2022-11-01

Assessing the impact of wastewater treatment works effluent on downstream water quality

Comber, Sean

http://hdl.handle.net/10026.1/19462

Assessing the impact of wastewater treatment works effluent on downstream water quality

S.D.W. Comber [a,*], M.J. Gardner [b], L. Ansell [a], B. Ellor [c]

[a] Biogeochemistry Research Centre, Plymouth University, A531 Portland Square, Drake Circus, Plymouth, Devon PL4 8AA, UK
[b] wca, Brunel House, Volunteer Way, Faringdon, Oxon SN7 7YR, UK
[c] UK Water Industry Research, 36 Broadway, London, UK

HIGHLIGHTS

- Analysis of over 600 sites upstream and downstream of wastewater treatment works
- Compliance taking account of bioavailability of metals is very high.
- Wastewater treatment works discharges show little local impact for many chemicals.
- Contaminations for many priority chemicals are on a catchment scale.

GRAPHICAL ABSTRACT
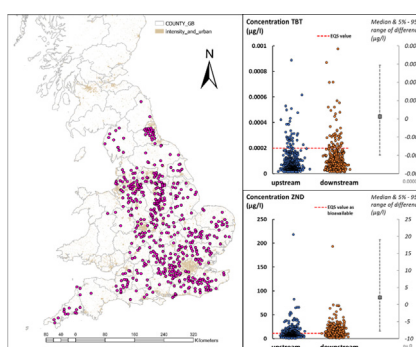
ABSTRACT

The impact of wastewater treatment works (WwTW) effluent on downstream river water quality is of increasing concern, particularly owing to the presence in effluents of a range of trace substances. In the case of contamination by metals the question of bioavailability has recently been accounted for in setting water quality standards for several metals. In the UK over the past decade the Chemical Investigations Programme (CIP) has generated upstream and downstream river quality data as well as associated WwTW effluent monitoring for over 600 sites, for the main contaminants of regulatory interest under the Water Framework Directive. Data presented here show that at a local level WwTW discharges have little impact for many contaminants. Soluble reactive phosphorus, hexabromocyclododecane (HBCDD), cypermethrin, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have been shown to be the principal substances where downstream concentrations were at least 10 % larger than the upstream value. Otherwise, poor compliance with riverine water quality standards tends to be associated with contamination at the river catchment scale, with corresponding implications for the nature of remedial actions that are likely to be successful. Compliance with water quality criteria for metals, taking account of bioavailability, is high overall.

1. Introduction

Wastewater treatment works in the EU27 and UK combined, discharge over 100 million m³ of effluent into receiving water a day (Eurostat, 2021)

making this sector a potentially important source of contaminants to the aquatic environment (Gardner et al., 2012; EEA, 2021). Stringent Environmental Quality Standards (EQS) are now established under the Water Framework Directive (WFD, EU, 2000) for chemicals. Hence there is increasing focus on identifying important contaminant sources and apportioning any measures required to meet the standards as part of a polluter pays 'fair share' approach. Related to this, is the importance of setting

* Corresponding author.
E-mail address: sean.comber@plymouth.ac.uk (S.D.W. Comber).

EQS for target chemicals based on rigorous scientific principles, particularly the bioavailability of the substance of interest. It has been long established that the form or "speciation" of many trace elements (e.g. copper, nickel, zinc, lead, aluminium, cadmium) controls their toxicity (Paquin et al., 2002). Specifically, it is the most chemically reactive forms of metals that are likely to be of the greatest concern from an ecotoxicological point of view. These forms (notably what has been referred to as the "free metal ion" concentration) is controlled by ambient water quality conditions including, but not exclusively, pH, hardness (or calcium concentration) and dissolved organic complexing agents (both natural and synthetic) generally estimated as dissolved organic carbon (DOC). Although free metal ion concentrations can be estimated analytically using a variety of somewhat empirical methods, typically voltammetry

(Dixon et al., 2000), none are easily applied as part of routine approaches to chemical analysis.

The development of metal speciation models such as the Free Ion Activity Model (FIAM) (Whitfield and Turner, 1979; Hudson, 2005), The Windermere Humic Acid Model (WHAM) (Tipping, 1994), PHREEQC (Marsac et al., 2011) and Visual MINTEQ (Ytreberg et al., 2011) allowed the prediction of metal speciation based on known water quality and reported dissociation constants. Combining the metal speciation with a better understanding of the fate of metals in the natural environment (Dwane and Tipping, 1998; Van Veen et al., 2002) coupled with ecotoxicology data, resulted in the production of biotic ligand models (BLM) for many metals (e.g. Paquin et al., 2002; De Schamphelaere and Janssen, 2004; Santore et al., 2006). These initial models have evolved into simplified
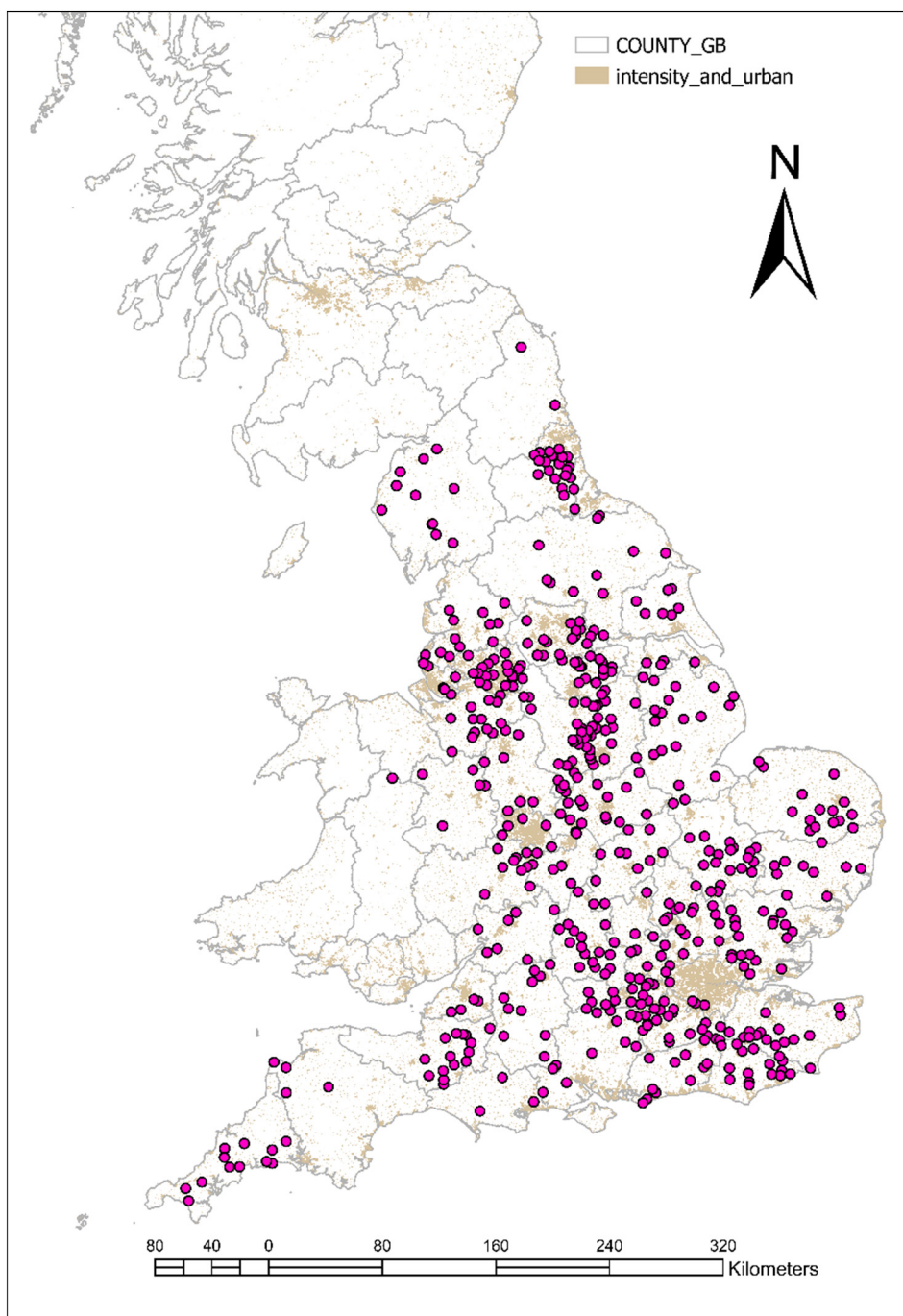

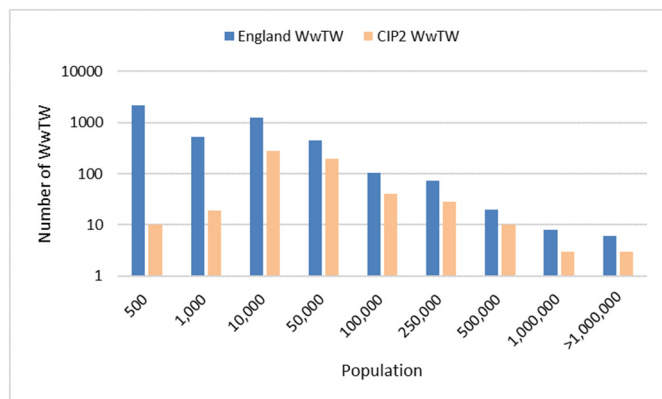**Fig. 1.** Map of CIP2 sampling locations.

Fig. 2. Histogram of frequency of WwTW size for CIP2 compared with England as a whole.

versions (wca, 2015), including BioMET (Peters et al., 2019), MBAT (Rüdel et al., 2015) and PNEC-pro (Verschoor et al., 2017). The reliability of the BLMs has led to the EU and Member States (and other regulators) setting annual average Environmental Quality Standards (EQS) for the Priority Substances lead and nickel and the Specific Pollutants such as copper and zinc, all expressed as bioavailable metal concentrations. The EQS values for the Priority Hazardous Substance cadmium is also set based on water hardness bands (a proxy for bioavailability) (EU, 2006) under the Water Framework Directive (WFD) (EU, 2000). The UK established a tiered approach to assessing bioavailable metal compliance utilising a combination of the bioavailable EQS, simplified BLMs and the 'full' BLM (Comber et al., 2008), which is now being adopted across Europe (EU, 2019). These requirements of the WFD have meant that other European Member States have started to develop and implement BLM based tools (De Schamphelaere and Janssen, 2004; Nys et al., 2016; Rüdel et al., 2015; Schlekat et al., 2010) as well as in other parts of the world (Peters et al., 2018). There is no (bioavailable) equivalent for organic chemicals and compliance is assessed based on samples that may, or may not, have been filtered through a variety of membrane types and pore sizes. This reflects a lack of standardisation, driven by a focus on achieving ever more challenging limits of detection, issues with determinand sorption on equipment and membranes, costs and practicalities etc.

Over 4600 WwTW in England discharge around 10 million m^3 of effluent a day into receiving waters including rivers, estuaries and coastal waters (Eurostat, 2021). A significant proportion (approximately 10 %) of these wastewater discharges are subject to <10 times dilution. The Chemical Investigations Programme (CIP) is a £250 million sampling and analysis programme investigating the sources and treatment of priority chemicals by UK WwTW as well as monitoring levels in effluents and upstream and

downstream receiving waters for over 600 sites with the least available dilution. Strict analytical performance requirements were set at environmentally relevant limits of detection and included total and dissolved metals and with supporting determinands required to run simplified BLMs (dissolved metal, calcium and dissolved organic carbon concentrations and pH). Samples were collected over the course of a year at a typically bi-weekly frequency.

It is often mistakenly assumed that any concerns about poor river water quality downstream of a WwTW discharge are a result of the particular nearby (local) effluent input. This can lead to calls for local remedial measures to be taken, when in fact the influence of the local discharge is often of limited importance because water quality upstream is already poor. The aims of this paper are, firstly, to demonstrate the benefits of the BLM approach to the regulation of metals in surface waters and, secondly, to present data on the local influence of WwTW effluent discharges on water quality and to emphasise the point that in many cases the sources of contamination might need to be identified on a wider river catchment scale, rather than at the local WwTW. The level of compliance with respect to metal concentrations is discussed in relation to recently implemented regulation that is specified in terms of "bioavailable" metal; local effluent impacts for other potential water quality contaminants are also presented.

2. Methodology

2.1. Chemical Investigations Programme

The core objective of the second phase of the CIP programme (2015–2020) was to determine concentrations of priority chemicals, including trace metals, leaving WwTW, including samples taken upstream and downstream of the WwTW discharge. WwTW were not selected at random, because it was a risk-based exercise, WwTW with the least dilution (and therefore likely to be the highest risk to receiving waters) were selected (Fig. 1). However, comparing profiles of size of works, type of treatment and geographic distribution, showed they were representative of the typical WwTW found in the UK (Fig. 2). Over 600 WwTW effluents were characterised across the programme, around 13 % of all WwTW in England. The CIP was split into phases relating to funding and developing objectives based on knowledge generated by ongoing data. The data used in this assessment relates to the second phase (CIP2) and was scheduled over four tranches of work that were undertaken primarily in successive years from 2016 to 2019, each tranche involving approximately 150 WwTW sites across England (605 WwTW sampled in total). Sampling of WwTW effluents involved 20 samples taken at approximately fortnightly intervals. Around 50 determinands were selected based on a previous prioritization exercise and included total and dissolved metal concentrations (aluminium, nickel, lead, copper, cadmium, chromium, mercury, iron and zinc with WFD EQS associated with them, including bioavailability based values) as well as priority and priority hazardous organic pollutants including

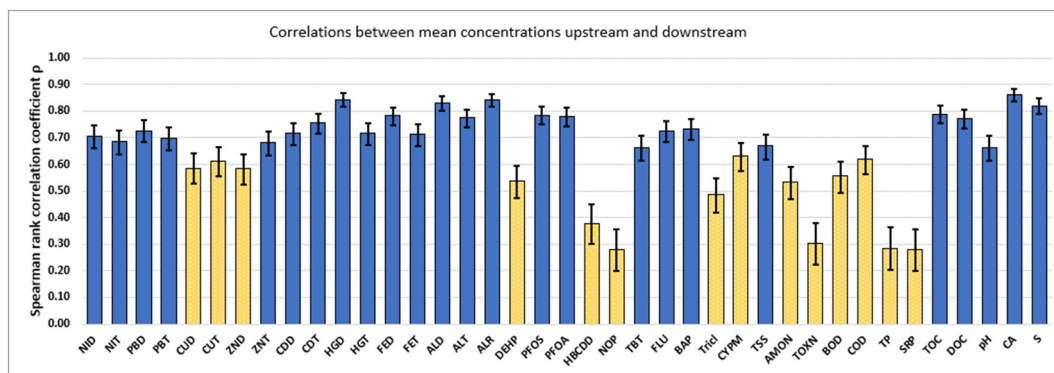**Fig. 3.** Spearman rank correlation coefficients for comparisons between upstream and downstream concentrations (abbreviations provided in Table 1). Blue bars denote higher correlation coefficients (>0.7) and yellow bars poorer correlation (<0.7) (rho, see text). Nb. error bars show the 95 % confidence interval of estimates of rho. BDEs removed on account of incidence of less than limits of detection upstream of >60 %.

Table 1
Summary of differences between paired upstream and downstream concentrations.

A	B	C	D	E	F	G
Data in µg/l unless stated otherwise		Median concn. upstream µg/l	Median concn. downstream µg/l	Median of paired differences µg/l	Mann Whitney "U" test p value	Median change in paired values as % of upstream value
Nickel (dissolved)	NID	1.9	2.38	0.21	0.00	11
Nickel (total)	NIT	2.6	3	0.21	0.00	8
Lead (dissolved)	PBD	0.19	0.21	0.0048	0.02	3
Lead (total)	PBT	1.49	1.25	−0.14	0.00	−9
Copper (dissolved)	CUD	2.03	2.7	0.38	0.00	19
Copper (total)	CUT	3.53	4.33	0.41	0.00	12
Zinc (dissolved)	ZND	6.49	10.8	2.1	0.00	33
Zinc (dissolved)	ZNT	15.1	18.6	1.6	0.00	11
Cadmium (dissolved)	CDD	0.016	0.018	0.00029	0.08	2
Cadmium (total)	CDT	0.036	0.0353	−0.00057	0.49	−2
Mercury (dissolved)	HGD	0.0018	0.0019	0.000023	0.20	1
Mercury (total)	HGT	0.00472	0.00464	0.000059	0.46	1
Iron (dissolved)	FED	70.6	77.1	1.2	0.05	2
Iron (total)	FET	526	477	−27	0.11	−5
Aluminium (reactive)	ALR	8.16	7.81	−0.25	0.56	−3
Chromium (dissolved)	CRD	0.30	0.29	−0.0027	0.09	−1
Chromium (total)	CRT	0.76	0.713	−0.035	0.08	−5
Diethylhexyl-phthalate	DEHP	0.17	0.22	0.016	0.00	10
BDE 47	BDE47	0.000251	0.000261	0.0000005	0.00	0
BDE 99	BDE99	0.000250	0.000255	2.6E−07	0.00	0
Perfluorooctane sulfonic acid	PFOS	0.00264	0.00318	0.00031	0.00	12
Perfluorooctanoic acid	PFOA	0.00248	0.0034	0.00049	0.00	20
Hexabromo-cyclododecane	HBCDD	0.00053	0.00136	0.00055	0.00	104
Nonylphenol	NOP	0.023	0.029	0.0025	0.00	11
Tributyltin	TBT	4.88E−05	6.42E−05	0.000007	0.00	14
Fluoranthene	FLU	0.025	0.021	−0.0018	0.00	−7
Benzo(a)pyrene	BAP	0.016	0.012	−0.0017	0.00	−11
Triclosan	Tricl	0.0077	0.017	0.0067	0.00	88
Cypermethrin	CYPM	0.00004	0.00006	0.00001	0.00	25
Total suspended solids mg/l	TSS	12.9	12.4	−0.35	0.26	−3
Ammoniacal nitrogen (as N) mg/l	AMON	0.15	0.21	0.034	0.00	22
A	B	C	D	E	F	G
Data in µg/l unless stated otherwise		Median concn. upstream µg/l	Median concn. downstream µg/l	Median of paired differences µg/l	Mann Whitney "U" test p value	Median change in paired values as % of upstream value
Total oxidised nitrogen (as N) mg/l	TOXN	5.08	9.9	2.8	0.00	55
Biochemical oxygen demand mg/l	BOD	1.83	2.07	0.16	0.00	9
Chemical oxygen demand mg/l	COD	19.8	23.7	2.1	0.00	10
Total phosphorus (as P) mg/l	TP	0.237	0.58	0.26	0.00	108
Soluble reactive phosphate (as P) mg/l	SRP	0.13	0.42	0.2	0.00	149
Total organic carbon mg/l	TOC	7.25	7.84	0.64	0.00	9
Dissolved organic carbon mg/l	DOC	5.62	6.5	0.67	0.00	12
pH value	pH	7.89	7.8	−0.053	0.00	−1
Calcium mg/l	CA	87.9	84.8	−0.04	0.62	0

brominated diphenylethers, polyaromatic hydrocarbons, flame retardants and other persistent organic pollutants listed under the WFD. Included in the analysis suite were pH, dissolved organic carbon, calcium, required to run the simplified BLMs for copper, lead, nickel and zinc (Table S1).

Minor adjustments were made in the analytical programme developed from the first phase of CIP (CIP1). These involved the requirement for improved limits of detection for metals including cadmium and mercury and the addition to the programme of further trace substances of more recent interest (e.g., two fluorocarbons, hexabromocyclododecane and cypermethrin). Analytical targets for limit of detection, precision of analysis and spiking recovery were specified to meet the main project aims of providing an accurate picture of effluent quality in relation to current river quality standards. Six laboratories took part, serving the needs of different water utilities (monitoring was organised by water utilities each operating within its own operational region); these laboratories were required to provide evidence that they could meet the specified requirements.

Sample collection for the CIP was organised on a stratified/random spot sampling basis (i.e. grab samples taken at relatively evenly spaced times). A minimum of 15 % of sampling was undertaken in non-working hours (evenings and weekends).

Samples for the determination of metals were collected with polyethylene samplers, filtered (0.45 μm) on-site then acidified and stored in polyethylene and transported at 4 °C to the laboratories. All data in the tables have been subjected to rejection of statistical outliers using the median absolute deviation z-score method as described in the NIST engineering handbook (NIST, 2021). Individual results reported as less than the required limit of detection (LOD) were substituted with a value 1/2 the reporting limit as specified in EU reporting regulations (EC, 2009).

Further details on sampling, analytical performance and quality control are provided in (ESI, S1).

2.2. BioMet BLM

The Bio-met tool v5 was funded by the European Copper Institute (ECI), International Zinc Association (IZA), and the Nickel Producers Environmental Research Association (NiPERA) as a simple MS Excel based application, developed collaboratively by ARCHE and WCA environment, freely available from the Internet. Its basis is the original chronic BLMs but requires fewer input parameters and therefore can also process samples more quickly. Briefly, the Bio-met bioavailability tool is a large database of >20,000 different combinations of the key input parameters, pH, DOC, and Ca concentrations, and corresponding HC5 (hazardous concentration for 5 % of the species assuming a lognormal species sensitivity distribution (SSD) for Cu, Zn, and Ni, from the original chronic BLMs). Other less critical parameters such as Mg, Na, and alkalinity were accounted for based on their correlation with Ca or pH (Rüdel et al., 2015).

The model was fitted over a parameter range as defined by the full BLMs: pH = 6 to pH = 8.5; DOC 0.1 to 100 mg/l; Ca from 1 to 200 mg/l and Na from 14 to 80 mg/l. The more insignificant parameters were set at reasonable worst-case values: temperature = 5 °C; K = 25 mg/L; SO_4^{2-} = 100 mg/l, and Cl^- = 160 mg/l. This generates a look up table that is used for the MS Excel macros and the minimum HC5 of the two best matching lookup table entries is selected for the site specific EQS (after application of an additional assessment factor which varies between the metals) (provided the input ranges are within calibrated ranges) (Table S4). If user inputs for pH or Ca are outside of its validated range, a prediction using the lower or upper limit value for pH, DOC, and Ca values is returned depending on the scenario. For some instances such as pH, values below the lower range will lead to a default of 100 %

bioavailability, whereas values above the upper range for Ca, DOC have been shown to have limited impact on metal bioavailability (see BioMet, 2019 for details).

Locations of the CIP sampling sites are shown in Fig. 1. As can be seen there was a good geographical spread across the country of WwTW locations.

The 605 CIP2 sites covered works size ranging from 12 to 3,140,000 population, with a mean of 40,000 and median of 9000. This provided a fair representation of works across England where there are approximately 4600 WwTW, with a mean and median population of 12,000 and 611 respectively (Fig. 2). The bias towards slightly larger WwTW reflects the CIP2 site selection methodology which targeted WwTW with lower receiving water dilution, in order to sample sites with greatest risk of not achieving downstream water quality targets. The smallest works a) treat <5 % of the total sewage load, b) they have greatest dilution and c) they generally offer lower risk and so they were deliberately not represented in proportion to their number in CIP2.

2.3. Statistical approach

The overall approach involved examination of the differences between the summary riverine concentrations upstream and downstream at each individual WwTW site for each water quality parameter included in the CIP. The results of a preliminary correlation analysis which was then followed by a more detail examination are presented below.

3. Results and discussion

The availability of the extensive CIP database of riverine contaminant concentrations upstream and downstream of a large number of WwTW discharges offered the opportunity of assessing the correlation between upstream and downstream concentrations for each discharge. The logical expectation is that correlation should be strong in the absence of factors caused by effluents (though other influences might also apply). The results are shown in Fig. 3, the blue bars exhibit a typical value of 0.7 to 0.8, with the deviation from 1.0 likely to be caused by various factors that affect all determinands, such as groundwater intrusions, drainage etc. (Wittenberg and Aksoy, 2010). Determinands highlighted in yellow relate to a rho value that is statistically significantly (p = 0.05) lower than 0.7. This is an arbitrary division apart from the fact that these contaminants tend to exhibit larger and more substance specific departures from the typical rho value of around 0.75 ± approximately 0.05. For some determinands, including the principal effluent sanitary parameters (COD, BOD, SRP, ammonia, total suspended solids), it might be proposed that effluent inputs might play a part (Gardner et al., 2012). In the case of other substances exhibiting low values of rho (DEHP, HBCDD, nonylphenol, triclosan and cypermethrin), the lower correlation coefficients could also be related to local perturbation, caused by the effluent discharge, of the otherwise simple correspondence of upstream to downstream concentration values (ESI Table S5).

It was recognised that this correlation analysis does not indicate the size, direction or importance of any potential impact that the effluent inputs may have on receiving water quality. It was therefore decided that a more detailed analysis of local effects was required. This comprised the quantification of upstream to downstream changes, an assessment of their statistical significance and the impacts of any changes on compliance with water quality standards.

3.1. Metals - impacts of assessing compliance using bioavailability

The EQS values for non-metals are taken directly from legislation (EU WFD and corresponding UK regulations). EQS values for some metals

---

Notes to Table 1: Column F - The "p" value for the Mann Whitney test represents the probability that the observed U statistic might have arisen if there were no true difference between the upstream and downstream median values – hence a p value of less than 0.05 indicates a statistically significant difference and the 5 % probability level. These values are highlighted in red. Column G Changes (in fact, increases) between upstream and downstream median concentration of larger than 10 % are highlighted in brown. It should be noted that the median of individual changes in pairs of upstream and downstream values concentration assessed across all sites (column E) is not the same as the difference between overall median concentrations (columns C and D).

(Cu, Ni, Zn, Pb and to a lesser degree Cd (accounting for hardness only)) are bioavailability corrected in response to ambient site specific characteristics (dissolved organic carbon, hardness and pH). This means that for each monitored location, the measured dissolved concentration must be compared with a calculated dissolved water quality criterion that takes account of bioavailability.

The BioMet tool was used to generate site-specific EQS for copper, nickel and zinc, which could then be compared with compliance values (Table 1). CIP2 sites with a full dataset of trace metal concentrations as well as BLM variables were run through the BioMet model. In total 462 and 602 sites had full datasets required to run the BioMet tool for upstream and downstream respectively. The BioMet model has limits for which pH, DOC and calcium are calibrated (Table S4). All CIP2 sites, both upstream and downstream were within range for pH and DOC and for the lower limit for calcium. However, the upper limit for calcium varies between 88 mg-Ca/l for Ni through to 204 mg-Ca/l for lead. The high prevalence of calcareous geology in England (chalk and limestone) means that just over half of the sites exceeded the 88 mg-Ca/l limit for Ni, reducing to <10 for lead. For copper there were 63 and 71 sites over the calcium application range for upstream and downstream respectively (BioMet, 2019). Given higher concentrations of calcium are likely to only reduce the bioavailability of the metal (Paquin et al., 2002), and that the simplified BLM tools are conservative in free metal ion estimation (BioMet, 2019), then it is justified to retain these samples in the compliance assessment.

The impact of not accounting for trace element bioavailability is clear. Assuming incorrectly that the observed dissolved copper concentrations were 100 % bioavailable leads to the majority of upstream and downstream (89 % and 96 % respectively) sites above the 1 μg/l worst case EQS. Similarly, if bioavailability is not taken into account for zinc, then 27 % and 49 % are non-compliant as a worst case (>10.9 μg/l) for upstream and downstream sites respectively; 11 % and 18 % respectively for nickel (>4.0 μg/l) and 1 % and 2 % respectively for lead (>1.2 μg/L). Taking account of bioavailability however, the situation changes dramatically.

Exceedances of the site specific EQS based on pH, calcium concentrations and DOC levels, reduced non-compliance to zero for lead, for copper only a 3 % non-compliance downstream (zero upstream), for nickel 3 % and 2 % upstream and downstream non-compliance respectively and zinc 4 % non-compliance up and downstream (Table 2). These data show the benefits of taking a scientifically robust risk assessment approach to addressing compliance (David et al., 2011; EU, 2019).

3.2. Local impacts of WwTW discharges on water quality

Examining the whole dataset in more detail, Table 1 summarises the changes in receiving water concentrations upstream and downstream of the WwTW discharges studied in CIP2. Differences in upstream and downstream concentrations were assessed using a Mann Whitney non-parametric test. Concentrations of trace substances in river waters are usually associated with relatively high variance (coefficient of variation of 0.5 to >1). Data distributions are also generally somewhat skewed. Under these circumstances it is quite possible for the differences between median concentrations across a number of sites to be in once direction and the median of pairs of individual differences to be in the opposite direction. The likelihood of this is increased if the overall median upstream and downstream values are very close in value, as is the case for total mercury. The conceptual difference between the difference between median values and the median of pairs of differences is noted in the footnote to Table 1.

Furthermore, the data shown in Table 1; the median river concentrations are presented in order to give the reader context of actual concentrations in relation to the statistic of primary interest here, the median change from upstream to downstream brought about by effluent discharges.

Of the nine metals monitored (counting dissolved metals and reactive aluminium) only four exhibit statistically significant increases downstream of the WwTW discharges. These (nickel, copper, lead and zinc) are listed in Table 2 with respect to downstream EQS compliance. Incidences of

Table 2
Upstream and downstream EQS compliance values (Mann Whitney 'U' test p value: red numbers are significant at 95% confidence, black numbers, not significant at 95% confidence).

Determinand	Code	Median concn. upstream μg/l	Median concn. downstream μg/l	Median of paired differences μg/l	Mann Whitney "U" test p value	Median change in paired values as % of upstream value	95%ile paired difference μg/l	5%ile paired difference μg/l	EQS value or concn. of potential concern μg/l	% upstream NON-compliance by works site	% downstream NON-compliance by works site
a) Metals											
Nickel (dissolved)	NID	1.9	2.38	0.21	0.00	11	3.15	−1.07	Site specific	3	2
Copper (dissolved)	CUD	2.03	2.7	0.38	0.00	19	4.89	−0.96	Site specific	0	3
Zinc (dissolved)	ZND	6.49	10.8	2.1	0.00	33	19	−7.74	Site specific	4	4
Cadmium (dissolved)	CDD	0.0161	0.0178	0.00029	0.08	2	0.0261	−0.021	Site specific	2	3
Iron (total)	FET	526	477	−27	0.11	−5	395	−944	730	32	26
b) Trace organic substances											
Diethylhexyl-phthalate	DEHP	0.174	0.218	0.016	0.00	10	0.532	−0.206	1.3	1	1
Nonylphenol	NOP	0.0234	0.0291	0.0025	0.00	11	0.127	−0.0249	0.3	1	1
Triclosan	Tricl	0.00766	0.0166	0.0067	0.00	88	0.063	−0.0043	0.1	1	3
Hexabromocyclo-dodecane	HBCDD	0.00053	0.00136	0.00055	0.00	104	0.00697	−0.00051	0.0016	11	43
Perfluorooctane sulfonic acid	PFOS	0.0026	0.0032	0.00031	0.00	12	0.0056	−0.0043	0.00065	86	93
Perfluorooctanoic acid	PFOA	0.00248	0.0034	0.00049	0.00	20	0.00341	−0.0024	0.00065	87	94
Tributyltin	TBT	4.88E-05	6.42E-05	0.0000068	0.00	14	0.00015	−0.000099	0.0002	9	10
Cypermethrin	CYPM	4.23E-05	6.33E-05	0.00001	0.00	25	0.00033	−0.000158	0.0008	29	43
c) Phosphorus											
Soluble reactive phosphate (as P)	SRP	0.134	0.416	0.2	0.00	149	2.48	−0.134	See text	65	94

Note 1EQS values are set generically as annual average concentration. In the case of metals this is expressed as a single value for "bioavailable" metal. This is then translated (on the basis of local water quality characteristics) into a site-specific dissolved concentration that can be compared with measured annual average concentrations to arrive at an assessment of compliance. The final right-hand columns of this table refer to this observed level of compliance for the CIP assessment of over 600 WwTW sites.

noncompliance are low as described above and changes in compliance from upstream to downstream are minimal.

Fig. 4 presents a visualisation of the upstream and downstream concentration data for four key metals, comparing these values with the bioavailable EQS standards. It is evident that in at least three of the four cases, cadmium being the exception, there is a high proportion of non-compliance with the EQS expressed as a face value bioavailability corrected metal concentration. The data in Table 2 record the correct interpretation with respect to quality criteria that are BLM-adjusted on a site-by-site basis. The rates of non-compliance are markedly reduced, demonstrating the benefit derived from use of the BLM. Furthermore, it should be noted that the bioavailability corrected EQS values for nickel, copper and zinc are based on a set of water chemistry conditions that provide high bioavailability and are therefore highly conservative, taking account of the precautionary principle under the WFD (BioMet, 2019). Consequently, instances of non-compliance are effectively limited to cases where specific local issues such a historic industrial contamination or naturally metalliferous sources lead to elevated metal concentrations. These site-specific exceedances require further data analysis under the Tiered Approach (Comber et al., 2008), including taking account of background concentrations for zinc for example.

Cadmium, being a 'Priority Hazardous Substance' under the WFD, means its EQS has been derived at a EU level using a different approach, only using hardness as a surrogate to derive a bioavailability corrected concentration for the EQS. The EQS boundaries are very narrow (<0.08 μg/l for <40 mg/l $CaCO_3$; 0.08 μg/l for 40–50 mg/l $CaCO_3$; 0.09 μg/l for 50–100 mg/l $CaCO_3$; 0.15 μg/l for 100–200 mg/l $CaCO_3$ and 0.25 μg/l for >200 mg/l $CaCO_3$) and in reality challenging to analytically distinguish at the softer range of waters. The fact that cadmium use has been banned or heavily controlled, and that concentrations in rivers are as a result declining, compliance, even against the tightest EQS is high, both up and downstream of WwTW, where median concentrations are significantly below the lowest EQS (0.08 μg/l).

On the right-hand side of each diagram the 5–95 percentile change in mean concentration is presented. In all cases this range overlaps with zero on the right-hand axis indicating that although the overall increase in concentration from upstream to downstream is statistically significant, the individual changes involve both increases and decreases.

For the twelve trace organic substances determined in the CIP there are 7 instances where the median downstream concentration exceeds the corresponding upstream median concentration by >10 %. All these increases in concentration are statistically significant, however, not all are of practical importance. On this basis, the impact of local discharges for DEHP nonylphenol and triclosan might be considered negligible from the perspective of pollution control. This is illustrated in Table 2 where it can be seen that the incidence of non-compliance with EQS values for these substances
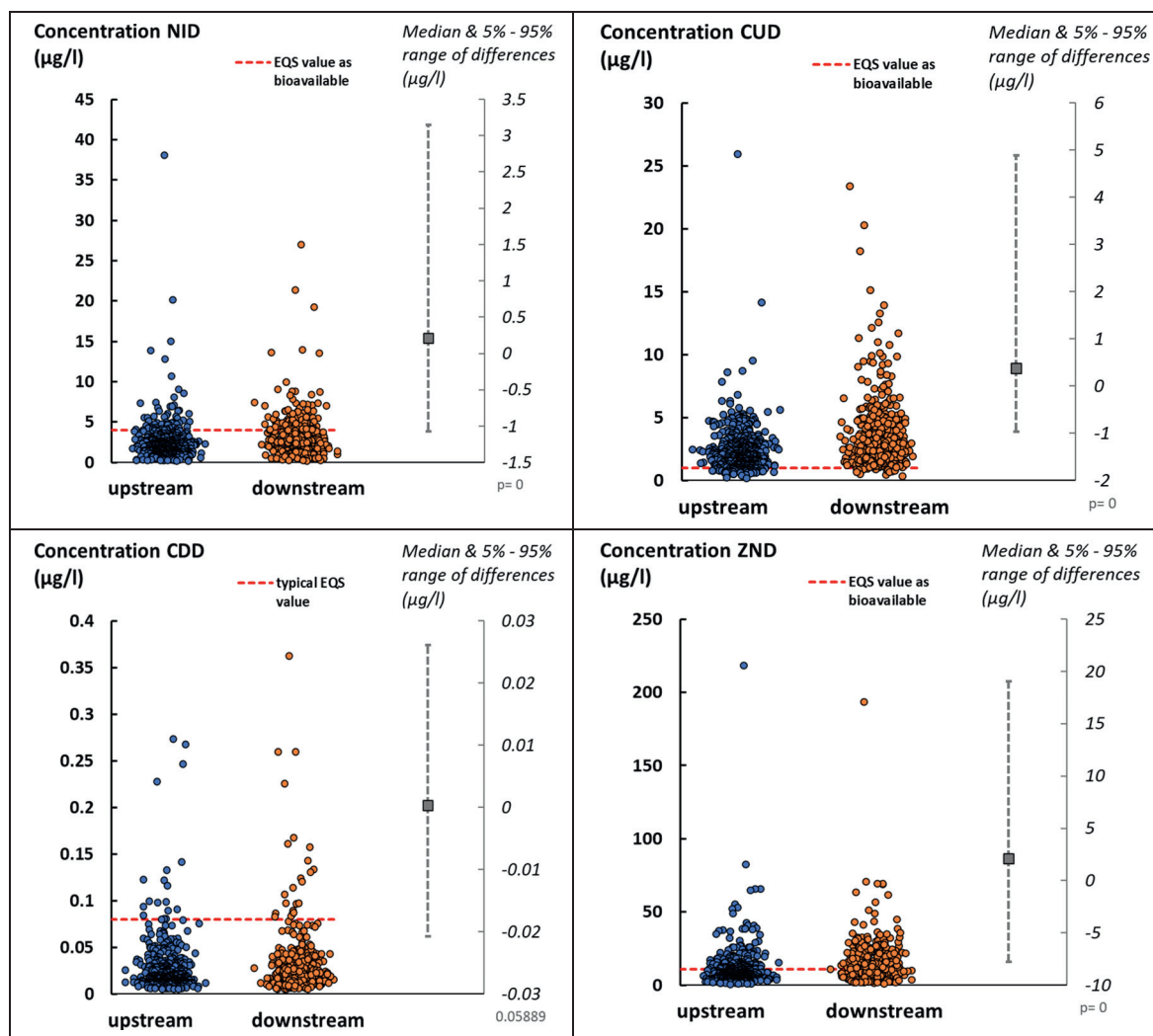

Fig. 4. Comparison of upstream and downstream concentrations for key metals. Metal concentrations are as dissolved metal. Red lines show the published EQS values expressed as bioavailable corrected metal concentration. Actual compliance with respect to the "BLM translations" of the published EQS values – expressed as dissolved concentrations - are listed in Table 2.

is very low. This leaves five trace organic substances that might be thought of as of potential concern on the basis not only of % downstream concentration increases, but also of changes in compliance (columns I and J – the two most right hand columns).

Fig. 5 features visualisations of data for these five substances for which the largest increases in downstream concentrations are observed. Data for soluble reactive phosphorus are also shown for comparison. All changes are statistically significant.

Consideration of this, as illustrated in Fig. 5, leads to the conclusion that only HBCDD, SRP and possibly cypermethrin and the PFAs appear to be of primary local concern on the grounds that a notable proportion of sites show an increase in concentration downstream of a WwTW discharge that is substantially larger than 10 %. However, it should also be noted that these cases also exhibit worryingly high levels of non-compliance with EQS value upstream of the local effluent discharge. The percentile range indicators show that cases of downstream reduction are relatively
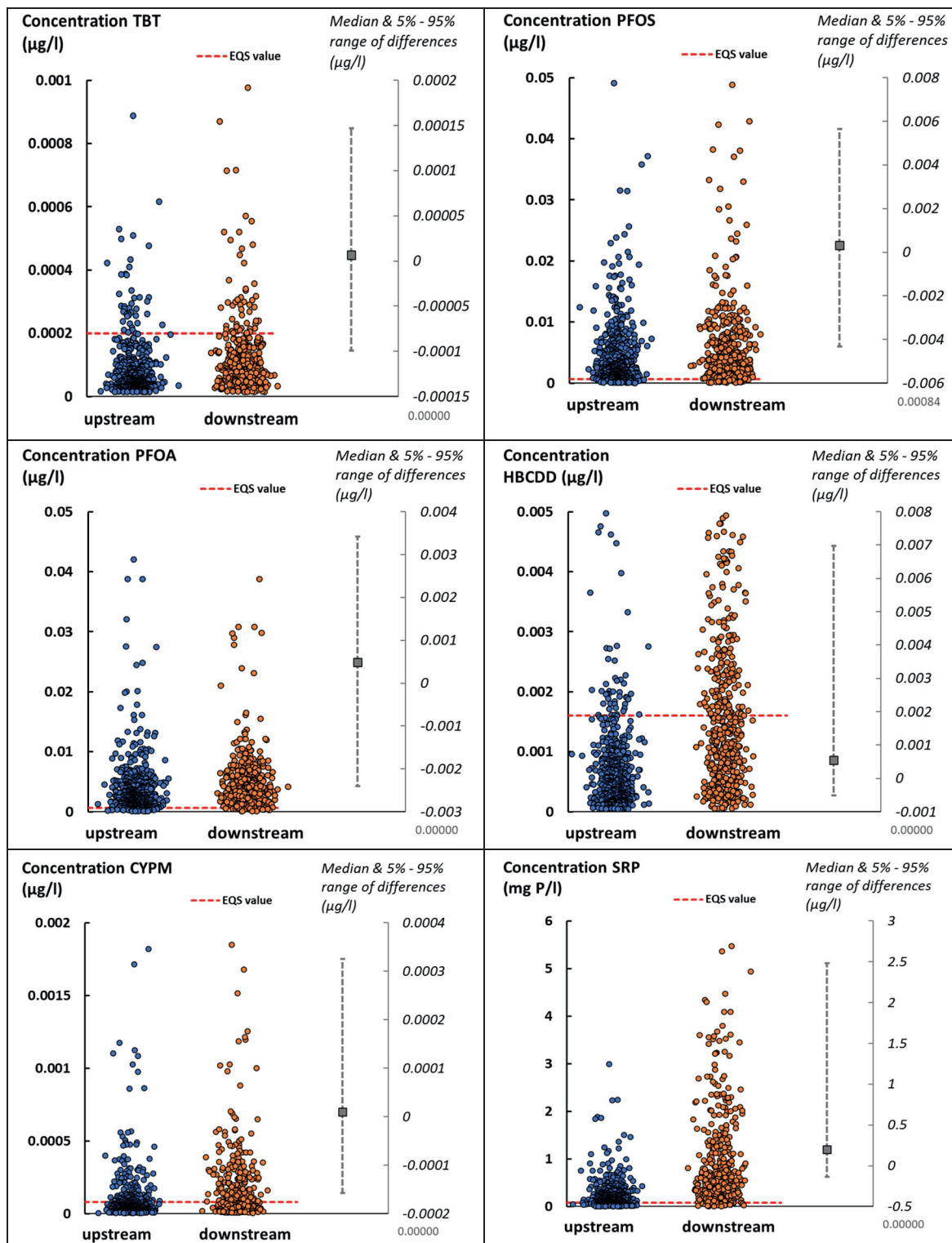

Fig. 5. Comparison of upstream and downstream concentrations for other chemicals of potential concern.

few for HBCDD, SRP and cypermethrin, suggesting that WwTW effluents are contributing to the overall river burden.

3.3. Geographical influences

Although the main objective of this paper was to provide a country-wide risk assessment, the data have been mapped (Fig. 6) in order to highlight any particular geographical influences that may be observed. Fig. 6 provides an illustration for an organic compound (HBCDD) for which the EQS value is low in relation to observed data and an example for a metal - iron. There appear to be no clear geographical trends. Some clustering of non-compliances is evident in the North West of England and in iron-rich locations in the South East.

For HBCDD where the ratio of downstream concentration to upstream was >10, the average dilution was 27, for upstream-downstream ratios <10, the mean dilution was 121 (Fig. S2). It must also be recognised that the CIP programme targeted lower dilution WwTW, as worst cases. The overall impression for HCBDD is of a predominance of yellow dots,
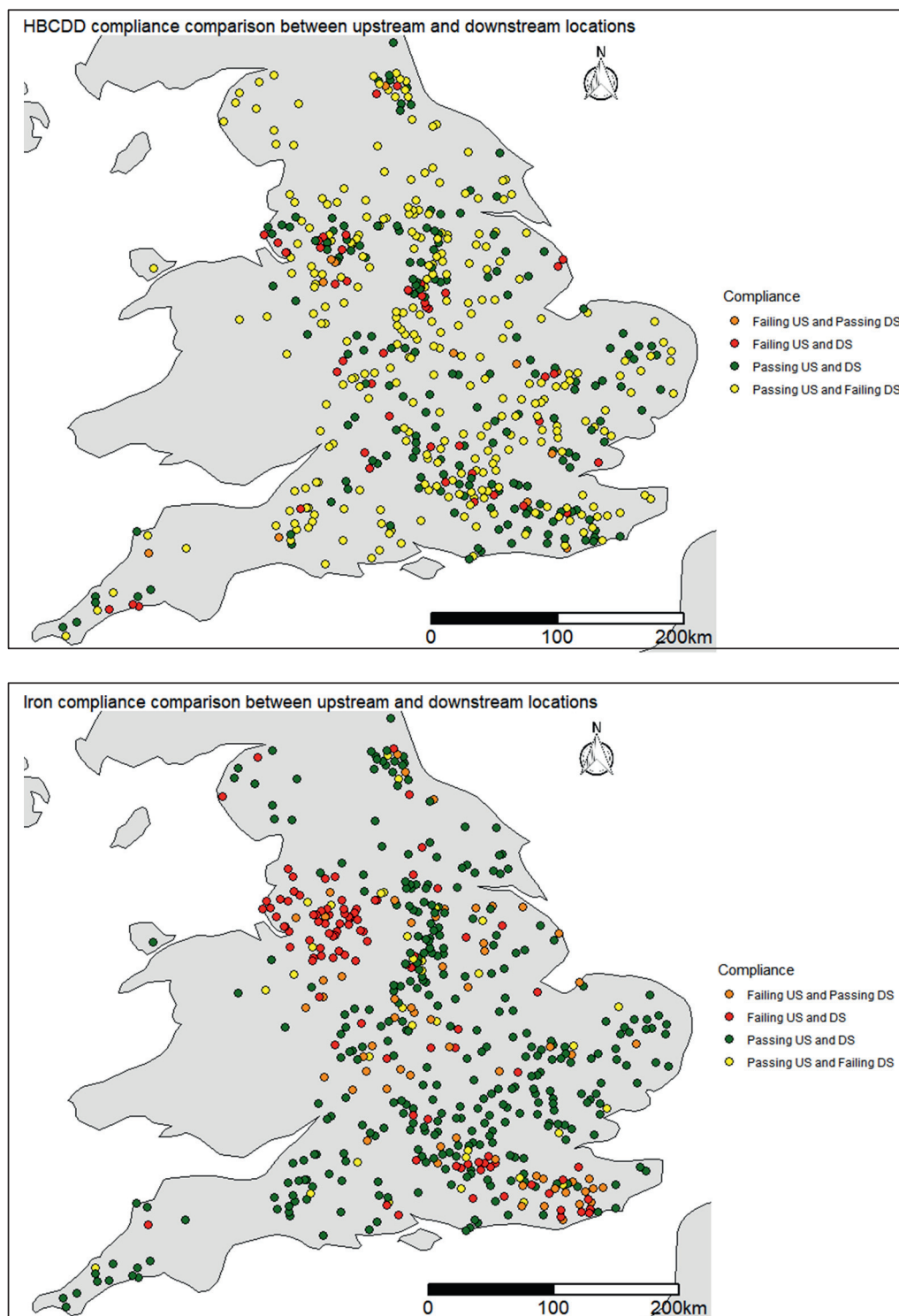

Fig. 6. Geographical representation of WwTW effluent influence for (top) HBCDD and (bottom) iron.

indicating change from upstream compliance to downstream non-compliance. By contrast, in the case of total iron, the picture is one that is characterised by red and green dots - indicating no change in compliance status from upstream to downstream of effluent discharges (red indicating non-compliance and green indicating compliance). It is likely that in the case of iron the main controlling influences relate to historic and geological factors.

These are two contrasting examples of the influence of WwTW on downstream concentrations of WFD priority chemicals. Consideration of important aspects controlling river concentrations such as seasonality, particularly flow conditions are beyond the scope of this research. All analysis here uses median or mean concentrations reflecting the application of EQS based on annual averages. However, it is well established that given WwTW discharge largely consistent flows throughout the year, they will influence downstream concentrations of contaminants more significantly in summer during low river flows, than during the winter (Comber et al., 2020a).

On a wider geographic scale, for metals the bioavailability based EQS has been slowly rolled out across Europe as countries adopt the tiered based approach. As with the UK, there are identified sites outside of the pH, DOC and Ca parameterisation, and high naturally salt concentrations have been identified in for example, Germany which lead to suggestions of further optimisation (Rüdel et al., 2015). Other BLM tools such as PNEC-pro have been used by the Netherlands for metals compliance, and showed between 8 and 97 % agreement with the full BLMs. For Spain, a case study in the North East part of the country demonstrated a high degree of compliance using both the BioMet tool and PNEC-pro (Rüdel et al., 2015).

For the WFD organic chemicals current focus is on non compliance with biota EQS, possibly more relevant than water EQS for persistent organic pollutants such as brominated diphenylethers, HBCDD, and perfluorinated chemicals for example. The very low EQS set for biota has led to European wide non compliance for these chemicals (e.g. EEA, 2022; Fliedner et al., 2016). Unlike the metals which have a natural background concentration, the xenobiotic organic substances are likely to demonstrate decreasing concentrations over time as bans and restrictions take effect (Comber et al., 2020b).

4. Conclusions

The data presented here lead to the following conclusions:

- Wastewater treatment works' discharges have been shown for many contaminants to have little local impact. Only HBCDD, SRP, cypermethrin and the PFAS appear to be of primary local concern on the grounds that a notable proportion of sites show an increase in concentration downstream that is substantially larger than 10 %. These cases also exhibit concerningly high levels of non-compliance with EQS value upstream of the local effluent discharge
- Otherwise, instances of poor compliance with riverine water quality standards tend to be associated with contamination at the river catchment scale, with corresponding implications for the nature of remedial actions that are likely to be successful in achieving environmental goals.
- Compliance with water quality standards for metals, taking account of bioavailability, is high overall. This conclusion shows the benefits of applying a rational approach to compliance assessment, taking account of the bioavailable proportion of the contaminant present. Marked elevation of contamination at a local level appears likely to occur primarily at sites with particularly low dilution in the receiving water.

CRediT authorship contribution statement

Sean Comber – Conceptualization, BLM background, review & editing, data discussion

Michael Gardner - Conceptualization, methodology, data curation, formal analysis, writing

Lauren Ansell – Mapping and data collation

Brian Ellor – Management, data quality, communication, review and editing.

Declaration of competing interest

The authors report no conflict of interest is producing this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.157284.

References

BioMet, 2019. bio-met bioavailability tool. User Guide (version 5.0), Guidance document on the use of the bio-met bioavailability tool.Available at www.bio-met.net 27/06/2019.
Comber, S.D.W., Merrington, G., Sturdy, L., Delbeke, K., van Assche, F., 2008. Copper and zinc water quality standards under the EU Water Framework Directive: the use of a tiered approach to estimate levels of failure. Sci. Total Environ. 403, 12–22.
Comber, S., Gardner, M., Ellor, B., 2020a. Seasonal variation of contaminant concentrations in wastewater treatment works effluent and river waters. Environ. Technol. 41 (21), 2716–2730.
Comber, S., Gardner, M., Constantino, C., Firth, S., Hargreaves, A., Davies, R., 2020b. Modelling scenarios of environmental recovery after implementation of controls on emissions of persistent organic pollutants. Environ. Sci. Process. Impacts 22 (9), 1865–1876.
David, M., Perceval, O., Batty, J., Rodriguez Romero, J., Niebeek, G., Delbeke, K., Van Assche, F., Merrington, G., Schlekat, G., 2011. Workshop on metal bioavailability under the water framework directive: policy, science and implementation of regulatory tools. Workshop Report June 2011.
De Schamphelaere, K.A.C., Janssen, C.R., 2004. Development and field validation of a BLM predicting chronic copper toxicity to Daphnia magna. Environ. Toxicol. Chem. 23, 1365–1375.
Dixon, E.M., Gardner, M.J., Comber, S.D.W., 2000. Copper speciation in UK rivers. Chem. Speciat. Bioavailab. 12 (1), 1–7.
Dwane, G.C., Tipping, E., 1998. Testing a humic speciation model by titration of copper-amended natural waters. Environ. Int. 24, 609–616.
EC, 2009. Technical Specifications for Chemical Analysis And Monitoring of Water Status. Directive 2009/90/EC.
EEA, 2021. The European Pollutant Release and Transfer Register (E-PRTR). European Environment Agency. https://prtr.eea.europa.eu/#/home.
EEA, 2022. Chemical status of surface waterbodies.Available atEuropean Environment Agency accessed July 2022 https://www.eea.europa.eu/themes/water/european-waters/water-quality-and-water-assessment/water-assessments/chemical-status-of-surface-water-bodies.
EU, 2000. Water Framework Directive (2000/60/EC) of the European Parliament And of the Council Establishing a Framework for the Community Action in the Field of Water Policy. European Union.
EU, 2006. Council Directive 76/464/EEC of 4 May 1976 on Pollution Caused by Certain Dangerous Substances Discharged Into the Aquatic Environment of the Community.
EU, 2019. Guidance Document No. 38. Technical Guidance for Implementing Environmental Quality Standards (EQS) for Metals Consideration of Metal Bioavailability And Natural Background Concentrations in Assessing Compliance. Document Endorsed by EU Water Directors at Their Meeting on Helsinki on 26-27 November 2019.
Eurostat, 2021. Eurostat. http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_ww_genv&lang=en.
Fliedner, A., Lohmann, N., Teuber, D., Wellmitz, J., Korschorreck, J., 2016. Environ. Pollut. 216, 866–876.
Gardner, M., Comber, S., Scrimshaw, M., Cartmell, E., Lester, J., Ellor, B., 2012. The significance of hazardous chemicals in wastewater treatment works effluents. Sci. Total Environ. 437, 363–372.
Hudson, R.J.M., 2005. Trace metal uptake, natural organic matter, and the free-ion model. J. Phycol. 41 (1), 1–4.
Marsac, R., Davranche, M., Gruau, G., Bouhnik, M., Dia, A., 2011. An improved description of the interactions between rare earth elements and humic acids by modeling: PHREEQC-model VI coupling. Geochim.Geochim. Acta 75 (19), 5625–5637.
NIST, 2021. Available at. https://www.itl.nist.gov/div898/handbook/eda/section3/eda35h.htm Accessed 10/9/21.
Nys, C., Janssen, C.R., van Sprang, P.V., de Schamphelaere, K.A.C., 2016. The effect of pH on chronic aquatic nickel toxicity is dependent on the pH itself: extending the chronic nickel bioavailability models. Environ. Toxicol. Chem. 35 (5), 1097–1106.
Paquin, P.R., Gorsuch, J., Apte, S., Batley, G., Bowles, K.C., Campbell, P.G.C., Delos, C.G., Di Toro, D.M., Dwyer, R.L., Galvez, F., Gensemer, R.W., Goss, G.G., Hogstrand, C., Janssen, C., McGeer, J., Naddy, R.B., Playle, R.C., Santore, R., Schneider, U., Stubblefield, W., Wood, C.M., Wu, K.B., 2002. The biotic ligand model: a historical overview. Comp. Biochem. Physiol. C: Toxicol. Pharmacol. 133 (1–2), 3–35.
Peters, A., Merrington, G., Schlekat, C., De Schamphelaere, K., Stauber, J., Batley, G., Harford, A., van Dam, R., Pease, C., Mooney, T., Warne, M., Hickey, C., Glazebrook, P., Chapman, J., Smith, R., Krassoi, R., 2018. Validation of the nickel biotic ligand model for locally relevant species in Australian freshwaters. Environ. Toxicol.Chem. 37 (10), 2566–2574.
Peters, A., Nys, C., Merrington, G., Verdonck, F., Baken, S., Cooper, C., van Assche, F., Schlekat, C.E., Garman, E., 2019. Demonstrating the reliability of bio-met for determining

compliance with environmental quality standards for metals in Europe. Environ. Toxicol. Chem. 12, 2361–2377.

Rüdel, H., Muñiz, C.D., Garelick, H., Kandile, N.G., Miller, B.W., Munoz, L.P., Peijnenburg, W.J.G.M., Purchase, D., Shevah, Y., van Sprang, P., Vijverr, M., Vink, J.P.M., 2015. Consideration of the bioavailability of metal/metalloid species in freshwaters: experiences regarding the implementation of biotic ligand model-based approaches in risk assessment frameworks. Environ. Sci. Pollut. Res. 22, 7405–7421.

Santore, R., Ryan, A., Paquin, P., 2006. Variability in NOM in surface waters and implications on trace metal speciation and bioavailability modelling. Annex to "7. Application of Biotic Ligand Models to the Risk Characterization for the Aquatic Compartment" Annex 7.2.e. Draft Report. Hydroqual, Inc., USA.

Schlekat, C., van Genderen, E., de Schamphelaere, K., Antunes, P.M.C., Rogevich, E.C., Stubblefield, W.A., 2010. Cross-species extrapolation of chronic nickel biotic ligand models. Sci.Total Environ. 408, 6148–6157.

Tipping, E., 1994. WHAM – a chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete-site electrostatic model of ion-binding by humic substances. Comput. Geosci. 20 (6), 973–1023.

Van Veen, E.M., Burton, N., Gardner, M.J., Comber, S.D.W., 2002. Speciation of copper in sewage effluents and its toxicity to Daphnia magna. Environ. Toxicol. Chem. 21 (2), 275–280.

Verschoor, A.J., Vink, J.P.M., Vijver, M.G., 2017. Refinement and cross-validation of nickel bioavailability in PNEC-Pro, a regulatory tool for site-specific risk assessment of metals in surface water. Environ. Toxicol. Chem. 36 (9), 2367–2376.

Wca, 2015. Technical Guidance to Implement Bioavailability-based Environmental Quality Standards For Metals. Drafted by wca (www.wca-environment.com) on Behalf of Eurometaux With Input From Member State And Stakeholder Experts April.

Whitfield, M., Turner, D.R., 1979. Critical assessment of the relationship between biological thermodynamic and electrochemical availability. In: Jenne, E.A. (Ed.), Chemical Modeling in Aqueous Systems. ACS Symposium SeriesVol. 93, pp. 657–680.

Wittenberg, H., Aksoy, H., 2010. Groundwater intrusion into leaky sewer systems. Water Sci. Technol. 62 (1), 92–98.

Ytreberg, E., Karlsson, J., Eklund, B., Ndungu, K., 2011. Effect of organic complexation on copper accumulation and toxicity to the estuarine red macroalga Ceramium tenuicorne: a test of the free ion activity model. Environ. Sci. Technol. 45 (7), 3145–3153.