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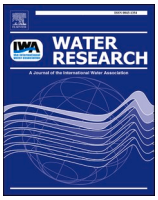

Spatial variation in the sensitivity of freshwater macroinvertebrate assemblages to chemical stressors

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ABSTRACT

Assessing spatial variation in the chemical sensitivity of natural assemblages will enhance ecological relevance and reduce uncertainty in ecological risk assessments and the derivation of environmental quality standards (EQSs). However, the majority of species in natural communities have not undergone toxicity testing for any chemical, which poses a major challenge when assessing their sensitivity. We investigated spatial variation and patterns in the sensitivity of 4084 freshwater macroinvertebrate assemblages across England to 5 general-acting chemicals (heavy metals) and 13 specifically acting chemicals (insecticides) using a novel hierarchical species sensitivity distribution method based on taxonomic relatedness. Furthermore, we explored how river typology relates to spatial variation in assemblage sensitivity to chemicals and the potential impacts of such variation on current EQSs. Our findings revealed that, whereas assemblages with similar taxonomic compositions exhibit comparable sensitivity distributions, assemblages with different taxonomic compositions could have very similar or very different sensitivity distributions. The variation in assemblage sensitivity was greater for specifically acting chemicals than for general-acting chemicals and exhibited spatial clustering patterns. These spatial clustering patterns varied depending on the chemical, and the regions where assemblages were most sensitive to metals were generally not the same as the regions where assemblages were most sensitive to insecticides. Spatial variation in assemblage sensitivity was related to river typology with sensitive assemblages being more common than expected in lowland calcareous (or mixed geology) rivers within very small to small catchments. Comparing spatial variation in assemblage-specific chemical sensitivity to EQSs, we found that the operational EQSs in England would protect most study assemblages (i.e., > 99.5 %), although a small proportion of assemblages may face potential risks associated with azinphos-methyl, copper, and malathion. In many cases the EQSs were very precautionary, potentially requiring expensive control measures or restricting beneficial chemical use with no additional environmental benefit. The development of spatially defined EQSs, possibly based on river types, could be developed to target areas that require the highest level of protection and thus strike a balance between the benefits of chemical use and environmental protection.

1. Introduction

Chemicals, many of which have brought tremendous benefits to modern human society, may be intentionally or unintentionally released into the aquatic environment, causing potentially adverse effects on natural assemblages and freshwater ecosystems (Johnson et al., 2020; Lu et al., 2020). Environmental regulatory thresholds (e.g., environmental quality standards (EQSs)) are commonly derived using a single threshold approach from toxicity data for a limited number of species, which may or may not occur in the ecosystems to be protected (Belanger et al., 2017; Liu et al., 2022). There is, therefore, considerable uncertainty regarding the level of protection environmental regulatory thresholds afford to species assemblages in natural ecosystems.

Freshwater macroinvertebrate species exhibit considerable variation in their sensitivity to toxic chemicals (Maltby et al., 2005). The magnitude of interspecies variation in chemical sensitivity is related to a chemical's toxic mode of action (Maltby et al., 2009): being smaller for general-acting chemicals (e.g., metals) than for specifically-acting chemicals (e.g., insecticides), where it may be as large as six orders of magnitude (Kienzler et al., 2019; Vaal et al., 2000). Given that

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freshwater macroinvertebrate assemblages exhibit variation in taxonomic compositions, interspecific variation in chemical sensitivity could result in the variation in assemblage sensitivity and hence risk to chemical exposure. Whereas two assemblages with the same taxonomic composition would have the same species sensitivity profile and hence assemblage sensitivity, two assemblages with different taxonomic compositions may have similar or different sensitivity profiles, depending on the relative sensitivity of the species involved. However, whereas interspecific variation in chemical sensitivity has been well described and forms the basis of the species sensitivity distribution (SSD) approach to assessing chemical risks (Posthuma et al., 2001), inter-assemblage variation in sensitivity to chemicals is rarely investigated. The main challenge in assessing the chemical sensitivity of assemblages is the lack of toxicity data for most species in natural assemblages.

Toxicity data are available for only a small percentage of freshwater macroinvertebrates in natural assemblages. Less than 15 % of the 993 freshwater macroinvertebrates in England (https://environment.data.gov.uk/ecology/explorer/) have toxicity data for any of the 5319 chemicals included in the U.S. Environmental Protection Agency ECOTOXicology Knowledgebase (Olker et al., 2022, available at https://www.epa.gov/ecotox/). Even for individual chemicals with extensive toxicity datasets, such as cadmium and copper, toxicity data is only available for less than 4 % of freshwater macroinvertebrate species in England. The challenge of assessing assemblage sensitivity is compounded by the fact that the relative sensitivity of individual species varies between chemicals. There is no specific species or group of species that is sensitive to all chemicals and which could therefore be used as sensitive surrogates for untested species (Cairns 1986).

Given that it is not feasible to perform toxicity tests on all freshwater species, even for a single chemical, methods for using existing toxicity data to predict the toxicity of chemicals to untested species are required (Van den Berg et al. 2021). Taxonomically similar species share toxicokinetic-toxicodynamic (TK-TD) traits and thereby exhibit similar responses to chemical stressors (Rubach et al., 2011). Trait-based approaches have been used to extrapolate toxicity data between freshwater invertebrate species for chemicals based on broad toxic modes of action. However, the general applicability of this approach is currently limited by the availability of appropriate trait data (Van den Berg et al. 2019). Extrapolation methods based on taxonomic relatedness are less constrained by data availability and hence more widely applicable. An example is the hierarchical species sensitivity distribution (hSSD) model, which uses taxonomic relatedness to predict the chemical sensitivity of untested species in natural assemblages (Craig 2013; Craig et al., 2012).

Freshwater macroinvertebrate assemblages exhibit considerable spatial variation in taxonomic composition driven, in part, by spatial variation in environmental variables, which may be classified as river typologies (Jupke et al., 2022; Solheim et al., 2019). Whereas the potential composition of macroinvertebrate assemblages is defined by river typology and associated physicochemical parameters, the actual species occurring at a site are influenced by the presence of anthropogenic stressors, including chemical contaminants (Soucek et al., 2023). Prior exposure to chemical stressors may therefore influence the sensitivity of assemblages by altering species composition.

The central question addressed in this research is: how does the sensitivity of freshwater macroinvertebrate assemblages to chemical stressors vary spatially, and what are the implications for current regulatory thresholds? We addressed this question using a novel application of the hSSD model, ecological and environmental information for over 4000 riverine sites across England, and toxicity data for 18 chemicals. The hSSD model utilises Bayesian estimations based on the hierarchical taxonomic relatedness between the species with known toxicity data and the species for which toxicity is to be predicted (Craig et al., 2012; Craig, 2013). Riverine macroinvertebrate assemblages in England were chosen as a case study due to the availability of information on macroinvertebrate assemblages at a large number of sites sampled in a consistent way. Study chemicals had rich toxicity datasets with high taxonomic diversity and included chemicals with narrow-spectrum and broad-spectrum toxicity.

The specific research objectives were to test the hypotheses that: (i) taxonomically dissimilar assemblages may not have dissimilar sensitivity profiles as taxonomically dissimilar species can be equally sensitive to a chemical (i.e., due to shared sensitivity mechanisms, such as the same adverse outcome pathways, which are not solely determined by taxonomy) (Fay et al., 2017; Van den Berg et al. 2021); (ii) variation in assemblage sensitivity will be greater for chemicals with a specific toxic mode of action (e.g., insecticides) than for chemicals with general modes of action. Variation in species sensitivity between major taxonomic groups (e.g., arthropods, molluscs, annelids, etc.) is expected to be greatest for chemicals that target specific taxonomic groups (Fay et al., 2017; Nyman et al., 2014; Sánchez-Bayo 2012) and consequently changes in species composition are predicted to have a greater impact on assemblage sensitivity for these types of chemicals; (iii) spatial patterns in assemblage sensitivity vary among different types of chemicals. The spatial patterns of assemblage sensitivity may vary depending on which taxonomic groups are affected by different types of chemicals (Van den Berg et al. 2020). Moreover, spatial variation in assemblage composition provides different combinations of sensitive and less sensitive species to different chemicals, potentially driving distinct spatial patterns in their assemblage sensitivity. (iv) The most and least sensitive assemblages to chemicals are associated with specific river types; The rivers with different typology descriptors provide different habitats, which drive variation in the taxonomic composition of assemblages (i.e., habitat templet theory, Southwood 1977) and hence variation in their chemical sensitivity. In addition, (v) the variation in the chemical sensitivity of macroinvertebrate assemblages was compared to operational environmental quality standards.

2. Methods

2.1. Chemical selection and toxicity data collection

Chemicals were selected if they had toxicity data for at least 25 different taxa representing the most common invertebrate phyla (i.e., Arthropoda, Mollusca, and Annelida) found in English rivers. Selected chemicals included general-acting chemicals and specifically-acting chemicals and for each chemical, fit to the hSSD model was assessed using a leave-one-out cross-validation process (Table S1).

Toxicity data for freshwater macroinvertebrates were extracted from Maltby et al. (2005) and the ECOTOXicology Knowledgebase (https://www.epa.gov/ecotox/). Criteria for toxicity data selection followed those used in previous studies (i.e., Maltby et al., 2005, 2009) where the endpoints were LC_{50} (mortality) and EC_{50} (immobility) and exposure times ranged from 1 to 7 days. Toxicity values based on measured concentrations were prioritised. For each chemical, all apparent outliers (e.g., toxicity data for the same species that differed by more than a factor of ten) were checked by reviewing the source references. If there were multiple toxicity values for the same toxicity endpoint, the lowest value was taken for each study and a geometric mean was calculated for values from different studies. Genera-specific toxicity data were collected when there was a lack of species-specific information in the ECOTOXicology Knowledgebase. Metal toxicity is strongly dependent on water hardness (Niyogi and Wood 2004) and therefore, all metal toxicity data were adjusted to water hardness of 50 mg/L as $CaCO_3$ using data extracted from the source references and the US EPA Aquatic Life Criteria Calculator (https://www.epa.gov/sites/default/files/2017–04/aquatic-life-criteria-calculator-beta-wqsa-version.xls). All toxicity data were expressed as μg/L.

2.2. Riverine assemblages in England

Information on macroinvertebrate assemblage composition was obtained from the Biosys database (https://environment.data.gov.uk/ecology/explorer/) and the RIVPACS (River Invertebrate Prediction and Classification System) reference database (https://www.ceh.ac.uk/services/rivpacs-reference-database). The Biosys database contains taxonomic information for over 28,000 riverine sites in England monitored by the Environment Agency since 1965 and includes sites of differing water quality. In contrast, the RIVPACS reference database contains information for 795 high-quality and minimally impacted sites throughout the UK sampled between 1978 and 2002. Macroinvertebrate records were extracted for English sites sampled during the period 2015 - 2020 (Biosys database) or 1978 - 1993 (RIVPACS reference database). For the Biosys database, the most recent sampling year was selected for any site sampled in multiple years, and a combined site-specific species list was generated for sites sampled on more than one occasion within a year. A combined site-specific species list was also generated for sites recorded in the RIVPACS reference database, as each site was sampled in spring, summer, and autumn. Each record comprised the sample date, location (Site ID), and taxon name. Apparent errors in taxonomy were corrected and any records for non-invertebrates and non-native species (categorised in the Biosys database) were removed (< 0.05 % of total records). Sites with marine and brackish water macroinvertebrates were also excluded (Gunn et al., 2018). The Biosys and RIVPACS databases use the same invertebrate sampling protocol (i.e., 3-minute active sampling (kick sampling) followed by a 1-minute hand search).

Some macroinvertebrate taxa were only recorded in the databases at the family, order, or class level, but toxicity data are usually recorded at the level of species or genus. Consequently, sites where more than 30 % of taxa, in terms of total richness, were recorded above the genus level, were excluded. In addition, sites, where the total number of taxa recorded was less than 10, were also excluded to meet the minimum number of species requirement for forming SSD curves. The final datasets consisted of 129,519 taxa records across 3663 Biosys sites (Fig. 1a) and 30,637 taxa records across 421 RIVPACS reference sites (Fig. 1b). The Biosys sites are subsequently referred to as 'diverse water quality' (DWQ) and the RIVPACS reference sites as 'high water quality' (HWQ).

2.3. Assemblage-specific sensitivity to chemicals

Taxonomic lists for all 4084 assemblages were combined to produce a single taxon master list consisting of 1145 taxa at the genus or species level. The taxonomic ranks from species to the kingdom level were completed for each taxon in the master list, using the R package taxize (Chamberlain and Szöcs 2013) and information from the National Center for Biotechnology Information (NCBI), Integrated Taxonomic Information System (ITIS) and the National Biodiversity Network databases. If taxonomic information for a species was not available in these databases, a Google search was performed.

For each chemical, the hSSD model, updated to run in R (Sinclair 2021), was used to predict toxicity values for all species of unknown sensitivity in the taxon master list based on hierarchical taxonomic relatedness. The hSSD model uses the Markov chain Monte Carlo (MCMC) method to sample from a Bayesian posterior distribution for sensitivities of species. An initial burn-in of 2500 MCMC time steps was followed by 10,000 further steps from which the geometric mean was calculated to obtain a single predicted toxicity value for each species. Toxicity values were not predicted for those species for which measured toxicity data was available. The hSSD model was validated using a leave-one-out cross-validation approach. The median R^2 value for the 18 study chemicals in this study is 0.67 (range: 0.24 – 0.83, Table S1).

Predicted or measured toxicity values for each chemical were allocated to the 4084 assemblages based on their taxonomic composition, resulting in an empirical SSD for each chemical and assemblage (73,512 combinations). For each empirical SSD, the mean and standard deviation were calculated from the log-toxicities and used to calculate the concentration hazardous to 5 % of species (HC5) using the "fitdistr()" function from the MASS package. The motivation for calculating the HC5 we used here is different from the traditional log-normal based HC5 (see SM Section 2). The function of HC5 in this study provides a summary measure of the sensitive end of assemblage sensitivity. It considers the full information on species composition and their chemical sensitivity (i.e., predicted or actual toxicity data) of the assemblage, stays neutral regarding the number of species, and enables the comparability with risk assessments and environmental quality standards.

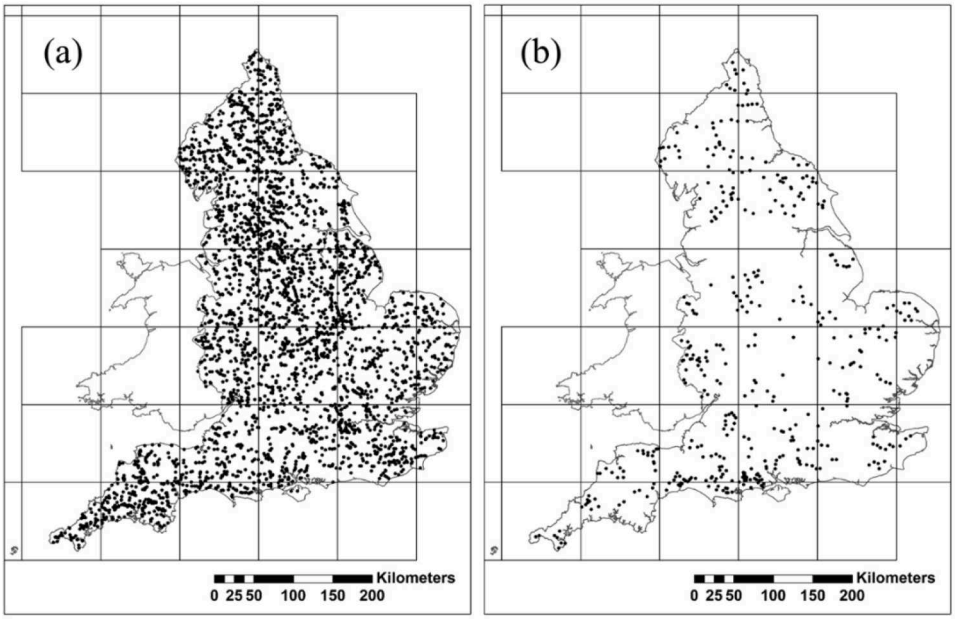

Fig. 1. Locations of 3663 diverse water quality (DWQ) sites (a) and 421 high water quality (HWQ) sites (b) across England.

2.4. Assemblage composition, toxic mode of action and sensitivity

The taxonomic similarity of assemblages within each of the datasets (i.e., DWQ and HWQ) was assessed by calculating a Jaccard similarity index (Jaccard 1912) for pair-wise combinations of assemblages. A Jaccard index (J) of 1 indicates that the taxonomic composition of the assemblages is identical and a value of 0 indicates that the assemblages have no taxa in common. The ratio of the largest HC5 value to the smallest HC5 value for each pairwise comparison (i.e., $HC5_{large/small}$) was used as a measure of similarity in assemblage sensitivity. A $HC5_{large/small}$ of 1 indicates that the chemical sensitivity of both assemblages is the same and values greater than 1 indicate that they are different. The hypothesis that assemblages with dissimilar taxonomic composition may have similar or dissimilar chemical sensitivities was investigated by comparing the Jaccard distance (i.e., 1 - J) and $HC5_{large/small}$ for pairwise comparisons within 421 HWQ and 421 selected DWQ assemblages, separately. The relationship between taxonomic dissimilarity and dissimilarity in assemblage sensitivity was visualised for each study chemical and assemblage type.

Study chemicals were divided into two groups based on their toxic modes of action: general-acting toxicants and specifically-acting toxicants (Barron et al., 2015). The hypothesis that variation will be greatest for chemicals with a very specific toxic mode of action was tested separately for the DWQ and HWQ assemblages. Variation in assemblage sensitivity to each chemical was described using the ratio of the maximum HC5 value to the minimum HC5 value for all DWQ or HWQ assemblages (i.e., $HC5_{max/min}$). The $HC5_{max/min}$ values for specifically-acting and general-acting chemicals were compared using a two-sample Wilcoxon-Mann Whitney test, where chemicals were the independent replicates.

2.5. Spatial variation in assemblage sensitivity to chemicals

For each dataset, spatial patterns in assemblage sensitivity to each study chemical were explored using hotspot analysis in ArcGIS (Scott and Janikas 2009). The HC5 values were log-transformed to meet the assumptions of the hot spot analysis before conducting the spatial cluster analysis, mitigating the impact of outliers and allowing important patterns to stand out. The results were visualised to show the spatial distribution of statistically significant ($\geq$ 95 % confidence level) clusters of more sensitive (small HC5 values) and less sensitive assemblages (large HC5 values). The threshold that distinguishes 'large HC5' values from 'small HC5' values is determined by the average of all log-transformed HC5 values for each chemical (i.e. large HC5 values are greater than the average and small HC5 values are less than the average for each chemical). The z-scores and p-values were calculated to determine which spatial cluster type (hot spots, cold spots, neither) individual assemblages belonged to. False discovery rate correction was applied when performing cluster analysis.

The spatial variation in sensitivity between chemicals was compared separately for DWQ and HWQ assemblages. Assemblage HC5 values were matched to 100 km^2 grid squares (Fig. 1), and the median sensitivity of all assemblages in the same grid square was calculated. The spatial variation in median sensitivity was then compared between chemicals using Spearman rank correlation. The spatial variation in sensitivity between DWQ and HWQ assemblages to the same chemicals was also analysed using Spearman rank correlation analysis to investigate whether the spatial patterns of assemblage sensitivity are affected by external stressors.

2.6. Relating spatial variation in assemblage sensitivity to river typology

A European river typology based on Water Framework Directive (WFD) river typology descriptors (i.e., catchment altitude, size, and geology) (Jupke et al., 2022; Solheim et al., 2019) was used to explore if and how chemical sensitivity of assemblages varies by river typology. Catchment altitude and catchment area data for all sites in the DWQ and HWQ datasets were obtained from the Catchment characterisation Model River and Catchment Database (CCM2; De Jager and Vogt, 2007). Catchment geology data were obtained from Solheim et al. (2019). All 4084 sites were matched to specific river typology descriptors (catchment altitude, geology, and size, Table S2) using the spatial join function in ArcGIS and categorised into seven river types: lowland, calcareous or mixed, medium-large (RT1), lowland, calcareous or mixed, very small-small (RT2), lowland, siliceous including organic, very small-small (RT3), mid-altitude, calcareous or mixed, very small-small (RT4), mid-altitude, siliceous including organic, very small-small (RT5), lowland and midland, organic calcareous, very small-small (RT6), lowland, siliceous including organic, medium-large (RT7)

For each chemical, the assemblages with the lowest 5 % of HC5 values (i.e., most sensitive assemblages) and the largest 5 % of HC5 values (i.e., least sensitive assemblages) were extracted from each dataset independently and assigned to a river type. For each chemical type (i.e., metals and insecticides), a Chi-squared test or Fisher's exact test was used to assess whether the distribution of sensitive and least sensitive assemblages across the river types was different from what would be expected if sensitivity was independent of river type.

2.7. Comparing chemical sensitivity distributions to operational environmental quality standards

The sensitivities of DWQ assemblages were compared to current environmental quality standards (EQSs) in England (https://www.gov.uk/guidance/surface-water-pollution-risk-assessment-for-your-environmental-permit). Environmental quality standards for a chemical may be expressed as the maximum allowable concentration (i.e., MAC-EQS) or the annual average concentration (i.e., AA-EQS) (European Commission, 2018). For each study chemical, the lowest HC5 value for all 3663 DWQ assemblages (i.e., $HC5_{min}$) was compared to the EQS values. The $HC5_{min}$ and MAC-EQS are based on short-term acute toxicity data and the AA-EQS is calculated using chronic toxicity data. Both the MAC-EQS and AA-EQS may be derived from species sensitivity distributions and a multiplication factor of 0.1 has been proposed to extrapolate acute HC5 values to chronic HC5 values (Hiki and Iwasaki 2020). The level of protection (i.e., at potential risk) provided by current EQS values was assessed by calculating the proportion of assemblages where the HC5 was less than the MAC-EQS or the 0.1 x HC5 was less than the AA-EQS. The margin of safety was expressed using the ratio of the minimum and maximum HC5 to the EQS values where assemblages are not at risk. The margin of safety, based on MAC-EQS, ranges from $HC5_{min}$/MAC-EQS to $HC5_{max}$/MAC-EQS, while the margin of safety based on AA-EQS ranges from (0.1 x $HC5_{min}$)/AA-EQS to (0.1 x $HC5_{max}$)/AA-EQS.

3. Results

This study involved an analysis of 4084 riverine macroinvertebrate assemblages and 1145 taxa; representing 4 phyla, 9 classes, 37 orders, 138 families, and 472 genera. The similarity in taxonomic compositions was compared for all pairs of DWQ or HWQ assemblages and then the mean and standard deviation of similarity were computed. On average, HWQ assemblages had a higher taxonomic similarity (mean = 0.26, SD = 0.10) and taxonomic richness (mean = 72.77, SD = 16.01) than DWQ assemblages (similarity mean = 0.16, SD = 0.09; richness mean = 35.36, SD = 13.02). The sensitivity of all assemblages was assessed for 18 chemicals; five metals (cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), zinc (Zn)), and 13 insecticides (azinphos-methyl (AZM), carbaryl (CBL), carbofuran (CBF), dichlorodiphenyltrichloroethane (DDT), deltamethrin (DTM), diazinon (DZN), endosulfan (EDS), fenitrothion (FNT), lindane (LIN), malathion (MLT), methoxychlor (MXC), parathion-ethyl (PAE), parathion-methyl (PAM)). Assemblage-specific HC5 values were derived from SSDs for each of the 4084 assemblages

and for each of the study 18 chemicals resulting in a total of 73,512 HC5 values for analysis.

3.1. Variation in assemblage-specific sensitivity: importance of taxonomic composition and toxic mode of action

As hypothesised, there was not a simple mapping between dissimilarity in the taxonomic composition of assemblages and dissimilarity in their chemical sensitivities. For all chemicals, a consistent pattern was observed. As illustrated for cadmium in Fig. 2 and for the other chemicals in Fig. S1 (DWQ assemblages) & Fig. S2 (HWQ assemblages), differences in taxonomic compositions may result in a wide variety of outcomes in assemblage sensitivity. Assemblages that are taxonomically very similar have very similar chemical sensitivities, but assemblages that are taxonomically very dissimilar may have very similar or very different chemical sensitivities

The hypothesis that the variation in chemical sensitivity (i.e., $HC5_{max/min}$ across all assemblages) would be greater for assemblages exposed to chemicals with a specific toxic mode of action was supported for DWQ assemblages (Wilcoxon-Mann Whitney test, $p < 0.001$, $n = 18$), but not for HWQ assemblages (Wilcoxon-Mann Whitney test, p-value = 0.246, $n = 18$) (Fig. 3a). The variation in chemical sensitivity was significantly less for HWQ assemblages than for DWQ assemblages, and this was consistent across all study chemicals (Wilcoxon-Mann Whitney test, $p < 0.001$, $n = 36$) (Fig. 3b). DWQ assemblages present greater differences in their taxonomic compositions (i.e., pairwise taxonomic similarity and taxonomic richness) than HWQ assemblages. For DWQ assemblages, $HC5_{max/min}$ ranged from 43 (nickel) to 6745 (azinphos-methyl), and for most specifically-acting chemicals, the maximum HC5 values are hundreds or even thousands of times greater than the minimum HC5 values. For HWQ assemblages, the highest $HC5_{max/min}$ value was 30 (azinphos-methyl).

3.2. Spatial variation and patterns of assemblage sensitivity to chemicals

Assemblage-specific sensitivity to chemical stressors was spatially patterned, with distinct clusters of more sensitive assemblages (low HC5 values) and less sensitive assemblages (high HC5 values) (Fig. 4 and Fig. S3). The strength of this clustering was greatest for DWQ assemblages, which is a function of their larger variation in assemblage sensitivity (Section 3.1), as well as their greater number and spatial coverage of sites (Fig. 1). The pattern of spatial clustering varied between chemicals. Whereas assemblages at DWQ sites in the north and southwest of England were less sensitive to metals, they were more sensitive to carbaryl and fenitrothion (Fig. 4). Sites in southern areas were generally more sensitive for insecticides (azinphos-methyl, carbofuran, DDT, deltamethrin, diazinon, endosulfan, lindane, malathion, methoxychlor, parathion-ethyl, and parathion-methyl), whereas sites in northern areas were less sensitive for these insecticides. Assemblage-specific sensitivity to metals exhibited stronger spatial clustering patterns than assemblage-specific sensitivity to insecticides.

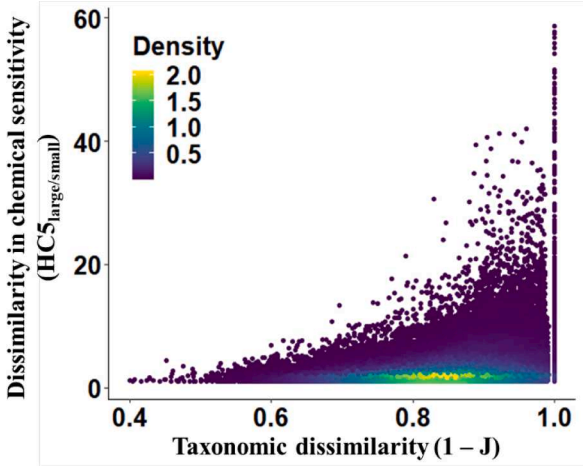

Fig. 2. The association between the dissimilarity in taxonomic composition and the dissimilarity in assemblage sensitivity to cadmium (for the other chemicals in Fig. S1 (DWQ assemblages) and Fig. S2 (HWQ assemblages)). Each data point is a pair of assemblages. Taxonomic dissimilarity is defined as 1 – Jaccard index (J) and the dissimilarity in assemblage sensitivity is defined as the ratio of the largest to smallest HC5 value within each pair of assemblages ($HC5_{large/small}$). The density of data points is indicated by the color coding.

The spatial patterns of the sensitivity for both DWQ and HWQ assemblages demonstrated greater similarity among metals compared to insecticides, as illustrated in Fig. 5 and Fig. S4. For HWQ assemblages, the spatial pattern for metal sensitivity was opposite to that of insecticide sensitivity (i.e. regions of high metal sensitivity were not the same as regions of high insecticide sensitivity), but for DWQ assemblages, this contrasting pattern was only observed for carbaryl and fenitrothion. Pairwise comparisons between different insecticides resulted in a large variation in correlation coefficients (Fig. S4), implying that there were multiple spatial distribution patterns for insecticides (Fig. 5). DWQ assemblages exposed to insecticides that act via AChE inhibition (azinphos-methyl, diazinon, malathion, parathion-ethyl, parathion-methyl, and carbofuran) generally exhibited high spatial similarity in their sensitivity, but this pattern was less strong for HWQ assemblages. Spatial patterns in the sensitivity of DWQ and HWQ assemblages exposed to the same chemical were also compared and are illustrated in Fig. S4. DWQ and HWQ assemblages share similar spatial patterns in their sensitivity to cadmium, copper, nickel, zinc, azinphos-methyl, and carbaryl (correlation coefficients > 0.6, Fig. S4).

3.3. Linkage between river typology and assemblage sensitivity

Whereas the DWQ assemblages covered all seven river types in England, HWQ assemblages did not include lowland rivers with siliceous geology and medium to large catchments (RT7). The number of sites per stream type for DWQ assemblages is as follows: 125 (RT1), 1766 (RT2), 1138 (RT3), 121 (RT4), 483 (RT5), 18 (RT6), and 12 (RT7). In the case of HWQ assemblages, the number of sites per stream type is as follows: 8 (RT1), 220 (RT2), 132 (RT3), 28 (RT4), 30 (RT5), and 3 (RT6). The breakdown of assemblage types by river types is provided in the Supplementary materials (Table S3). Overall, both DWQ and HWQ assemblages were mainly present in lowland rivers with very small to small catchments (RT2, RT3). The distribution of the 5 % most sensitive and the 5 % least sensitive assemblages deviated from the overall distribution (Fig. 6). For metals, the most sensitive assemblages were more common than expected under independence of river type and sensitivity in RT2 (lowland, calcareous or mixed, very small-small), while the least sensitive assemblages were more common than expected in RT5 (mid-altitude rivers with siliceous geology and very small-small catchments). For insecticides, the most sensitive DWQ assemblages were more common than expected in RT2, and the most sensitive HWQ assemblages were more common than expected in RT3 (lowland, siliceous including organic, very small-small). The least sensitive assemblages to insecticides were more common than expected in RT5 as metals. These differences in occurrence, which were most marked for metals, were statistically significant for all chemical and assemblage types (a chi-squared test or Fisher's exact test, DWQ assemblages: df = 6, p $\langle$ 0.05, $\chi 2 \geq 107.86$; HWQ assemblages: df = 5, $p < 0.05$, $\chi 2 \rangle$ 17.20).

3.4. The comparisons of variation in assemblage-specific sensitivity on EQSs

Both MAC-EQS and AA-EQS values were available for cadmium, nickel, lead, diazinon, and endosulfan and AA-EQS values were available for azinphos-methyl, copper, DDT, fenitrothion, malathion, and

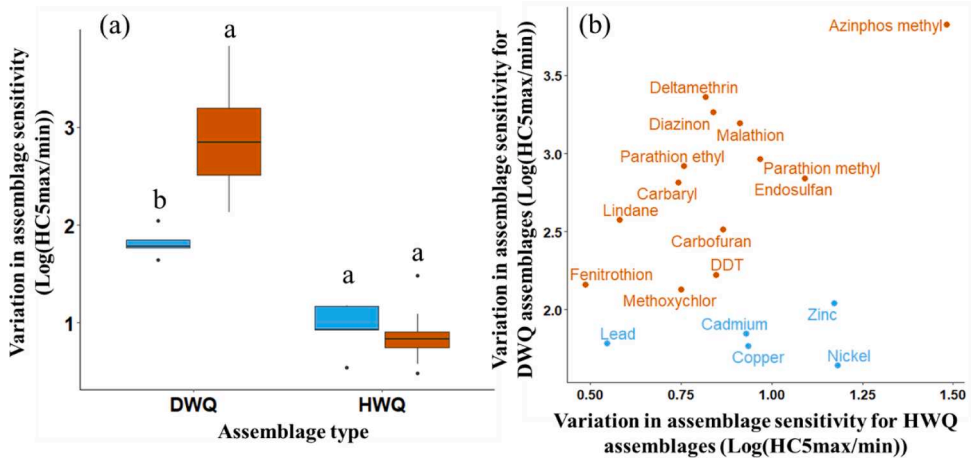

Fig. 3. (a) Variation in assemblage sensitivity ($HC5_{max/min}$) of diverse water quality (DWQ) or high water quality (HWQ) assemblages exposed to general-acting (blue boxes) or specifically-acting (orange boxes) chemicals. All data are presented logarithmically with a base of 10. Boxes indicate the interquartile range, the horizontal lines are the median values, the vertical whiskers are quartiles and the dots are outliers. The different letters above the boxes within each assemblage type indicate significant differences in median variation in chemical sensitivity ($p < 0.05$). (b) Comparison of the variation in sensitivity ($HC5_{max/min}$) of DWQ or HWQ assemblages for each of the 18 study chemicals. Blue symbols and blue labels indicate general-acting chemicals and orange symbols and red labels indicate specifically-acting chemicals.

zinc (Table 1). There was evidence that the EQS may not be sufficiently protective for three of the study chemicals (Table 1). The $HC5_{min}$ was 4.76 to 33.95 times greater than the MAC-EQS for five chemicals for which a comparison was possible (Table 1 and Fig. S5). The 0.1 x $HC5_{min}$ was lower than the AA-EQS for azinphos-methyl, copper, and malathion (Table 1 and Fig. S5), but the proportion of assemblages at potential risk is very small (0.03 – 0.49 %). DWQ assemblages to these chemicals are less sensitive than expected, with potential overprotection. In cases where the EQS was found to be protective of all assemblages, the margin of safety (acute) between the MAC-EQS and the most sensitive assemblage ranged from a factor of 5 to 34 (Table 1). The margin of safety (acute) between the MAC-EQS and the least sensitive assemblages ranged from a factor of 290 to 26,957 (Table 1). The margin of safety (chronic) between the MAC-EQS and the most sensitive assemblage ranged from a factor of 1.3 to 23. The margin of safety (chronic) between the MAC-EQS and the least sensitive assemblages ranged from a factor of 43 to 5391 (Table 1).

4. Discussion

Spatial variation in the taxonomic composition of natural communities is a well-known phenomenon (Castro et al., 2019; Wilkes et al., 2020). However, when it comes to chemical ecological risk assessment, the relationship between taxonomic composition and the chemical sensitivity of assemblages is still unclear. The main issue is that, although interspecific variation in chemical sensitivity has been described (Esteves et al., 2017; Maltby et al., 2009), the chemical sensitivity of most species in natural communities is unknown. In this study, we have used a novel application of a taxonomy-based extrapolation method (hSSD) to predict the chemical sensitivity of untested species and hence to estimate the chemical sensitivity of specific assemblages.

Based on the analysis of over 4000 freshwater macroinvertebrate assemblages, we have demonstrated that, as expected, assemblages with similar taxonomic compositions exhibit similar sensitivity to chemicals. However, the converse is not necessarily true. Assemblages with varying taxonomic compositions can exhibit similar or different sensitivities to a chemical. Previous studies have reported that species assemblages with similar taxonomic compositions share similar sensitivity to a chemical. Nearly half of the species in the toxicity data sets for parathion-ethyl overlap, with 55.6 % of indigenous species in China and 43.5 % of indigenous species in the USA being shared, resulting in similar HC5 values (Wang et al., 2014). Similarly, very similar HC5 values for linear alkylbenzene sulfonate (e.g., 0.85 and 0.73 mg/L, respectively) were derived for two river invertebrate assemblages in England that share 70 % of the same species (Blake 2002). It should be noted that these previous studies are based on a subset of species for which toxicity data are available, rather than on the whole assemblage of species present, as is the case for the current analysis. Assemblages with different taxonomic compositions may exhibit very similar chemical sensitivity, possibly because the sensitive species within these assemblages belong to the same major taxonomic groups or have similar TK-TD traits. Independent of chemical effects, the spatial variation in taxonomic composition (such as the replacement of sensitive species by less sensitive species along the river continuum) likely contribute to the differences in assemblage sensitivity among river types (Van den Berg et al. 2020). With respect to insecticides, the replacement of insect species within an assemblage with other insect species may have a limited impact on assemblage sensitivity, as many insects exhibit similar sensitivity to insecticides. However, the replacement of insect species by non-insect species could have a major impact on assemblage sensitivity. Similarly, taxonomically dissimilar cladoceran communities have been shown to exhibit high similarity in their sensitivity to copper and zinc (Bossuyt et al., 2005). Taxonomically dissimilar assemblages may contain species that share similar TK-TD trait profiles and hence exhibit similar chemical sensitivities (Dalhoff et al., 2020; Rubach et al., 2011). Species traits were reported to be more important than species identity in determining interspecific variation in sensitivity to a pyrethroid insecticide (λ-cyhalothrin) (Wiberg-Larsen et al., 2016). Small body size and gill respiration were identified as the main predictors of interspecific variation in the sensitivity of macroinvertebrates to the insecticide chlorpyrifos (Rubach et al., 2012). Assemblages that are taxonomically very dissimilar exhibit large variations in their chemical sensitivities, with some assemblages comprising sensitive taxa, while others are composed of less sensitive taxa (Van den Berg et al. 2020). These studies support the contention that taxonomic composition may significantly influence assemblage sensitivity to chemicals, which underscores the importance of considering taxonomic compositions when evaluating the sensitivity of assemblages across different sites.

Inter-specific variation in chemical sensitivity is dependent on a chemical's toxic mode of action. Whereas some chemicals such as metals are toxic to a wide diversity of species, others have much more specific toxic modes of action (e.g., insecticides). Interspecies variation in sensitivity to specifically-acting chemicals has been demonstrated to

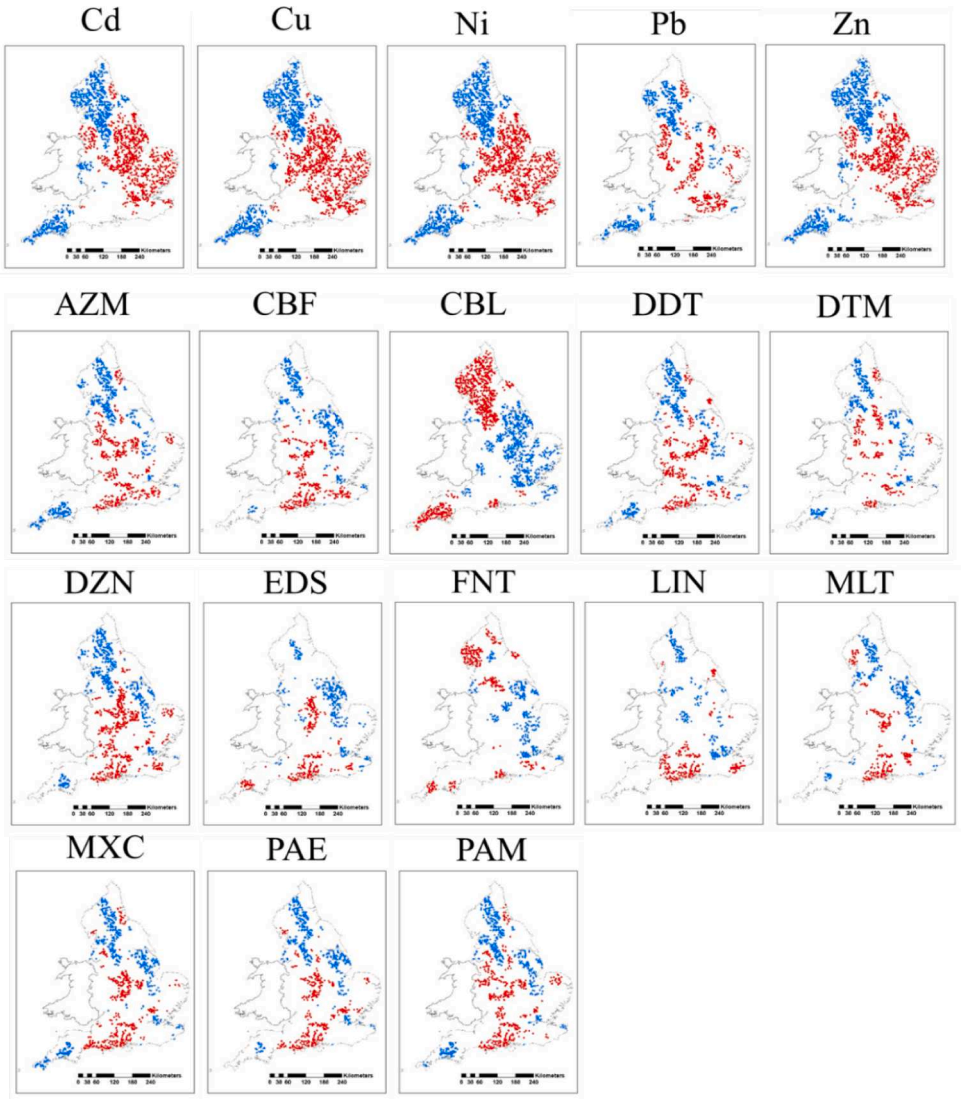

Fig. 4. Spatial patterns of the sensitivity of DWQ assemblage to 18 chemicals (cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), zinc (Zn)), azinphos-methyl (AZM), carbaryl (CBL), carbofuran (CBF), dichlorodiphenyltrichloroethane (DDT), deltamethrin (DTM), diazinon (DZN), endosulfan (EDS), fenitrothion (FNT), lindane (LIN), malathion (MLT), methoxychlor (MXC), parathion-ethyl (PAE), parathion-methyl (PAM)). Blue clusters indicate assemblages with large HC5 values and therefore less sensitive to the chemical. Red clusters indicate assemblages with small HC5 values and therefore more sensitive to the chemical.

vary by six orders of magnitude, while variation in sensitivity to general-acting chemicals is small (i.e., two orders of magnitude) (Vaal et al., 2000). We hypothesised that variation in assemblage sensitivity would be significantly greater for specifically-acting chemicals (i.e., insecticides) than for general-acting chemicals (i.e., metals). This hypothesis was supported for DWQ assemblages but not for HWQ assemblages. This is because DWQ sites contain a wider diversity of assemblages including those that are insect-poor and insect-rich. The proportion of insects in the DWQ assemblages ranged from 0 to 100 % and variation in assemblage sensitivity to insecticides (i.e., $HC_{max/min}$) ranged from 925 to 6745. In contrast, the proportion of insects in the HWQ assemblages ranged from 41 % to 98 % and variation in assemblage sensitivity to insecticides ranged from 9 to 30. The taxonomic composition of DWQ assemblages can therefore be dominated by either sensitive insect species or less sensitive non-insect taxa, resulting in large inter-assemblage variation in the sensitivity to specifically-acting chemicals.

Variation in the sensitivity of assemblages to chemical exposure was spatially patterned and distinct clusters of more sensitive and less sensitive assemblages were observed for all study chemicals. These clusters were most prominent for the DWQ assemblages and metals. Freshwater invertebrates could exhibit spatial autocorrelation patterns which may be linked to ambient (e.g., altitude, geology) and non-ambient factors (e.g., dispersal ability, species interactions) (Bonada et al., 2012; Cañedo-Argüelles et al. 2020), thus affecting the spatial patterns in assemblage-specific sensitivity. In England, species composition showed positive spatial autocorrelation patterns within the 150 km geographical distance (Murphy and Davy-Bowker 2005). This suggests that these areas exhibit similar taxonomic composition and, consequently, similar sensitivity to specific chemicals. Additionally, similar spatial patterns in assemblage sensitivity are more commonly observed within the same chemical type, indicating that considering the toxic modes of action of chemicals is also important when interpreting clustering patterns. Both DWQ and HWQ assemblages exhibit highly similar spatial patterns in their sensitivity to metals, which share the same toxic mode of action, primarily impairing osmoregulatory processes (Braz-Mota et al., 2018; Capparelli et al., 2020). The insecticides analysed in this study exhibit several specific toxic modes of action (Barron et al., 2015). Generally, the assemblages show a higher similarity in spatial patterns of sensitivity to insecticides acting via AChE inhibition than acting via other toxic modes of action. The similarity in spatial patterns for insecticides is significantly different from that observed for heavy metals.

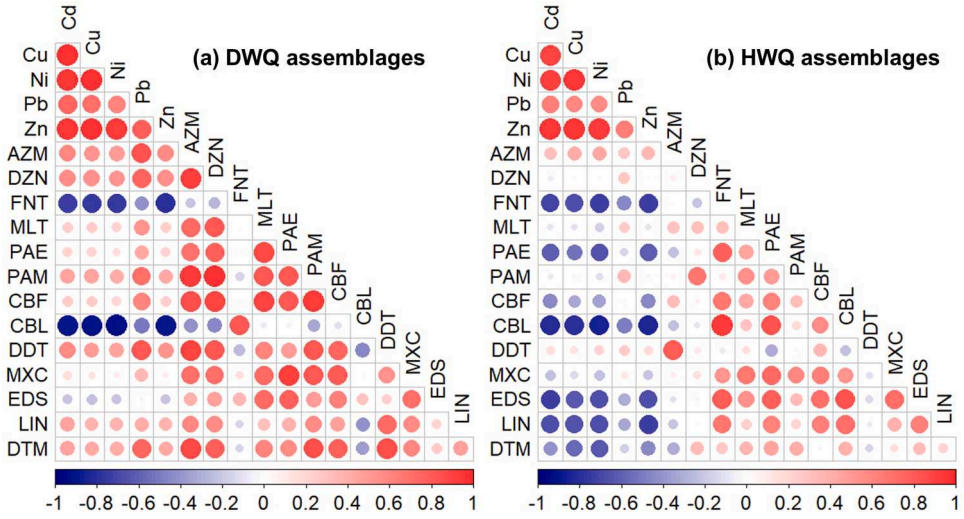

Fig. 5. Spearman correlation matrices indicating the similarity in the spatial pattern of sensitivity values for diverse water quality (DWQ) assemblages (a) and high water quality (HWQ) assemblages (b) exposed to different chemicals. Metals: cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn)). Insecticides grouped by toxic mode of action: Organophosphate AChE inhibition: azinphos-methyl (AZM), diazinon (DZN), fenitrothion (FNT), malathion (MLT), parathion-ethyl (PAE), and parathion-methyl (PAM); Carbamate AChE inhibition: carbaryl (CBL) and carbofuran (CBF); Diphenyl sodium channel modulation: dichlorodiphenyltrichloroethane (DDT) and methoxychlor (MXC); Alicyclic GABA antagonism: endosulfan (EDS), and lindane (LIN); Pyrethroid sodium channel modulation: deltamethrin (DTM).

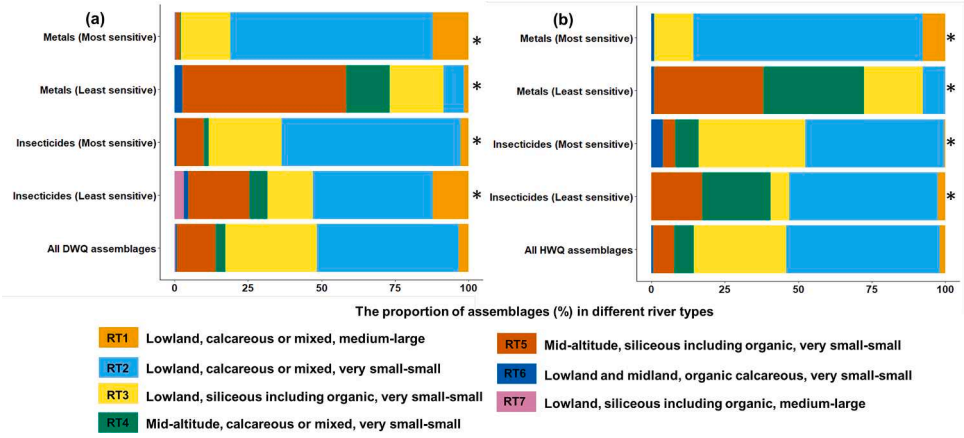

Fig. 6. The proportional distribution of (a) DWQ assemblages and (b) HWQ assemblages across seven river types (RT1–7). For each dataset, distributions are presented for all assemblages, for the 5 % most sensitive assemblages to metals or insecticides and for the 5 % least sensitive assemblages to metals or insecticides. The asterisk indicates a significant difference in the proportions of assemblages across river types compared to what would happen under the independence of river type and sensitivity (i.e., all DWQ assemblages, or all HWQ assemblages) ($p < 0.05$).

Deriving assemblage-specific sensitivity thresholds that consider the taxonomic composition of assemblages that occur under particular conditions (e.g., river typology, region) enables risk assessment to be more tailored and spatially explicit (Belanger et al., 2017). Previous studies addressing spatial variation in chemical risk have mainly focused on the spatial variation in the environmental exposures of chemicals without considering the spatial variation in the sensitivity of the exposed assemblages (Holmes et al., 2022; Posthuma et al., 2019; Spurgeon et al., 2022). An exception is the study by Van den Berg et al. (2020), which used a trait-based method to investigate the spatial pattern of sensitive invertebrates to narcosis and AChE-inhibiting insecticides in the UK. Our results are consistent with their findings that assemblages sensitive to AChE-inhibiting insecticides are mainly distributed in the south of England. However, our approach provides greater spatial coverage and chemical-specific assessment within toxic modes of action. It extends the analysis to other chemical groups (i.e., metals) and toxic modes of action (i.e., alicyclic GABA antagonism, diphenyl sodium channel modulation) (Barron et al., 2015).

Rivers are nested within a hierarchical structure in the catchment and exhibit diverse morphological and hydrological characteristics (Polvi et al., 2020). The physicochemical characteristics of rivers (e.g., catchment altitude, size, and geology) can influence assemblage sensitivity to chemicals by shaping the taxonomic composition of natural assemblages (Jupke et al., 2022; Solheim et al., 2019). The proportions of the most sensitive and least sensitive assemblages in different river typologies were significantly different from the overall distribution of assemblages across river types, indicating a possible association between river type and assemblage sensitivity to chemicals. For most chemicals investigated in this study, particularly heavy metals, the most sensitive assemblages were over-represented in lowland rivers with calcareous or mixed geology and very small or small catchments (RT2). Molluscs (i.e., gastropods and bivalves), which are known to be particularly sensitive to metals (Al-Taher et al., 2022), require substantial amounts of calcium ions to construct and sustain their shells (Chakraborty et al., 2020) and are commonly found in lowland calcareous rivers (Sinclair 2021).

Table 1
Annual average environmental quality standard (AA-EQS), maximum allowable concentration environmental quality standard (MAC-EQS), and lowest HC5 value for 3663 DWQ assemblages ($HC5_{min}$) for 11 study chemicals. All concentrations are given as micrograms per liter. Bold and italic highlighting denotes where the $HC5_{min}$ is less than the MAC-EQS or 0.1 x $HC5_{min}$ is less than the AA-EQS. The sixth column indicates the percentage of assemblages at risk and the final columns indicate the margin of safety for assemblages not at risk. The margin of safety based on the MAC-EQS is calculated as $HC5_{min}$/MAC-EQS to $HC5_{max}$/MAC-EQS, and the margin of safety based on the AA-EQS is calculated as (0.1 x $HC5_{min}$)/AA-EQS to (0.1 x $HC5_{max}$)/AA-EQS.

Chemical	MAC-EQS(acute)	AA-EQS(chronic)	$HC5_{min}$	$HC5_{max}$	Assemblages at risk (%)	Margin of safety	
						Acute	Chronic
Cadmium (dissolved)[a]	0.6	0.09	20.37	1424.27	0	34 - 2374	23 - 1583
Nickel (dissolved)	34	4	287	12,610	0	8 - 371	7 - 315
Lead (dissolved)	14	1.2	66.7	4061.7	0	5 - 290	6 - 338
Diazinon	0.02	0.01	0.29	539.13	0	15 - 26,957	3 - 5391
Endosulfan	0.01	0.005	0.077	53.632	0	8 - 5363	1.5 - 1073
Azinphos-methyl	-	0.01	0.06	406.63	*0.49*	-	NA - 4066
Copper (dissolved)	-	1	7	434	*0.41*	-	NA - 43
DDT	-	0.025	0.541	90.461	0	-	2 - 362
Fenitrothion	-	0.01	1.66	240.67	0	-	17 - 2407
Malathion	-	0.01	0.08	118.37	*0.03*	-	NA - 1184
Zinc (dissolved)	-	10.9	147.0	16,231.5	0	-	1.3 - 149

[a] water hardness: 50– 100 mg.

A comparison of current Environmental Quality Standards in England to the sensitivity of 3663 freshwater invertebrate assemblages across England indicated that current EQS values would protect all the assemblages studied from the adverse effects of eight of the eleven chemicals evaluated (i.e., cadmium, nickel, lead, diazinon, endosulfan, DDT, fenitrothion, and zinc). However, they may fail to adequately protect a small proportion of assemblages (i.e., < 0.5 %) from chronic exposure to three of the study chemicals (azinphos-methyl, copper, and malathion). Where the EQS was protective of all assemblages, the margin of safety between the EQS and the most sensitive assemblage ranged from a factor of 1.3 to 34, and between the EQS and least sensitive assemblages ranged from a factor of 43 to 26,957, indicating that operational EQS value may be extremely precautionary for some chemicals and assemblages.

Many chemicals that provide important benefits to society may also have adverse environmental impacts. The challenge of setting environmental thresholds to protect ecosystems from the adverse impacts of chemicals is to balance being overly cautious and underprotective. Being overly cautious may lead to unnecessary mitigation costs or the restriction of chemicals that provide societal benefits, whilst providing no additional environmental benefits (Belanger et al., 2017). Being underprotective may also have societal impacts by resulting in the loss of biodiversity and associated ecosystem services (Maltby, 2013). Our work contributes to a move away from single 'one-size-fits-all' protective thresholds to spatially-defined thresholds that facilitate the targeting of mitigation and control measures to maximize environmental protection, thereby helping address the balance between being overly cautious and underprotective (Maltby et al., 2022).

This study has demonstrated how the sensitivity of invertebrate assemblages to chemical stress is clustered spatially and that the relative sensitivity of assemblages depends on the chemical to which they are exposed. Central to this approach is the use of hSSD to predict the toxicity of chemicals to untested species. Alternative approaches for addressing the challenge of missing toxicity data are the interspecies correlation estimation model (Awkerman et al., 2014; Raimondo and Barron 2020), which has been used to derive the protective thresholds for chemicals (Feng et al., 2013; Wu et al., 2015), and trait-based approaches (Van den Berg et al. 2020). However, in contrast to the current study, previous studies have either only predicted the sensitivity of a very small number of untested species at the national scale, with limited consideration of inter-regional variation in assemblage sensitivity, or have been restricted to a few specific toxic modes of action. The hSSD approach can be used to predict the sensitivity of most species that occur in natural assemblages at an individual site level to any chemicals for which sufficient toxicity data exist. It therefore reduces the uncertainties in deriving assemblage HC5 values, increases spatial resolution, and expands applicability to the diverse range of chemicals to which ecosystems are exposed. Taxonomy-relatedness methods offer a practical option for predicting species sensitivity since taxonomy data are readily accessible from databases like NCBI and ITIS. A more comprehensive integrated approach, incorporating taxonomy, species traits, and genomic information, could be developed in the future, pending the availability of detailed toxicokinetic-toxicodynamic trait information and genetic data (Van den Berg et al., 2021). The fact that the sensitivity of assemblages is clustered spatially and linked to river typologies provides a framework for establishing ecological scenarios where the most and least sensitive assemblages exist and for developing scenario-specific EQS values that protect the environment and enable society to benefit from chemical use.

5. Conclusion

This study assessed spatial variation in the sensitivity of 4084 freshwater macroinvertebrate assemblages to 18 chemicals using a novel taxonomy-based extrapolation method (hSSD). It demonstrated that assemblages sharing similar taxonomic compositions exhibit similar chemical sensitivities, but those with different compositions could vary slightly or greatly. Additionally, the variation in sensitivity of DWQ assemblages was significantly higher for specifically-acting chemicals than for general-acting chemicals. Sensitive and less sensitive assemblages displayed significant spatial clustering, which was chemical-specific and related to river typology. The most sensitive assemblages were more prevalent than expected in lowland rivers with calcareous or mixed geology and very small to small catchment areas, while the least sensitive assemblages were more abundant than expected in mid-altitude rivers with siliceous geology and very small to small catchment areas. The operational EQSs, available for 11 of the 18 study chemicals, protected most assemblages (> 99.5 %), but a few were potentially at risk from azinphos-methyl, copper, and malathion. These results highlight the importance of considering spatial variation in taxonomic composition when assessing the risk of chemicals to freshwater ecosystems and deriving protection thresholds. The risk of a given chemical is not the same everywhere and areas of high risk vary depending on chemical type. The development of spatially defined environmental quality standards, possibly based on river types, could be used to target areas requiring the highest protection, striking a balance between chemical use benefits and environmental protection.

CRediT authorship contribution statement

Ruoyu Liang: Writing – original draft, Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation,

Methodology. **Thomas M. Sinclair:** Methodology, Investigation, Data curation, Writing – review & editing. **Peter S. Craig:** Methodology, Writing – review & editing. **Lorraine Maltby:** Writing – review & editing, Supervision, Conceptualization, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120854.

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