Ratio to Acute Limit	% Imidacloprid	% Clothianidin	% Thiamethoxam	% Acetamiprid	% Thiacloprid
River Blyth, Bedlington Bridge	0.008	0.22	0.04	2	92	2	2	2
River Ancholme, Horkstow Bottom	0.043	1.24	0.22	18.2	70.4	10.3	0.6	0.6
River Waveney Ellingham Mill	0.172	4.93	0.86	9.8	53.8	36.2	0.0	0.2
River Wensum, Sweet Briar Rd.	0.043	1.23	0.21	30.4	58.0	11.1	0.0	0.4
River Chelt, Princess Elizabeth Way	0.011	0.30	0.05	91.0	4.5	1.5	1.5	1.5
River Eden, Sheepmount	0	0	0					
River Irwell, Old Ringley Bridge	0.012	0.34	0.06	85.7	3.6	3.6	3.6	3.6
River Ouse, Nether Poppleton	0.011	0.32	0.06	52.6	44.8	1.1	0.1	1.4
River Ouse, Roxton Lock	0.059	1.68	0.29	80.0	18.8	0.9		0.3
River Tame, Coleshill	0.443	12.66	2.22	8.3	87.9	3.7	0.1	0.1
River Teme, Powick	0.023	0.64	0.11	2.8	97.0			0.2
River Test, Longbridge	0.009	0.25	0.04	100				
Sincil Dyke, Washingborough	0.088	2.52	0.44	38.9	56.4	4.1	0.3	0.3
Somerhill Stream, Old Forge Fm	0.135	3.84	0.67	99.3	0.2	0.2	0.2	0.2
Windermere, South Basin	0	0	0					
Wyke Beck, Knostrop Works	0.051	1.46	0.26	83.7	14.9	0.5	0.5	0.5
Allt an Dubh Loch	0.007	0.20	0.04	100				
River Clyde	0.002	0.05	0.01	100				
River Ugie	0	0	0					
River Ythan	0	0	0	_				
River Mawddach, Ty'n y Groes Hotel	0	0	0					
River Trothy, Onen	0.002	0.06	0.01	54.55	45.45			
River Towy, Nantgaredig	0	0	0					

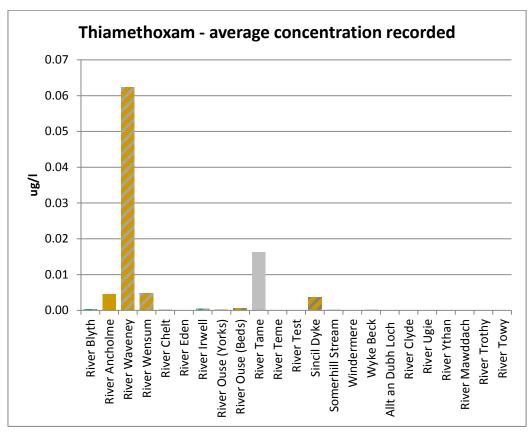
^{*}Observations below the limit of quantification (LOQ) factored in at 50% of LOQ in table.

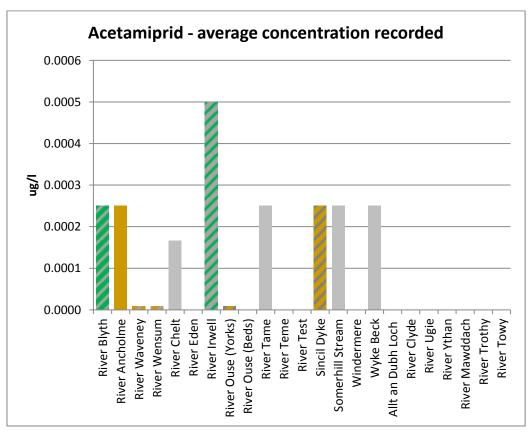
Figure 22 – Average concentrations of each neonicotinoid recorded at each site with indication of catchment type.

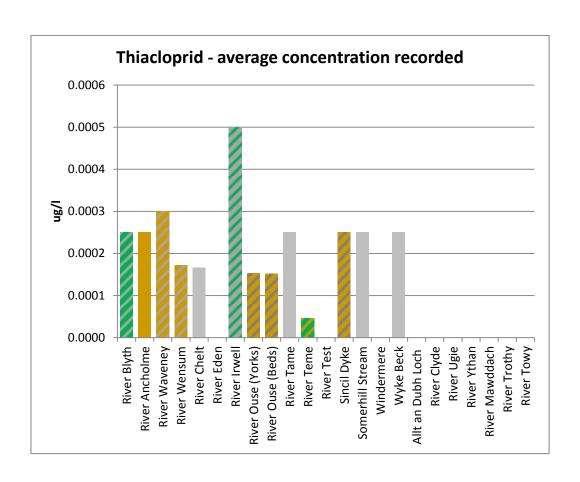
Colour of bars represents catchment; Grey = urban, Brown = arable, Green = grassland











Discussion

The results of the first year of Water Framework Directive 'Watch List' monitoring in the UK indicate that in line with many parts of the world the UK has a significant problem with neonicotinoid pollution in freshwater.

Eight rivers exceeded their annual average chronic pollution limits and two of those rivers also exceeded their acute limits, although one of these, the Tame, only had two data points, one of which was very high. Based on scientific studies in laboratories and in the Netherlands it can be concluded that these rivers will have suffered from significant ecological harm. The levels of contamination are sufficient to cause a range of sublethal effects on mayflies, caddisflies, flies and other invertebrates, and to result in steep declines in invertebrate abundance and declines in bird populations.

The Riverfly Census (Measham 2016) assessed the invertebrate health of 12 English rivers in 2015, including the Eden, Test and Wensum. The Wensum, a river designated as an SSSI and Special Area of Conservation for its river life, was the worst ranked river. Compared with the Eden and Test (Table 6) the Wensum was also the worst polluted with neonicotinoids. Although there may be other correlated factors, the high levels of neonicotinoids in the Wensum alone would be sufficient to explain the observed differences.

Table 6 – Riverfly Health Scores from the 2015 Riverfly Census (Measham 2016) compared with UK Government data on neonicotinoid concentrations in 2016.

River	Average	Spring	Riverflies	WFD	Average 2016
	ranking	riverfly	average	classification	Neonicotinoid
	score	species	abundance		Concentration
		richness			μg/L
Eden	37.3	17	335	Good	0
Test	34.8	16	314	Good/Moderate	0.009
Wensum	33.3	12	127	Moderate	0.045

The River Waveney was the most heavily polluted river in this sample, not only did it exceed the average annual chronic pollution limit, it also exceeded the acute pollution level for over a month, peaking at 1.03 μ g/L. This would undoubtedly have impacted significantly on the insect life of the river. Worryingly both the Wensum and Waveney supply water to the Norfolk Broads, an internationally important wetland that supports many endangered aquatic species.

To better understand the source of neonicotinoid pollution the nature of the catchment and the actual insecticides present need to be considered (see Figure 22), this is reviewed below.

Primarily polluted with Imidacloprid (failing rivers in red)

River Chelt – Urban, no waste water treatment plant, some grassland.

River Irwell – Urban, waste water treatment plants, grassland and upland catchment.

River Ouse (Bedfordshire) – Mixed arable/grassland, with waste water treatment plant.

River Test – Grassland and arable, catchment sensitive farming.

Somerhill Stream – Urban, with waste water treatment plant.

Wyke Beck – Urban, with waste water treatment plant.

Allt an Dubh Loch - Reference Site.

River Clyde – Urban, with waste water treatment plant, large grassland and arable catchment.

Primarily polluted with Clothianidin

River Blyth – Industrial/urban, arable and some grassland catchment.

River Ancholme – Arable with small waste water treatment (NOT Industrial/urban).

River Tame – Urban, with waste water treatment plants.

River Teme – Grassland, arable, fruit, catchment sensitive farming to 2015, and WWTPs.

Polluted with both Clothianidin and Imidacloprid

Sincil Dyke – Arable with urban, with waste water treatment plants (River Witham). River Trothy – Grassland and arable.

Polluted with both Clothianidin and Thiamethoxam

River Waveney – Arable, catchment sensitive farming, with waste water treatment plants.

River Wensum – Arable, catchment sensitive farming, with waste water treatment plants.

River Ouse (Yorks) – Arable, some grassland & upland, catchment sensitive farming, WWTPs.

There is now very little use of Imidacloprid in arable or vegetable crops, however because of its persistence in soil it is likely to continue to pollute water for several more years, this is the probable source of Imidacloprid in the Ouse (Beds), Ancholme, Sincil Dyke, Waveney and Wensum. However, all the four most polluted sites have significant areas of urban catchment and waste water treatment inflows, and three of these are very predominantly urban. This strongly suggests arable land is not the primary source of Imidacloprid pollution. Two potential alternative sources exist: treatments on potted plants, in greenhouses, garden centres, amenity areas or gardens, and ectoparasite treatments on pets.

Four Imidacloprid sprays are authorised for greenhouse use in the UK, however the Horticultural Trades Association's "Statement on Neonicotinoids" (2017) says "only two neonicotinoids which are currently used widely in UK ornamental plant production (Thiacloprid and Acetamaprid), and a third [Imidacloprid] which is used sparingly as the only current year-round effective treatment to control vine weevil". However, Lentola et al. (2017) found Imidacloprid in 38% of ornamental plants in sale in UK garden centres (11 of 29), with an average contamination concentration of 3.9 ppb (Standard Deviation ± 8.4 ppb). In addition Reuter et al. (2014) found that 43% of plants in garden centres across several EU states contained Imidacloprid. As the UK imports over £1 billion worth of potted plants every year (Trading Economics 2016) the volume of Imidacloprid being released into gardens and amenity areas is difficult to quantify.

The UK population of dogs is 8.5 million (24% of households) and there are 8 million cats (17% of households) (PFMA 2017) many of these pets are regularly treated for fleas or ticks, and Imidacloprid is one of the more commonly used treatments, however it's prevalence and volume of use is not reported.

There may be a small number of commercial greenhouses, garden centres or composting sites within the catchments of these rivers that could form point sources of Imidacloprid, however most potted plants are dispersed widely and sparsely in gardens from where significant leaching into storm drains and water courses seems unlikely. On the other hand pets are washed in bathrooms and their bedding is washed, resulting in a significant

likely input into waste water; pets are active on sealed soils resulting in a storm drain risk; and dogs particularly enter water bodies directly.

While the indirect effects of horticultural use may be contributing to Imidacloprid pollution in urban areas, the pathways from veterinary use on pets are more direct and this suggests that veterinary pour on and collar uses are likely to be the prime source of pollution, and are therefore implicated in three waterbodies – the Tame, Wyke and Somerhill Stream - exceeding their chronic pollution limits.

The presence of Imidacloprid at the Allt an Dubh Loch, a remote stream in the Cairngorms, above Loch Muick, is an important detection. Allt an Dubh Loch was chosen as a reference site, none of the Watch List substances were supposed to occur there. The watercourse was monitored on two dates 27 September and 10 December, Imidacloprid was only detected on the second date. There is no arable or forestry in the valley upstream of the site. It seems unlikely that sufficient agricultural Imidacloprid would persist, blow up the mountains and cause the pollution. Imidacloprid is not licenced for use on sheep and they are unlikely to still be on the mountains in December. On both dates the mammalian female hormone Estrone was detected, and on the second date the oral contraceptive Ethinylestradiol was detected, neither of these chemicals have approved UK veterinary uses. By deduction the most likely source of this pollution is a dog entering the outlet stream. There have been a number of reports of aquatic devastation where the most likely cause is flea treatments on dogs (e.g. Taylor et al. 2005), but the issue has not been tackled.

Kreuger et al. (2010) studied pesticides in surface water next to vegetable crops and greenhouses in different regions in Sweden and found Imidacloprid in all sample sites draining areas with greenhouse cultivation, with the highest Imidacloprid concentration being 9.6 μ g/L. However, none of the catchments studied in Britain were dominated by greenhouses, only the Clyde has a significant number of horticultural operations, and this is a large and varied catchment with only two sampling dates, so despite their indictment as a key source of water pollution in other studies it is not possible to assess their impact in the UK.

More Clothianidin was encountered than all the other neonicotinoids put together. The primary use of Clothianidin is on cereals, and the most polluted waterbodies were associated with arable catchments – Ancholme, Wensum, Waveney and Sincil Dyke. Clothianidin alone would have been sufficient to cause the last two water bodies to exceed the chronic pollution level. However, the pollution of the River Tame was an exceptional event, there were only two samples taken, one in February and the second in September (Table 7). There was no Clothianidin detected in February but 0.78 μ g/L was detected in September. The River Tame above the sampling site is almost entirely urban and industrial (see Figure 23). The most likely cause of the September peak was a pollution event; this may have arisen from a chemical factory, seed treatment facility or the disposal of a farm pesticide into the sewage system.

Table 7 - River Tame neonicotinoid pollution

Date	Substance	ug/l
08.02.2016	Imidacloprid	0.012
	Imidacloprid	0.062
	Thiamethoxam	0.032
	Clothianidin	0.78

THE CATCHMENT OF THE TAME Major urban areas Outside catchment River Tame Other rivers Km Tamworth WOLVERHAMPTON Atherstone Coleshill Wednesbury Coldfield DUDLEY Oldbury BIRMINGHAM Sheepwash Urban Park Solihull Sandwell Valley COVENTRY Perry Hall Park LadywalkReserve Kingsbury Water Park Whitemoor Haye Croxall Lakes National Memorial Arboretum

Figure 23 - Catchment of the River Tame showing sampling site.

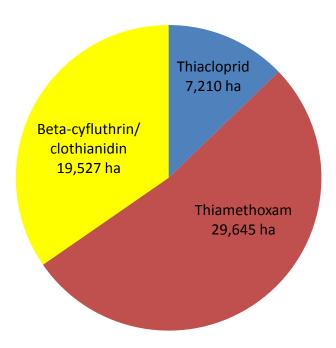
By Sjwells53 - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=4401415

Since the partial ban in 2013 most Thiamethoxam is used as a seed treatment on Sugar beet – 29,645 ha in 2016. There are also smaller areas of other vegetables (lettuces, swedes and/or turnips) with Thiamethoxam seed treatments, 1,497 in 2015, and 2,200 ha of potatoes was sprayed with Thiamethoxam in 2016 (see Figure 24).

Most sugar beet is grown in an arc from the Humber through Lincolnshire, Cambridgeshire, Norfolk, Suffolk and North Essex, often in light, free draining soils. Four of the five rivers with significant Thiamethoxam levels were in this arc – Waveney, Wensum, Ancholme and Sincil Dyke. Of these the River Waveney was the most heavily polluted with an average reading of 0.06 µg/L and a peak of 0.77 µg/L on 20 June 2016. The Waveney catchment contains large areas of sugar beet, it was the only river where Thiamethoxam alone would have exceeded pollution thresholds.

Figure 24 - Area of UK Sugar Beet Crop Treated with Neonicotinoids in 2016

Fera PUSSTATS Data



Interestingly the second most Thiamethoxam polluted river was the Tame, as with Clothianidin this occurred as a peak on the second of the two dates monitored (Table 7), although the concentration of Thiamethoxam present was one twenty-forth that of the Clothianidin. Clothianidin is very close chemically to Thiamethoxam, could it be that their occurrence in the Tame was linked and they were both part of the same pollution incident – Thiamethoxam released and degrading into Clothianidin or a partially processed batch?

A sliver of good news is that there were fairly low levels of Thiamethoxam in the river Ouse in Bedfordshire - average $0.0005~\mu g/L$ with a peak of $0.0063~\mu g/L$ on 14 June 2016. Its catchment contains large areas of Oilseed rape and if accumulations of Thiamethoxam in arable soils, resulting from its common use on the crop up until 2014, had still been causing significant aquatic pollution then a higher concentration might have been expected. This gives hope that after neonicotinoids are banned the recovery of aquatic chemical quality status might happen within a few years.

Pollution levels of Acetamiprid were low with no readings above the limit of quantification and only a single detection on each river where it was found.

Thiacloprid pollution was low; it was most frequently detected in the Ouse in Yorkshire (eight times), the Waveney (six times) and the Wensum (five times). The peak concentration was on the Waveney on 24 June when a level of 0.01 μ g/L was recorded. This pattern suggests the main source was insecticide sprays on vegetable and/or sugar beet crops.

Conclusions

The Water Framework Directive Watch List monitoring has been very successful in relation to neonicotinoids in the UK. In England particularly, where more sites were included and more sample dates undertaken, the monitoring has presented an informative snap shot of the pattern of neonicotinoid pollution.

It is clear from the data that neonicotinoid pollution is a significant problem in Britain and that harm to the environment has doubtlessly been done. Unless measures are put in place this harm is likely to continue and potentially worsen.

Invertebrate populations in rivers and other waterbodies represent an important part of the UK's biodiversity, they provide valuable ecosystem services, recycling organic matter and keeping rivers clean. In addition they provide food for fish and birds. Given the impacts caused by pollution at comparable levels in other countries, these results are an alarm bell for the health of our invertebrate, fish and bird populations.

While there has been concern in other countries about neonicotinoid pollution from arable farming for several years, it is now clear that the problem is prevalent in the UK, particularly in Eastern England. The treatment of Sugar beet with Clothianidin and Thiamethoxam is clearly problematical for the aquatic environment, with some of our most precious rivers and wetlands in Sugar beet growing areas being polluted to a damaging level. Particular concern is expressed in relation to the Broads, although it is likely that the Fens and other areas may be similarly impacted.

The limited number of sites made an assessment of the risk posed by neonicotinoid use in greenhouses impossible, as none of the catchments were dominated by greenhouses. There were also no water bodies representing areas with extensive orchards, soft fruit production or commercial forestry.

It is apparent from the data that the use of Imidacloprid as a veterinary medicine is a cause of serious concern. Pollution from flea treatments is the most likely source of chronic and harmful pollution on several urban rivers, and the insecticide was detected in one of the UK's most pristine environments. The threat posed to aquatic life by high levels of Imidicloprid are clearly established, and immediate action to bring rivers back into a good chemical status is essential.

There is a bewildering array of toxins available to treat ectoparasites on pets in the UK, in addition to Imidacloprid another neonicotinoid Nitenpyram is used, as is the similar toxin Fipronil. Pyriproxyfen, Methoprene, Indoxacarb, Diazanon, Permethrin, Flumethrin, Fluralaner, Propoxur, Dicyclanil, Spinosad, Deltamethrin, Lotilaner, Afoxolaner, Sarolaner, Cyromazine and Cypermethrin are also used, only the latter is currently included under Water Framework Directive monitoring requirements. Some of these toxins are endocrine disrupters and may be further regulated by the EU. Having discovered that Imidacloprid pet treatments appear to be the cause of harmful pollution of waterbodies, it would be short sighted not to consider that other ectoparasite treatments may pose similar risks.

The apparent pollution event on the River Tame indicates that monitoring of neonicotinoids has the potential to detect damaging insecticide pollution incidents in rivers; events that can be difficult to observe directly.

There is some good news in the data, a suggestion that the partial ban on neonicotinoids may have already reduced aquatic contamination from Thiamethoxam, and reassuringly low levels of Acetamiprid and Thiacloprid contamination. Although it should be noted that neither of these latter neonicotinoids insecticides have been as widely used as

Clothianidin or Thiamethoxam, and the waterbodies selected do not represent the areas where they are likely to be commonly used.

The ecologically damaging levels of neonicotinoids detected in British freshwaters is a further example, were one needed, that current regulatory procedures are failing to provide sufficient protection to ecosystems. This problem has been recognised by Prof. lan Boyd, the Defra Chief Scientist:

"The current assumption underlying pesticide regulation—that chemicals that pass a battery of tests in the laboratory or in field trials are environmentally benign when they are used at industrial scales—is false."

"The United Kingdom has one of the most developed regulatory and monitoring systems for pesticides. Yet, it has no systematic monitoring of pesticide residues in the environment."

"Better regulation is needed to control how pesticides are used and affect the environment at a landscape scale."

(Milner and Boyd 2017).

The regulatory agencies should take the opportunities currently presented to address the short comings in insecticide regulation, as a model for a better future approach to pesticide regulation that would establish stronger regulatory tests prior to the initial approval of pesticide uses, and default post-approval monitoring of both environmental presence and impacts. It should not come as a surprise from the blue every time we realise that an insecticide is causing environmental harm, it can be predicted and managed. Finally, the process of insecticide approval, monitoring, risk management and review must be made vastly more independent, transparent and open.

Recommendations

- Monitoring of these five neonicotinoids should be continued, regardless of their future Watch List status, and the number of sites and sample dates expanded. In particular more rivers should be included that are a) at risk of, or in probability are already, being impacted by arable insecticides and veterinary medicines, and b) representative of areas with greenhouses, extensive orchards, soft fruit production and commercial forestry.
- A comprehensive EU wide ban on the agricultural use of Imidacloprid, Clothianidin and Thiamethoxam should be introduced due to the unacceptable harm they are causing to the aquatic environment; this ban should include greenhouse uses. There is no obvious alternative way to reduce or mitigate their impact on aquatic life.
- 3. Urgent action is required to reduce Imidacloprid pollution in water bodies and return them to a good chemical condition:
 - a) The use of Imidacloprid as an externally applied veterinary medicine should be suspended in the UK - this is the measure most likely to rapidly reduce chronic pollution levels.
 - b) A thorough review of the use of ectoparasite treatments, including a full risk assessment in relation to the aquatic environment, must be urgently undertaken. The report should make recommendations that address all risks of environmental harm. Currently ectoparasite medicines do not even come with a warning to pet owners indicating that they should keep treated animals out of streams, rivers, ponds and lakes.
 - c) If it becomes apparent that chronic pollution of aquatic habitats by ectoparasite treatments is originating via storm drains and/or waste water treatment works outflows then mitigation measures may not be feasible and permanent bans may be required.
- 4. The Environment Agency should develop a clear regulatory approach to responding to neonicotinoid pollution This should include:
 - a) Adopting and applying formal EQS standards based on a rational assessment of risk, considering the wealth of evidence relating to Imidacloprid and the likely comparable toxicity of the other neonicotinoids.
 - b) A clearly communicated approach to investigating and resolving neonicotinoid pollution events identified by monitoring.
- 5. The apparent pollution incident on the River Tame should be investigated and potential sources examined. Monitoring on this river should be stepped up to become at least fortnightly so that any future incidents can be detected.
- 6. Defra should establish an initiative to transform insecticide environmental risk management so as to ensure future generations have a better protected environment, in line with the Defra Chief Scientist's recent call for improved "pesticidovigilance". This should include:

- a) Formal engagement between the Environment Agency, SEPA, NRW, Chemicals Regulation Directorate and Veterinary Medicines Directorate on a joint project.
- b) The development of a new, independent, transparent and open approach that uses a more ecologically comprehensive evidence base in approving insecticide uses, monitoring environmental prevalence, researching environmental impacts, and reviewing post-approval use.

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Appendix 1 - UK methodology submission

Description of the Watch List monitoring stations and the monitoring strategy for surface waters sampled in the Administrations of United Kingdom.

1. Introduction.

The Water Framework Directive's (WFD) chemical Watch List (WL) was established in March 2015 as a mechanism to gain information on whether the selected chemicals pose a risk across the European Union's river basins. It includes 17 substances which must be monitored at least once annually at a minimum number of monitoring sites allocated to each Member State. Substances cannot remain on the WL longer than four years, but can be removed after only one year. Following deselection, substances are either dropped completely or are prioritised for inclusion under WFD as priority substances. Monitoring for the first year of the WL substances should commence six months after the list was established (*i.e.* 20th September 2015), and must be completed within one year (i.e. before 20th September 2016). Results must be reported to the Commission within 21 months of the establishment of the WL and no later than 20th December 2016.

This paper describes monitoring WL substances in the United Kingdom (UK) and by the UK's devolved administrations (DAs). It covers sampling and analysis, and draws on work undertaken by the DAs and on the guidance provided by the European Commission. The objectives of the UK's planning for monitoring and reporting concentrations of WL substances were, to the best of our abilities, to:

- Ensure as far as possible, similar and harmonised approaches to monitoring and reporting WL substances are taken across England, Wales, Scotland and Northern Ireland;
- Detect and quantify some of the more novel WL substances using best available and fit-for-purpose analytical methods and technologies not entailing excessive costs; and
- Ensure concentration data are representative of typical conditions at higher risk sampling stations due to the low number of monitoring stations and low sampling frequency. Simultaneously, we needed to be mindful of unusual or atypical conditions which may skew the overall picture of substance distribution and their quantities.

2. Description of sampling procedure.

The sampling procedure was based on 2015 EU JRC WL draft sampling guidance. A summary of the WL substances, their relevant intrinsic properties and uses, and when and where they should be monitored is presented here and in Annex 1. Substances have been grouped into four classes (pesticides, pharmaceuticals, steroidal oestrogens and industrial chemicals) with sub-classes for pesticides and pharmaceuticals. Groupings have been based on chemical use and reflect substance type and when a substance is used on a seasonal basis. These details were then used to identify and establish sample stations and the time of the year when samples were to be collected for chemical analyses.

3. Selection process for sample station locations.

A pre-requisite for WL site selection and sampling was that it would follow the general principles outlined in Common Implementation Strategy guidance documents 7,19 and 25 (i.e., risk based, reflecting realistic pressures but including sites that are not atypical, and spatial and temporal sampling reflecting use pattern and substance properties).

Stations were thus selected based on likely risk and from information mainly drawn from evidence that has emerged from existing surveillance exercises. There are eight pesticides on the WL and monitoring effort focussed on diffuse agricultural sources. For the other nine substances including three oestrogens, four pharmaceuticals and two industrial chemicals, monitoring focussed on water bodies with significant municipal (or industrial) waste water treatment plant (WWTP) effluent inputs on the whole.

The UK was allocated a total of 18 WL monitoring stations (England has 14 stations, Scotland 2, Northern Ireland 1 and Wales 1). Clearly for those DAs with an allocation of only one or two stations, this represented a problem. Two options existed: (1) to select, if available, a catchment with a waterbody that has multiple (agricultural and urban) pressures, or (2) incorporate an additional site so that one site targeted agricultural inputs and the other urban pressures. The latter option was decided upon.

Within their sampling stations, Wales, Scotland and Northern Ireland also included a "background" site for monitoring all WL substances. These stations were selected where no known chemical inputs due to urban, agricultural or industrial pressures were apparent. Although this approach would provide more useful information, it was recognised that with additional stations, this would greatly increase sampling and analytical effort above what was expected. The timing for sample collection for the different WL chemicals was an additional complicating factor, and again resulted in an increase in effort. Especially for the DAs with such a lower number of allocated monitoring stations, a trade-off was necessary which still provided meaningful risk-based information.

It was agreed that WL sampling should focus on freshwater only, and that voluntary sediment sampling for the sunscreen chemical did not need to be carried out. The DAs would organise monitoring in sub-sets of their allocation for groups of WL substances with related pressures. The following summaries how sampling stations were allocated and specific details regarding sampling regimes can be found in Annexes 2 to 5:

- Of England's 14 allocated stations, monitoring was organised into four agricultural sites (for pesticides), four industrial sites and six sites reflecting urban pressures (Annex 2).
- For Wales (see Annex 3), four stations were established and included one urban with surface waters impacted by waste water treated effluent as well as diffuse source inputs, two rural locations representing livestock and arable agricultural practices, and one background station.
- For Scotland, the four stations include one background site, two rural stations encompassing agricultural production and one urban river where surface waters were impacted by treated waste water effluents and diffuse source inputs (Annex 4).
- For Northern Ireland (see Annex 5), three stations included a background site, one river in a highly urbanised catchment and a rural location representing high agricultural production.

3.1 Diffuse source inputs - pesticides.

Of the WL pesticides, most are used in some way for the control of pests on vegetables, cereal crops and oil seed rape. Note that oxadiazon is mainly used for the control of grasses, and the use-up period for the main use of methiocarb (slug pellets) has recently expired. This pesticide is a UK Specific Pollutant and it was decided site selection for pesticides could include one or more existing methiocarb sites. Therefore sites that had already been prioritised for pesticide risk were considered in the process of WL sample station selection. Catchments with higher farm numbers were targeted where possible so that factors such as crop rotation or changes in crop types year on year were less likely to affect overall annual usage and water body concentrations at the catchment scale.

3.2 Point source inputs - industrial chemicals, oestrogens and pharmaceuticals.

The majority of WL substances for which point source emissions are more relevant will be more associated with treated effluents discharges from municipal WWTPs. The industrial chemical 2,6-di-tert-butyl-4-methylphenol will also be associated with WWTPs treating industrial sewage and will have diffuse releases from for instance, vehicle tyre wear. However, the contribution from latter to aqueous concentrations was difficult to estimate at the time. Monitoring of this substance in water bodies associated with urban run-off pressures as well as municipal WWTWs' effluents would aim to cover the latter aspect.

It is known that livestock are a significant source of 17- β oestradiol (E2) and this substance can be associated with diffuse inputs from rural-agricultural areas. The sunscreen chemical, 2-Ethylhexyl-4-methoxycinnamate is used in personal care products so, in addition to 'down the drain' releases, direct environmental release to bathing waters (inland as well as coastal) in summer months may be a significant source for some DAs.

Especially for Wales, Scotland, and Northern Ireland, site selection for chemicals more associated with point sources emissions focussed on catchments with significant urban density and associated WWTPs' pressures. Sites that had already been selected for the detection and reporting of Priority/Priority Hazardous Substances (*e.g.* Diethylhexyl Phthalate, 4-nonylphenol, polybrominated diphenyl ethers) with a similar use and release profiles were considered for sample station selection.

4. Timing of sample collection.

4.1. Surface water sample collection for pesticide measurements.

The WL pesticides fall into three sub-categories based on when they are used. According to the information in the Commission draft guidance:

- Spring/summer (Methiocarb, Imidacloprid, Thiacloprid and Acetamiprid);
- Summer/autumn use (Thiamethoxam and Clothianidin); and
- Winter use (Oxadiazon and Tri-allate).

Information from pesticide usage in the UK indicates that Tri-allate was last used in Scotland, albeit in small amounts, in 2012. For the rest of the UK, use is high (300 t across the UK in 2014). Oxadiazon is not currently used on major crops in Scotland and UK usage overall has

declined greatly (200 kg in 2014). Some sources indicate that neonicotinoids in Scotland are mainly used on winter crops, which conflicts with the Commission draft guidance.

It was decided that the competent authorities (CA) for England and Wales would undertake sampling during pesticide use periods. For monitoring in Scotland, sampling was designed to take place during the months of September and October to 'catch' the use of neonictinoids and any (post use-period) use of methiocarb on winter crops.

4.2. Sampling for oestrogens, pharmaceuticals and industrial chemicals.

Only 2,6-di-tert-butyl-4-methylphenol has no seasonality associated with its use. The literature and the Commission's guidance indicate that steroidal oestrogen concentrations are higher in summer months (although this is more related to low flows than seasonal differences in use/release).

The pharmaceuticals may see increased use in winter; antibiotic use associated with infections may be more prevalent in winter, conditions that require anti-inflammatories are arguably worsened in cold weather. Use of 2-ethylhexyl-4-methoxycinnamate in personal care products with down-the-drain release will occur year round, although use of sun screens will be much higher in the summer possibly resulting in higher down-the-drain release as well as direct release in bathing waters.

The English CA proposed rotating seasons annually for the monitoring of oestrogens, pharmaceuticals and industrial chemicals. The approach taken in Scotland for these chemical groups was to have two sampling events – late winter (March) and late summer (September) with the objective of gathering information on effects of seasonality and concentrations.

4.3. Surface water sample pre-treatment.

Samples were collected using amber glass vessels with PTFE-lined caps. Given that some WL substances are susceptible to hydrolysis at low pH while others at higher pH, surface water samples were not acidified. The Commission guidance stated that samples should be extracted within seven days or 48 hours if natural sample pH has not been modified and that samples should be stored/transport chilled (4°C) and in the dark. This guidance was adhered to by the UK Administrations with the exception of Wales (Annex 3).

5. Chemical analyses of WL substances.

It was agreed amongst the UK Administrations that the QAQC Directive only applies to concentration data used for compliance assessment (river classification) and not to the WL substances. This meant that less costly, unaccredited methods could be used so long as they provided "high quality (of sufficient quality) for the purpose of risk assessment", as stated in the Commission's guidance (which also discusses results relative to limits of detection /maximum residue limits rather than limits of quantitation).

Since not all CAs had access to methods of analyses for all WL substances, one laboratory [National Laboratory Services (NLS), England] where methods were available undertook analyses for samples obtained from Scotland and Northern Ireland. The same laboratory also analysed samples acquired in Wales but only for the determination of the pesticide, Methiocarb and the steroid compounds; all other substances were analysed in-house. Applied methods performed by NLS included:

- A fully quantitative, liquid chromatographic mass spectrometric (LC-MS) technique for the steroid compounds;
- A semi-quantitative LC-MS approach for Diclofenac, the three macrolide antibiotics and the five neonicotinoids; and
- A semi-quantitative gas chromatographic mass spectrometric (GC-MS) method for 2,6-ditert-butyl-4-methylphenol, 2-ethylhexyl 4-methoxycinnamate.

Methods applied to extracts from samples collected from Welsh surface waters included:

- Semi-quantitative techniques, using a range of calibration standards appropriate to the levels of interest. Appropriate QC standards and typically five calibration standards were applied. Reporting is based on the bottom calibration standard as statistical data, which would have supported a lower reporting limit, was not available.
- A fully quantitative, liquid chromatographic mass spectrometric (LC-MS) technique for the steroid compounds (carried out by NLS);

Annex 1.

Summary of Watch List substances: Substance classification; properties; uses in the United Kingdom; and proposed sampling station areas and sample collection timings.

Watch List substance	Chemical class	Summary of physico-chemical, fate and behaviour properties	Main uses	Grouped site selection – where and when to sample
Imidacloprid	Pesticide (Neonicotinoid systemic insecticides)	Not adsorbing, moderately water soluble, non-ionised. Little hydrolysis, slow biodegradation, slightly photodegradable. No stability issues .	Seed treatments, foliar spray OSR, apples	WHERE: Rural zones with high agricultural production. WHEN: winter (seed treatment), Apr, May, Jun
Thiacloprid	Pesticide (Neonicotinoid systemic insecticides)	Not adsorbing, moderately water soluble, non-ionised. Little hydrolysis & photodegradation, but biodegradable. No stability issues.	Foliar use on OSR, (root) vegetables, late application and pre-harvest.	WHERE: Rural zones with high agricultural production. WHEN: Apr, May, Jun
Thiamethoxam	Pesticide (Neonicotinoid systemic insecticides)	Not adsorbing, water soluble, non-ionised. Hydrolysable pH >7, photodegradable and moderately biodegradable. Moderately stable	Seed treatment, soil and foliar treatment vegetables, cereals	WHERE: Rural zones with high agricultural production. WHEN: summer/autumn
Clothianidin	Pesticide (Neonicotinoid systemic insecticides)	Not adsorbing, moderately water soluble, non-ionised. Little hydrolysis & biodegradation, but photodegradable. Light instable.	Seed treatment, soil and foliar application	WHERE: Rural zones with high agricultural production. WHEN: summer/autumn
Acetamiprid	Pesticide (Neonicotinoid systemic insecticides)	Not adsorbing, moderately water soluble, non-ionised. some hydrolysis pH >7, moderately biodegradable, little photodegradation. Moderately stable	Foliar application vegetables, OSR, fruits	WHERE: Rural zones with high agricultural production. WHEN: Spring, summer, autumn
Methiocarb	Pesticide (non- systemic contact insecticide); biocide (rodenticide and insecticide)	Moderately adsorbing, moderately soluble, non-ionised. Hydrolysis pH >7, volatilisation possible, slow biodegradation Moderately stable	Seed treatment (maize and sweetcorn), garden products Slug pellet use withdrawn.	WHERE: Rural zones with high agricultural production. WHEN: spring sowing (Apr, May)

Oxadiazon Tri-allate	Pesticide (pre- emergent selective herbicide) Pesticide (pre- emergent selective herbicide)	Highly adsorbing, poorly soluble, non-ionising Photodegradable, hydrolysable pH >7, not biodegradable Moderately stable Highly adsorbing, poorly soluble, non-ionising, volatilisation possible in lower OC waters Hydrolysable pH >7, not bio- or photodegradable Moderately stable	Control of summer weeds, esp annual grasses. Pre-emergence soil application for winter barley and wheat.	WHERE: Rural zones with high agricultural production. WHEN: Late winter/early spring (Jan, Feb, Mar, Apr) WHERE: Rural zones with high agricultural production. WHEN: Late winter/early spring (Sept, Oct, Nov, Dec, Apr)
17-alpha- ethinylestradiol (EE2)	Steroidal oestrogen (synthetic)	(volatility) Adsorbing, poorly soluble, non-ionised Some hydrolysis and photodegradation, not readily biodegradable Fairly stable	Contraceptive pill	WHERE: Highly urbanised areas impacted by WWTP effluents WHEN: summer (low flows)
17-beta-estradiol (E2)	Steroidal oestrogen	Adsorbing, poorly soluble, non-ionised Some hydrolysis, Photodegradable and biodegradable Lower stability	Naturally released female hormone	WHERE: Highly urbanised areas impacted by WWTP effluents WHEN: summer (low flows)
Estrone (E1)	Steroidal oestrogen	Slightly Adsorbing, poorly soluble, non- ionised Some hydrolysis, Photodegradable and biodegradable Lower stability	Degradation product of E2	WHERE: Highly urbanised areas impacted by WWTP effluents WHEN: summer (low flows)
Diclofenac	Pharmaceutical (anti- inflammatory)	Slightly adsorbing, lower solubility, ionised Very Photodegradable, potentially biodegradable, no hydrolysis Light unstable	Human and veterinary med.	WHERE: Highly urbanised areas impacted by WWTP effluents; high intensity livestock farmland WHEN: Winter
Erythromycin	Pharmaceutical (macrolide antibiotic)	Adsorbing, soluble, ionised at neutral pH Hydrolysis pH >7, some photodegradation, not readily biodegradable Moderately stable	Human and veterinary med.	WHERE: Highly urbanised areas impacted by WWTP effluents WHEN: Winter

Clarithromycin	Pharmaceutical (macrolide antibiotic)	Adsorbing, poorly soluble, ionised Hydrolysis pH <7, some photodegradation, not readily biodegradable Moderately stable	Human medicine	WHERE: Highly urbanised areas impacted by WWTP effluents WHEN: Winter
Azithromycin	Pharmaceutical (macrolide antibiotic)	Adsorbing, poorly soluble, ionised Hydrolysis pH <7, some photodegradation, not readily biodegradable Moderately stable	Human medicine	WHERE: Highly urbanised areas impacted by WWTP effluents WHEN: Winter - stability and use
2,6-di-tert-butyl- 4-methylphenol	Industrial chemical	Highly adsorbing, poorly soluble, nonionising, volatilisation possible in lower OC waters Photodegradable, but adsorption and turbidity may lower photodeg. rates. Not biodegradable, no hydrolysis. Moderately stable	Constituent of rubbers (incl. tyres), plastics, oils, foods cosmetics; antioxidant	WHERE: Highly urbanised areas impacted by WWTP effluents; diffuse sources WHEN: any time.
2-ethylhexyl-4- methoxycinnama te	Industrial chemical (personal care (sunscreen) products)	V adsorbing, poorly soluble, non-ionising Biodegradable and some photodegradation, no hydrolysis. Adsorption may limit degradation. Moderately stable	UVB filter in sunscreen and PCPs, also light stabiliser in plastics	WHERE: Highly urbanised areas impacted by WWTP effluents, possibly bathing waters WHEN: Summer.

Adapted from Water Framework Directive Watch List Sampling Guidance DRAFT 01.09.2015 (G. Umlauf, A. Duffek, S. Polesello, S. Eisenreich, H. Clayton).

Annex 2.

Description of the representativeness of the Watch List monitoring stations and of the monitoring strategy for surface waters in England.

For the purpose of acquiring concentration data on the Watch List (WL) substances in English surface waters, 17 monitoring stations representing different land use types were selected. Only freshwater rivers and one lake were chosen and no transitional and coastal waters were included. Some stations were selected which were likely to demonstrate elevated WL substance concentrations. This approach was taken instead of a separate and fixed network of stations tailored on perceived risks for each WL substance. Thus for each substance, it was likely that a range of lower to higher risk conditions may be encountered. At the time and given the limited knowledge of sources of WL substances, this was considered an acceptable approach to identify typical levels and provide information on the significance higher risk sources

Draft sampling guidance (*Water Framework Directive Watch List Sampling Guidance*) was published by the Joint Research Centre in September 2015 and this post-dated some of the planning for the Watch List programme for England. However, the guidance states that: "Member States are not obliged to follow the guidance, as long as they satisfy the requirements of Directive 2008/105/EC) and of Commission Decision (EU) 2015/495 (Watch List Decision). However, the processing and interpretation of data is likely to be easier if all Member States take a similar approach to the monitoring and reporting." Thus, it was not considered essential to strictly adhere to the guidance, particularly given that the relatively high number of sampling points for the England.

The likely sources of the WL substances were identified and are described in Table 2.1. The adopted sampling guidance sets out thematic groupings for these substances (see Table 2.2). The guidance also refers to the time of year considered most at risk. For monitoring in England and rather than varying the timing of monitoring of each substance to account for specific risks, it was planned to stagger the time of the sampling the whole set of sites over a period of years i.e. spring 2016, summer 2017, autumn 2018, winter 2019, etc., Thus, if the first sampling occasion was not at the same time of highest risk, a subsequent sampling occasion would coincide with the risk period.

Selection of English monitoring stations

As described above, a range of stations were chosen to reflect various surrounding land uses. In England as well as other UK Administrations, it is rarely possible to find watercourses influenced by single land uses in isolation. For example, agricultural catchments will still receive wastewater from (albeit small) wastewater treatment works (WWTWs) and/or domestic systems, and urban catchments will rarely be free from some upstream agricultural use. However, sites were chosen on the basis of broad land uses as presented in Table 2.3.

The network expanded after the first sampling occasion in response to changes in the Catchment Sensitive Farming(CSF) network, and also in response to renewed interest by the English fishing sector in chemicals in surface waters including some WL substances. This, in combination with some problems with sampling and/or analysis has meant that varying numbers of sampling occasions have occurred for some substances.

Table 2.1. Watch List Substances in first list (EU Decision 2015/495), their use and likely sources.

Name of substance or	Nature of substance	Likely sources
group of substances 7-α-ethinylestradiol (EE2)	Synthetic oestrogen – main use as contraceptive pill	Human population - Urban wastewater
17-β-estradiol (E2) Estrone (E1)	Natural oestrogenic substances	Human population - Urban wastewater Farm livestock
Diclofenac	Pharmaceutical (NSAID) drug (humans only - no veterinary use approved in UK).	Human population - Urban wastewater.
2,6-Ditert-butyl-4- methylphenol	Industrial chemical. Antioxidant. Various uses including as a food additive.	Human population – industrial areas, urban wastewater.
2-Ethylhexyl 4- methoxycinnamate	Sunscreen.	Human population – Bathing waters, Urban wastewater
Macrolide antibiotics: Erythromycin Clarithromycin Azithromycin	Pharmaceuticals.	Human population - Urban wastewater.
Methiocarb	Pesticide - Carbamate insecticide and molluscicide. Many approvals withdrawn – uses restricted to maize crops and container grown ornamental garden plants.	Agriculture. NB -should be on downward trend (if detected).
Neonicotinoids: Imidacloprid Thiacloprid Thiamethoxam Clothianidin Acetamiprid	Pesticide - Insecticide. Agricultural use and some pet medicines (Imidacloprid).	Agriculture and human population - Urban wastewater.
Oxadiazon	Pesticide previously used on fruit, ornamental plants, and paved surfaces. Products withdrawn June 2015.	Agriculture and urban areas. NB- should be on downward trend (if detected).
Tri-allate	Pesticide approved for use for cereals, peas and beet. Some products withdrawn 2015 and 2016.	Agriculture – there may be a decline in use.

Table 2.2. Thematic grouping of Watch List (WL) substances and at-risk seasons.

	Thematic grouping of WL substances	Potential at-risk sampling locations	At-risk season
(a)	Human medicines with an emission peak in the cold season (macrolides, anti-inflammatory drugs).	Highly urbanised areas impacted by WWTP effluents.	Cold season.
(b)	Industrial chemicals and human medicines including hormones with continuous releases (contraceptives, human hormones, medicines applied for chronic diseases).	Highly urbanised areas impacted by WWTP effluents.	Low rainfall - dry season.
(c)	Herbicides and animal hormones.	Rural zones with high agricultural production. Urban zones to some extent.	Low rainfall - dry season. Pre-emergent herbicides also in the pre- and post-growing period coinciding with rainfall.
(d)	Insecticides.	Rural zones with high agricultural production.	Dry season.
(e)	Veterinary medicines.	Rural zones with high farming activity, pasture or animal housing.	Dry season.
(f)	Sunscreen chemical	Highly urbanised areas impacted by WWTP effluents. Swimming lakes, coastal zones with high tourist activity and low mixing.	Year round with summer maxima.

Table 2.3. English monitoring stations, and indicative land use and rationale for sampling.

Region	Site I.D.	Site name	Land use and rationale
North West	88016096	WINDERMERE SOUTH BASIN	Grassland, forestry. Bathing water (lake).
North West	88002324	RIVER IRWELL AT OLD RINGLEY BRIDGE	Urban (no WWTP impact)
Midlands	50050	RIVER LUGG AT MORDIFORD BRIDGE	CSF - Grassland

Midlands	04465640	RIVER CHELT PRINCESS ELIZABETH WAY	Urban (no WWTP impact)
Midlands	13598380	RIVER TEME AT POWICK	Grassland (and fruit- growing) CSF to 2015
Midlands	59010550	RIVER TAME - U/S COLESHILL STW	Urban - d/s WWTP - Minworth
Thames	E0000770	SOMERHILL STREAM OLD FORGE FM	Urban - d/s WWTP - Tunbridge Wells North.
Anglia	WAV120	R.WAVENEY ELLINGHAM MILL	CSF - Arable
Anglia	WEN250	R.WENSUM SWEET BRIAR RD.BR	CSF - Arable
Anglia	ANCOC	R.ANCHOLME HORKSTOW BOTTOM	Industrial/urban
Anglia	SIND4	SINCIL DYKE WASHINGBOROUG H	Urban - d/s WWTP - Lincoln
North East	49100488	RIVER OUSE AT NETHER POPPLETON (SKELTON)	CSF - Mixed
North East	49400709	WYKE BECK BELOW KNOSTROP WORKS FE	Urban - d/s WWTP - Knostrop
North East	42600397	BLYTH AT Industrial/urban BEDLINGTON BRIDGE	
Anglia	12M08	RIVER OUSE ROXTON LOCK	Mixed arable/grassland
Anglia	ANCN5	R.ANCHOLME CADNEY BOTTOM	CSF Arable (vegetables)
North West	88006427	RIVER EDEN AT SHEEPMOUNT	CSF1 – grassland
Southern	G0003890	RIVER TEST LONGBRIDGE	CSF1 – grassland

CSF – Catchment Sensitive Farming area.
CSF1 - Regular monitoring at these two sites does not include pesticides.
WWTP – Wastewater treatment plant.
U/S – Upstream.
d/s – Downstream.

Annex 3.

Description of the representativeness of the Watch List monitoring stations and of the monitoring strategy for surface waters in <u>Wales</u>.

Selection of monitoring stations.

Across Wales and during 2016, four freshwater river stations were selected for monitoring Watch List (WL) substances. Monitoring was targeted to those sites where they were most likely to be detected, based on expected usage or route to the environment. The stations are described below and were selected to represent:

- Background levels. RIVER MAWDDACH TY'N Y GROES HOTEL BRIDGE (UK0CYMW20003). This station is unaffected by major wastewater treatment works (WWTWs), industrial discharges nor intensive agriculture;
- Urban-affected concentrations. RIVER ALYN AT ITHELS BRIDGE (UK0CYMW6). This location is significantly impacted by urban WWTWs, combined sewer overflows and industry;
- Rural-arable farming-affected levels. TROTHY AT ONEN (UK0CYMW50319). This site
 is significantly impacted by arable agriculture; and
- Rural-livestock affected concentrations. TOWY NANTGAREDIG, near CARMARTHEN (UK0CYMW31601). This station is significantly impacted by livestock agricultural practices.

All of the17WL substances were analytically screened for in samples taken at the background station (see Table 3.1). For surface water samples acquired at the urban station, the pharmaceutical (diclofenac), synthetic and natural steroids (E1, E2 and EE2), the antibiotics (erythromycin, clarithromycin, and azithromycin) and the industrial and sunscreen chemicals (2,6 di-tert-butyl-4-methylphenol and 2-ethylhexyl-4-methoxycinnamate sunscreen) were monitored. The three steroids as well as the pesticides (methiocarb, oxadiazon, Tri-allate) and the five neonicotinoids (Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin and Acetamiprid) were monitored at the rural livestock) station. The pesticides (methiocarb, oxadiazon, Tri-allate) and the five neonicitinoids were monitored at the rural arable station.

Monitoring frequency and period of monitoring.

Two sampling occasions were performed; one in August and one in November 2016. For each class of WL substance, the sampling month and station location is summarised in Table 3.1.

For those samples taken in August, chemical analyses were conducted for the following substances: diclofenac; the three antibiotics, methiocarb, oxadiazon and Tri-allate pesticides, and the industrial and sunscreen substances. This was based on the fact that dilution in waste water treatment works and receiving rivers would be expected to be lowest during the summer even though use of the antibiotics is generally higher in winter months. Due to technical issues, analytical concentration data were not available for the three steroids Sampling for neonicotinoid pesticides took place in early November 2016, as well as resampling for the three steroids. This was later than would have been ideal to reflect the expected period of greatest usage especially for the pesticides.

Table 3.1. Description of sampling month and sample station locations in Wales for each group of WL substances.

Watch List	2016 sampling	Station
substance	month	locations
Pharmaceutic	August.	Background
al		and
Diclofenac		Urban.
Antibiotics:		
Erythromycin		
Clarithromycin		
and		
Azithromycin.		
Natural and	November.	Background,
synthetic		urban and
steroids		rural
E1		(livestock).
E2, and		
EE2.		
Industrial and	August.	Background
sunscreen		and
2,6 di-tert-		urban
butyl-4-		
methylphenol, and		
2,6 di-tert-		
butyl-4-		
methylphenol		
Pesticides	August.	Background,
Methiocarb	August.	rural (arable)
Oxadiazon and		and
Tri-allate.		rural
Til-allate.		(livestock).
Neonicotinoid	November	Background,
pesticides	TAOVOITIDGI	rural (arable)
Imidacloprid		and
Thiacloprid		rural
Thiamethoxam		(livestock).
Clothianidin		(
and		
Acetamiprid.		

Surface water sample pre-treatment in Wales

Samples in Wales were collected in clear glass bottles. These were stored chilled (4C) in the dark and were extracted within 30 days.

Annex 4.

Description of the representativeness of the Watch List monitoring stations and of the monitoring strategy for surface waters in Scotland.

Selection of monitoring stations.

Across Scotland, four freshwater river stations were selected for monitoring Watch List (WL) substances.

Pesticide monitoring sites were chosen from the Competent Authority's Priority Catchment Programme. Large catchments with a high density of farms were targeted. Thus factors such as crop rotation or changes in crop types year-on-year were less likely to affect overall annual usage and water body concentrations of the likes of pesticides at the catchment scale.

The sample stations are described below and were selected to represent:

- Background station. Allt an Dubh Loch (Location 204173). No known inputs of WL substances.
- Urban. River Clyde (Location: 12115). Highly urbanised catchment impacted by WWTP effluents and urban diffuse sources.
- Rural #1. River Ugie (Location 205225). Rural catchment with high agricultural production; and
- Rural#2. River Ythan (Location 205148). Rural catchment with high agricultural production (which is different in terms of crop production and pesticide usage compared to Rural#1).

Frequency of sample collection.

Table 4.1 details the month in which surface water samples were collected for chemical analyses of WL substances.

Table 4.1. Frequency of surface water sample collection from Scottish Watch List samples station.

Substance	Location	Sample	Sampling	Method of analysis
class	type	station	month	
Pesticides	Rural	River Ugie	Septembe	LC-MS semi-quantitative
	catchment	(Rural#1)	r	method for:
	with high		2016	Imidacloprid, Thiacloprid,
	agricultural			Thiamethoxam,
	production			Clothianidin, Acetamiprid,
		River Ythan		Methiocarb*, Oxadiazon,
		(Rural#2)	Septembe	Tri-allate
			r	Erythromycin,
			2016	Clarithromycin,
				Azithromycin, Diclofenac)
Steroidal	Highly	Catchment:	March	Fully quantitative LC-MS
oestrogens,	urbanised	Glasgow coastal	2016	analysis for:
Pharmaceuti	catchment	Waterbody: Clyde	and	17-alpha-ethinylestradiol
cals,	impacted by	Coordinates:	Septembe	(EE2), 17-beta-estradiol
Industrial	WWTP	59500, 64400	r	(E2), Estrone (E1),

chemicals	effluents and diffuse sources	Location code: 121157	2016	GCMS screen: 2,6-di- tert-butyl-4- methylphenol, 2- ethylhexyl-4- methoxycinnamate Semi-quantitative LC-MS analysis for: Erythromycin, Clarithromycin, Azithromycin, Diclofenac Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin, Acetamiprid, Methiocarb*, Oxadiazon, Tri-allate)
All substances	Background site	Catchment River Dee (Grampian) Waterbody: Allt an Dubh-loch Coordinates: 326596, 782091 Latitude 56.9242677, longitude - 3.2075254 Location code: 204173	Septembe r 2016 and October 2016	All substances (4 methods: 3 sub- contracted methods + in- house analysis for Methiocarb*)

^{*}In-house fully quantitative Methiocarb analysis also carried out for information but not reported – none detected).

Annex 5.

Description of the representativeness of the Watch List monitoring stations and of the monitoring strategy for surface waters in Northern Ireland.

Monitoring regime and stations.

The sampling regime applied in Northern Ireland (NI) as well as the other UK Administrations reflected where a watch list (WL) substance is expected to be used and the effect of seasonality (see Tables 1 and 2, above). As number of WL substances have documented usage in NI (http://www.afbini.gov.uk/index/services/services-specialist-advice/pesticide-usage/pesticide-reports-table.htm). These include the neonictionoid pesticides: Imidacloprid, Thiacloprid, and Clothianidin; and the carbamate pesticide, Methiocarb.

Surface water sampling was applied in river catchments where water bodies are subjected to agricultural- and urban-related pressures. This consideration was important for NI to allow adequate cover based on these criteria. A background (control) station and two monitoring stations were identified for the purpose of collecting samples and these are described in Table 5.1:

Table 5.1. Locations of surface water sampling stations for Watch List substance Monitoring in Northern Ireland.

WL substance class	WL substance	Location type	Selected NI River Basin District sites	Comment
Pesticides.	Imidacloprid, Thiacloprid, Thiamethoxa m, Clothianidin, Acetamiprid. Methiocarb Oxadiazon Tri-allate.	Rural catchment with high agricultural production.	Quoile River at Quoile Bridge, North East RBD Sampled in autumn and spring/summe r months. [Total 2 samples].	Sample timing within relevant catchment more important.
Steroidal oestrogens, anti-biotics, pharmaceutica I, industrial and sunscreen chemicals.	E1 E2 EE2. Erythromycin, Clarithromycin , Azithromycin. Diclofenac. 2,6-di-tert- butyl-4- methylphenol 2-ethylhexyl-4- methoxycinna mate.	Highly urbanised catchment impacted by WWTP effluents and diffuse sources.	River Lagan at Stranmillis Weir station, North East RBD. Sampled in summer month with low flow and winter month. [Total 2 samples].	Antibiotics and diclofenac: livestock as a source not being investigated.

All WL	As above.	Background	Dunnyboe	Unimpacted
substances.		'Control' site.	Burn at	remote
			Dunnyboe	location.
			Bridge,	
			North West	
			RBD	
			Sampled	
			winter	
			[Total 1	
			sample].	

Contact us: Buglife, Bug House, Ham Lane, Orton Waterville, Peterborough, PE2 5UU

www.buglife.org.uk

Tel: 01733 201210

Email: info@buglife.org.uk

@buzz_dont_tweet

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