Using water industry data to assess the metaldehyde pollution problem

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Abstract

The presence of metaldehyde in raw and treated water has become a recognised problem recently. The current study used water industry monitoring data collected over a two and a half year period (2008-11) to quantify the presence of metaldehyde in rivers and finished waters. Measured surface water concentrations were then compared to catchment characteristics in an attempt to identify those factors driving losses of the pesticide to water. An assessment was also made of the robustness of the monitoring strategy used, which was assumed to represent typical water industry practice, and is currently being used to develop catchment management plans. It was found that exceedance of the European Union pesticide standard (0.1 µg/l) during the October to December slug pellet application period is commonplace. Peak concentrations were generally in the 0.4-0.6 µg/l range although sometimes were an order of magnitude higher.

Keywords: metaldehyde; monitoring; pesticide; pollution; water industry; water quality.

1. Introduction

Metaldehyde is a synthetic aldehyde pesticide used globally in agriculture, usually in pellet form, for the control of slugs and snails (i.e. a molluscicide) (Li et al., 2010; NFU, 2011). It has been used since the 1940's and is the active ingredient in 80 % of slug pellets (PPDB, 2011). With the advent of improved analytical techniques metaldehyde has now began to be detected in surface waters (Gillman et al., 2012) and was identified in a recent review as a pesticide of emerging concern for water pollution (Stuart et al., 2012). To-date, very few studies have quantified the presence of the substance though. A recent investigation in northern France (Lazartigues et al., in press) found that metaldehyde was frequently present in fish farming ponds receiving agricultural runoff at concentrations above the 0.1 µg/l EU regulatory

standard (EC, 1998). Peak concentrations were as high as 6.98 µg/l. It is proposed that the compound reaches waters in three ways; point sources (e.g. due to spillage during pesticide spreader filling operations), accidental direct application to waterbodies, and diffuse runoff. In an unpublished study in the Cherwell catchment, UK, 1.8 % of the applied active ingredient was lost to surface waters and very high peak concentrations of up to 9.8 µg/l were reported (NFU, 2011).

Available environmental fate data show that metaldehyde can be very mobile in the environment with measured K_{oc} (organic carbon sorption coefficient) values ranging between 34 and 240 l/kg (IPCS, 1999; PAN, 2010; PPDB, 2011). K_{oc} values are routinely used to describe the mobility of pesticides and range from less than 100 l/kg to hundreds of thousands, lower values indicate that a substance will be more mobile in the environment. This concurs with monitoring data that have shown losses to waterbodies within 1-4 days of application to land (Calumpang et al., 1995; Lazartigues et al., in press). Degradation in soil varies depending on conditions and reported half-life ranges between 3.17 and 223 d (IPCS, 1999; PAN, 2010; PPDB, 2011; Ma et al., 2012). These data would indicate that in agricultural environments at the time of application (autumn/winter) metaldehyde has the potential to be persistent and mobile. Furthermore, metaldehyde's characteristics mean that it is not amenable to removal from water using Granular Activated Carbon (GAC); the process normally used to reduce pesticide concentrations in drinking water. It is also a simple molecule that cannot be broken down by other treatment processes, including chlorination and ozonation (NFU, 2011).

The dearth of data to describe the presence of this commonly used pesticide in the aquatic environment, its physicochemical properties, excessive initial monitoring values and its recalcitrance in treatment processes mean that further studies are merited. The first objective of this paper was therefore to quantify the presence of

metaldehyde in a range of surface and drinking waters. A second aim was to determine key sources of metaldehyde in river catchments. This task was important as catchment management is likely to be the only way of addressing concentrations in drinking water given the inability of current treatment techniques to remove the substance.

2. Methodology

2.1 Monitoring sites and sampling

The data used in the current study was produced by a regional water utility in the UK for regulatory purposes and to develop catchment management plans to alleviate pollution. Water samples were collected between April 2008 and August 2011 at 9 water treatment works (WTW) and 21 river channel sites throughout the Ouse catchment in the Yorkshire region of the UK (Figure 1). The WTW were selected for the study as previous occasional detections of metaldehyde had been made at them following the development of an analytical method for metaldehyde in water (Environment Agency, 2009). The surface water monitoring sites provided a range of accessible locations (close to roads) that covered various stream orders along watercourses providing untreated water to the different WTW. At each of the WTW samples were collected at the inlet and outlet in order that concentrations reaching the drinking water distribution system could be quantified. In the first year of monitoring samples were collected at WTW every 2-4 weeks although this frequency was increased to weekly for the remainder of the study. Samples were collected from the river monitoring sites between February 2010 and July 2011 and the sampling interval varied between 1 and 4 months, being most intensive during the autumn/winter metaldehyde application period. Samples were collected in 500 ml glass bottles, returned to the laboratory, stored in the dark at 4 ˚C and analysed within 2 weeks.

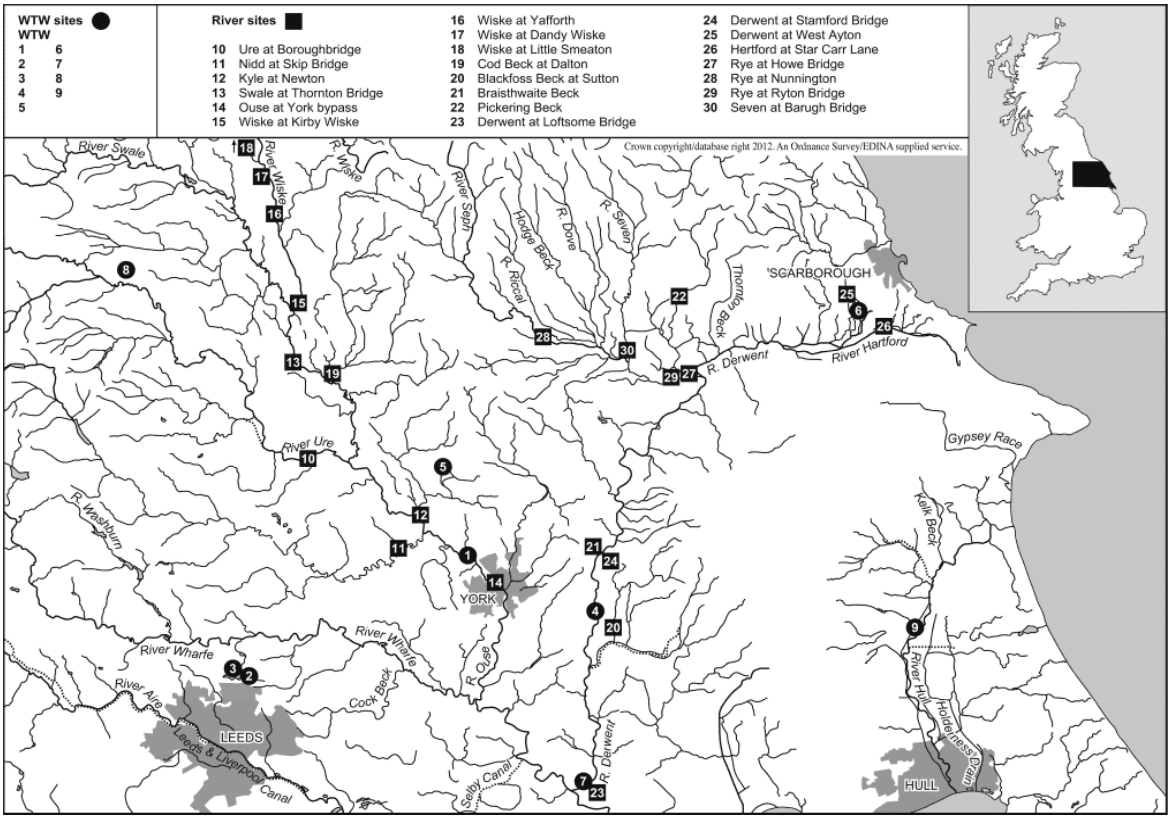

Figure 1. The location of sampling sites where water was collected for analysis of metaldehyde. These were situated at water treatment works (WTW) and river channels throughout the Ouse catchment, Yorkshire, UK.

2.2 Chemical analysis

A 250 ml volume of each water sample was filtered through a 0.8 µm Whatman membrane and metaldehyde extracted using pre-rinsed Phenomenex Strata-X solid-phase extraction cartridges at a flow rate of 10 ml/min. The compound was then eluted using a mixture of ethyl acetate and acetone followed by iso-octane. Laboratory recovery tests where river water was spiked with known concentration of metaldehyde showed that this method produced recoveries of 93.39 %. Metaldehyde concentrations in extracts were then determined using a Hewlett Packard Agilent 6890 Gas Chromatography-Mass Spectrometry (GC-MS) system. The limit of quantification was 2 ng/l.

2.3 Catchment characteristics dataset

In order to determine those catchment attributes associated with metaldehyde losses to water a range of catchment characteristics were selected which were likely to be important and for which datasets were available. These were percentage cover of wheat, winter barley, oil seed rape, permanent grassland, and soils likely to generate quickflow (Hydrology of Soil Types (HOST) classes 18, 19, 21, 22, 24 and 25; Boorman et al., 1995), as well as the mean slope of land in the catchment. Catchment characteristics were then compared to peak metaldehyde concentrations using regression analysis.

To compile the Geographical Information System (GIS) database the location of each sampling point was first added so that its effective catchment could be determined. Flow direction and accumulation were calculated from a digital terrain model (DTM; Ordnance Survey Land-Form Panorama DTM dataset with 50 x 50 m resolution) in ArcGIS using the Hydrology Toolbox. The Watershed Tool was then used to calculate the catchment area draining to each sampling point and a raster dataset created for each catchment. Defra annual farm survey data for 2005 were used to estimate crop and livestock production in the study catchments as since 2006 these data have only been available at the county scale, thus providing a much poorer spatial resolution. An average percentage cover of each land use type was calculated for each catchment. Using the National Soil Map for England and Wales (NATMAP) the HOST class was calculated for each soil type present in the study catchments and the data converted into a 50 x 50m resolution raster. The percentage of each catchment covered by the selected HOST classes was determined. WTW 6 was not included in this analysis as raw water is abstracted from groundwater, the chemical characteristics of which may not reflect current land use in the catchment given the long transit times of water through aquifers. Similarly, WTW 8 was not included as raw water is blended from different sources and contributions

from the different catchments could vary. Although data from WTW 7 and 9 have been included it should be noted that samples were taken from storage reservoirs and so degradation of metaldehyde may have occurred here before the water was sampled.

3. Results

3.1 Metaldehyde concentrations in river and drinking water

Peak concentrations of metaldehyde were in excess of 0.1 µg/l at eight of the nine WTW investigated (Table 1) and were generally in the range 0.2-0.4 µg/l, although higher concentrations of up to 2.7 µg/l were detected. Due to the transient nature of metaldehyde detections median concentrations were an order of magnitude lower than this though. A one-way ANOVA showed that there was no significant difference ($p=>0.05$) in metaldehyde concentrations in water at the inlet and outlet of any of the WTW. A distinct seasonal pattern existed in metaldehyde detections (Figure 2) with peaks generally being experienced between October and December. Those measured at WTW 9 spanned a greater period however; covering the months of September through to February. Maximum metaldehyde concentrations measured at the additional river monitoring sites varied between 0.016 and 1.08 µg/l (Table 2). Even though these monitoring locations were only sampled between 4 and 8 times (with the exception of the River Derwent at Loftsome Bridge) the regulatory limit was exceeded at 11 of the 21 sites.

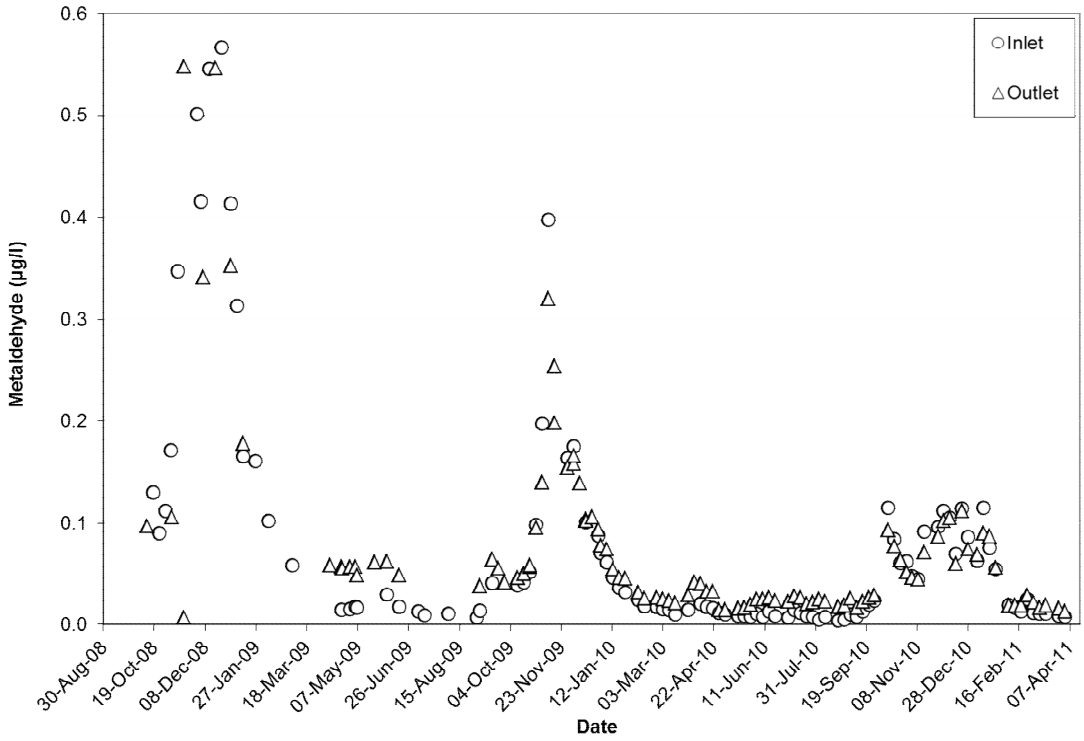

Figure 2. Metaldehyde concentrations measured at the inlet and outlet to water treatment works 7, Yorkshire, UK, in the current study.

3.2 Comparison of metaldehyde concentrations and catchment characteristics

Data describing catchment attributes in the study areas are given in Table 3. Regression analysis showed that there was no significant relationship (p=>0.05) between any of the catchment attributes measured and peak metaldehyde concentrations recorded in raw water at WTW and additional river monitoring sites (Table 4).

4. Discussion

4.1 Concentrations of metaldehyde in surface waters

Peak concentrations of metaldehyde were in excess of the EU regulatory limit (0.1 µg/l) at 8 of the 9 WTW and 11 out of 21 additional river monitoring sites. Despite the substance having been in use for around seventy years this is one of the first studies to measure its presence in rivers. The maximum concentration detected was 2.72

µg/l which is of the same order of magnitude as reported in the few other existing studies that have monitored metaldehyde in waters (NFU, 2011; Lazartigues et al., in press). Despite the very small number of published studies it appears that metaldehyde represents a very significant water quality concern, having already been found at concentrations as high as other pesticides that have previously been monitored in rivers and deemed to be problematic (Espigares et al., 1997; Power et al., 1999; Brown et al., 2002; Du Preez et al., 2005). For instance, these concentrations are of the same order of magnitude as the highest reported in the study by Brown et al. (2002) who used a comprehensive pesticide monitoring database comprising of over 1.5 million analyses undertaken in the UK between 1992 and 1998 by the Environment Agency and water utilities. Even though median concentrations of metaldehyde are generally an order of magnitude lower than peak detections, as has been demonstrated in other studies of pesticides in surface water (e.g. Schulz et al., 1998), a problematic period typically exists for several months of the year (October-December). Recent research by the Metaldehyde Stewardship Group (MSG) in the Cherwell catchment, UK, has shown that most metaldehyde is lost in the initial storm event following application (Kilburn, 2010). Because of this, it may be the case that concentrations at catchment outlets represent inputs from individual areas of land where slug pellets were applied at different times during the autumn/winter application period and that for ditches and small streams draining individual fields concentrations above 0.1 µg/l will only be measured in the first runoff generation event following application.

4.2 Effects of measured metaldehyde concentrations

As there was no significant difference in WTW inlet and outlet concentrations, the current study has also supported the available evidence to show that metaldehyde is not removed by contemporary drinking water treatment methods. Nevertheless, the Acceptable Daily Intake (ADI) for the substance is 20 µg/kg/d in humans. Minor

effects (e.g. vomiting) have been observed at several mg/kg and serious impacts do not occur until concentrations above 100 mg/kg are reached, with death being reported at 400 mg/kg (Ellenhorn, 1997). In the environment, a 21 d NOEC (No Observed Effect Concentration) of 37.5 mg/l has been reported for fish whilst the respective figure for aquatic invertebrates was 90 mg/l. A 72 h EC_{50} (Effect Concentration for 50 % of test population) of 75.9 mg/l was reported in a growth test on algae and an LC_{50} (Lethal Concentration for 50 % of test population) of >1000 mg l^{-1} was reported for earthworms (PPDB, 2011). Even though such high concentrations of metaldehyde have been measured in rivers and drinking water it would thus seem, given the available data, that impacts in humans and aquatic organisms are unlikely. Nevertheless, exceedence of the EU drinking water standard would necessitate removal of the active ingredient from the market. This raises questions about regulatory limits being based on arbitrary values (0.1 µg/l) rather than effects data.

4.3 Relationships between catchment characteristics and metaldehyde pollution

Regression analysis indicated that there were no significant relationships between the catchment characteristics measured and metaldehyde detections. This may indicate that it is not catchment attributes such as soil type and land use that are driving differences in metaldehyde losses to water but practices carried out on individual farms for which data were not available. These may include factors such as the metaldehyde product used, application rate, technique and timing.

Other useful observations can be made. Data from WTW 2 has a much lower peak concentration when compared to the other WTW sites of 0.07 µg/l which is hypothesised to be due to the catchment containing little arable agriculture, unlike all of the others. The catchment contained 93 % permanent grassland and no arable agriculture whereas in the other study catchments the maximum area of grassland

was 51 %. The data for this catchment support the logical hypothesis, given that slug pellets are applied predominantly to arable crops, that catchments which contain more arable agriculture will experience higher levels of metaldehyde losses to water.

4.4 Influence of sampling regime on the dataset

One of the most important parts of any water quality monitoring study is the use of an appropriate sampling regime so that the data collected accurately reflect conditions at the study site (Ort et al., 2010). In fact, samples that do not do this are often the main source of error in a dataset (Martin et al., 1992), particularly as advances in analytical chemistry are made (Ort et al., 2010). The dataset that was used in the current study was obtained from a water utility and so the sampling design could be assumed to reflect standard water industry practice. In addition to providing some of the first data on metaldehyde in the environment the current study is therefore also able to critique contemporary monitoring practices used by the water industry to develop management strategies. It is likely that the sampling regime employed has had a significant influence on the dataset and it has been concluded by some authors (Petersen et al., 2005; Rabiet et al., 2010) that grab sampling is not suitable for accurately measuring pesticide losses to surface waters. Indeed, in the current study grab samples were often collected days or weeks apart so that metaldehyde concentrations in the interim are unknown. Rabiet et al. (2010) found that weekly grab sampling underestimated pesticide losses to water by five times when compared to composite sampling using an automatic water sampler. Their work highlighted the importance of capturing storm events, which accounted for 89 % of diuron losses, in agreement with other studies which have reported that between 84 and 90 % of pesticides are lost, at the catchment scale, during high flow events (Louchart et al., 2001; Chen et al., 2005). Moreover, sampling was not undertaken at the same time at different WTW and so comparison between them is sometimes difficult. The impact of the sampling regime is exemplified by the case of WTW 1, 3

and 5 which take raw water from the same source but for which peak concentrations were an order of magnitude different at 2.72, 0.46 and 0.42 µg/l respectively. This is likely to be because sampling was not carried out at WTW 1 and 5 on the day that this very high concentration was measured at WTW 1. Nevertheless, from a practical viewpoint, it is difficult to imagine a study with such great spatial coverage as the current one where these problems can be avoided entirely. More spatially and temporally intense sampling has been recommended recently as a necessity to overcome similar criticisms made of diffuse pollution sampling in general. This would allow better identification of pollution sources and quantification of the effects of mitigation actions (Kay et al., 2012). If the metaldehyde pollution problem is to be dealt with effectively it will be necessary to improve the water industry sampling regimes that are being used to develop mitigation plans.

4.5 Future research directions

Despite metaldehyde having been in use since the 1940s it is seen as an emerging pollutant (Stuart et al., 2012) and the dearth of existing research means that there are still many questions to be answered regarding the compound's environmental occurrence, fate, effects and management. Further monitoring of metaldehyde is urgently needed as there are almost no studies assessing its presence in the environment and those that have been undertaken (NFU, 2011; Gillman et al., 2012; Lazartigues et al., in press) have detected it at extremely high concentrations in waterbodies of almost 10 µg/l, an order of magnitude higher than the EU regulatory limit. This research is therefore needed to determine the severity of the metaldehyde pollution problem which will then provide a basis for further investigations on fate, effects and management. Moreover, improved monitoring strategies, based on composite sampling for instance, are needed to produce datasets which robustly describe the substance's presence in aquatic systems. Environmental fate data for metaldehyde are limited and further work to assess persistence and mobility under

different environmental conditions would be useful. This should include studies of the presence and fate of chemical metabolites in the environment as the main metabolite of metaldehyde, acetaldehyde, has recently been identified as having the potential to be mobile (Stuart et al., 2012).

Similarly, effects data are limited to a few standard laboratory studies that have used acute end points in short-term microcosm tests (PPDB, 2011). Whilst no negative impacts have been observed to date, these studies offer a rather simplistic viewpoint in ecological terms and longer-term chronic studies are needed to provide a more detailed understanding of the impacts that metaldehyde might be having in the environment. Practical studies are also needed to assess the effectiveness of best management practices for reducing metaldehyde pollution as currently none of those that have been undertaken (e.g. see Kay et al. (2009) for a review of pesticide research) has studied metaldehyde.

5. Conclusion

1. This is one of the first papers to quantify concentrations of metaldehyde in the environment
2. The EU pesticide regulatory standard of 0.1 µg/l is frequently exceeded for metaldehyde in surface waters during the autumn/winter slug pellet application period and peak concentrations may be an order of magnitude higher than this.
3. Beyond being a problem associated with arable catchments, it was not possible to determine those factors driving metaldehyde pollution. The lack of correlation with the crop and soil types tested, as well as slope, suggests that other variables are important, which may include application technique, timing and the specific product used.
4. Contemporary water treatment techniques do not remove metaldehyde and it may be present in drinking water. Nevertheless, toxicity data indicate that the

316 metaldehyde concentrations measured do not represent a health risk to humans or
317 aquatic ecosystems.
318 5. This raises questions about setting a regulatory limit for pesticides that is not
319 compound specific and does not take effects data into account.
320 6. Under the current regulatory system, effective actions are urgently needed to
321 eliminate the risk of the compound being withdrawn from the market.
322 7. Water quality monitoring strategies have been discussed and future studies should
323 endeavour to ensure that the samples collected are as representative of
324 environmental conditions as possible which will subsequently aid the development of
325 effective management strategies.
326

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330

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Figure captions

Figure 1. The location of sampling sites where water was collected for analysis of metaldehyde. These were situated at water treatment works (WTW) and river channels throughout the Ouse catchment, Yorkshire, UK.

Figure 2. Metaldehyde concentrations measured at the inlet and outlet to water treatment works 7, Yorkshire, UK, in the current study.

Tables

Table 1. Summary data describing metaldehyde concentrations measured at the inlet and outlet of nine water treatment works (WTW) in Yorkshire, UK.

WTW	Metaldehyde concentration (µg l^{-1})							
	Inlet				Outlet			
	n	Max	Median	Min	n	Max	Median	Min
1	105	0.435	0.018	0.002	92	0.490	0.021	0.003
2	28	0.071	0.014	0.007	88	0.071	0.014	0.007
3	97	2.724	0.018	0.002	88	0.380	0.020	0.006
4	91	0.276	0.016	0.002	90	0.567	0.018	0.002
5	84	0.417	0.020	0.005	87	0.735	0.022	0.006
6	68	0.362	0.007	0.002	47	0.048	0.006	0.002
7	101	0.567	0.024	0.004	104	0.548	0.049	0.007
8	72	0.407	0.007	0.002	46	0.021	0.008	0.002
9	75	0.180	0.012	0.002	73	0.126	0.014	0.002

462

463 Table 2. Metaldehyde concentrations measured in rivers throughout the Yorkshire

464 region, UK, during the period 2010-11.

Sampling site	Metaldehyde concentrations (µg l^{-1})			
	n	Max	Median	Min
Ure at Boroughbridge	7	0.026	0.009	0.002
Nidd at Skip Bridge	8	0.090	0.022	0.007
Kyle at Newton	8	0.230	0.054	0.018
Swale at Thornton Bridge	8	0.369	0.022	0.007
Ouse at York bypass	8	0.169	0.027	0.008
Wiske at Kirby Wiske	6	0.517	0.078	0.012
Wiske at Yafforth	4	0.557	0.088	0.013
Wiske at Danby Wiske	4	0.658	0.082	0.013
Wiske at Little Smeaton	4	0.259	0.090	0.013
Cod Beck at Dalton	6	0.168	0.053	0.005
Blackfoss Beck at Sutton	5	0.070	0.023	0.017
Braisthwaite Beck	4	0.107	0.076	0.017
Pickering Beck	4	0.026	0.011	0.017
Derwent at Loftsome Bridge	113	1.080	0.023	0.005
Derwent at Stamford Bridge	5	0.037	0.024	0.002
Derwent at West Ayton	4	0.037	0.023	0.009
Hertford at Star Carr Lane	4	0.362	0.207	0.004
Rye at Howe Bridge	5	0.023	0.015	0.025
Rye at Nunnington	4	0.016	0.009	0.011
Rye at Ryton Bridge	4	0.026	0.020	0.004
Seven at Barugh Bridge	4	0.043	0.018	0.010

Table 3. Individual catchment characteristics for those attributes that were compared to measured peak metaldehyde concentrations in order to assess catchment predictors of pollution. For catchment names refer to Figure 1. HOST = Hydrology Of Soil Types (Boorman et al., 1995). The classes included in this analysis are associated with quickflow generation.

Attribute	Catchment																												
	1	2	3	4	5	7	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Wheat (%)	22	0	22	27	22	15	39	6	23	6	15	12	26	28	28	23	18	23	22	24	15	15	13	22	12	8	8	11
Winter barley (%)	7	0	7	11	7	6	4	2	7	2	5	4	7	7	7	6	7	2	8	1	6	6	2	7	5	4	5	3
Oil seed rape (%)	5	0	5	7	5	4	10	1	7	2	3	3	5	5	6	5	5	5	8	5	4	4	5	7	3	2	3	1
Permanent grassland (%)	51	93	51	34	51	19	14	33	15	35	24	27	24	22	22	24	23	12	18	13	19	19	12	14	22	23	22	25
Mean slope (˚)	4	7	4	4	4	4	2	5	1	4	4	4	2	2	2	3	4	2	2	4	4	4	3	2	5	6	5	5
HOST classes 18, 19, 21, 22, 24, 25 (%)	38	35	38	31	38	28	27	20	48	48	42	49	83	87	86	80	62	69	85	4	28	26	0	24	24	0	22	35

469 Table 4. Regression analysis of the relationship between catchment characteristics
470 and peak metaldehyde concentrations measured at water treatment works intakes
471 and other river monitoring sites (n = 30). HOST = Hydrology Of Soil Types (Boorman
472 et al., 1995). The classes included in this analysis are associated with quickflow
473 generation.

Catchment attribute	R^2	p
% wheat	0.05	>0.05
% winter barley	0.13	>0.05
% oil seed rape	0.02	>0.05
% permanent grass	0.06	>0.05
Mean slope (º)	0.01	>0.05
% HOST classes 18, 19, 21, 22, 24 and 25	0.02	>0.05

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