An ecosystem service impact assessment framework applicable to any chemical pollutant

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Data availability

The underlying data used in the step 1 potency ranking and step 2 exposure ranking are available within the supporting information linked to this article, as well as the template (with calculations) used in the step 3 community impact assessment.

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Conflicts of interest

The authors confirm that they have no competing financial or non-financial interests.

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ABSTRACT

This paper outlines a generic and broadly applicable proof-of-concept framework linking ecosystem services to relative Environmental Risks and Impacts of Chemicals (ENRICH) to quantify the impacts of chemical pollution at a national (UK) level. The ENRICH framework utilises sources of chemical exposure and ecotoxicological data to establish the overall community and taxonomic group-level impacts of chemical pollution and the resulting effects on ecosystem processes and services. A proof-of-concept analysis is carried out for three case study chemicals: fipronil, copper (Cu) and perfluorohexanoic acid (PFHxA) that differ in their mode of action (MoA), usage, and data availability. The results indicate that each case study chemical has different predicted impacts on different taxa: fipronil strongly affects arthropod groups, Cu affects a wider range of taxa and PFHxA mainly vertebrate species. These predicted taxa impacts are linked through logic chains to different ecosystem service provision consequences. The three case studies demonstrate the generalisability and value of the hazard, exposure, community and ecosystem service impact assessment steps of the framework, and also highlight the remaining uncertainties and data gaps in its use. The ENRICH framework illustrates that, despite challenges, a chemical-agnostic approach to impact characterisation support prioritisation of chemicals and the evaluation of ecosystem services benefits arising from chemical pollution management policies.

KEYWORDS: Exposure, Hazard, Prioritisation, Environmental impact, Chemical management policy

INTRODUCTION

International conventions on biodiversity and ecosystem services, which are the benefits that humans derive from natural ecosystems, identify pollution, alongside climate change, habitat loss, unsustainable exploitation, and invasive species and diseases, as a major environmental threat. Chemical pollution is currently recognised to exceed the planetary boundary safe operating space (Persson et al., 2022), reflecting that there is a vast number of substances that require evaluation, many of which remain poorly studied. Even when the potential for substances to cause adverse effects is well recognised, current or past uses may still lead to harmful effects on people and ecosystems (Slabe et al., 2022).

Understanding and valuing the environmental impact of chemicals and associated societal consequences is a priority for chemical regulation (European Chemicals Agency, 2023). Policymakers are faced with difficult decisions when determining which chemicals to monitor, evaluate and regulate. A major challenge is to balance the benefits of chemical use against the health and environmental costs of the associated pollution. Challenges such as chemical diversity, data gaps, and the absence of models linking ecotoxicological data to ecosystem service impacts have to date limited the development of pollution impact valuation frameworks (Faber et al., 2019). As a result, decisions on chemical management often have to rely on risk assessments that have high uncertainty and which often poorly link substance effects to the intended ecological protection goals (Fairbrother and Bennett, 1999).

In seeking to develop a foundation for economic valuation of chemical pollution, the OECD (2022) identified some major challenges for impact assessment framework development. These issues included data availability, incorporating species variation, linking taxa impacts to ecosystem changes and undertaking economic valuations amid uncertainty. Past efforts to link chemical pollution to ecological impact have to date focused on quantitative relationships between “toxic pressure” and ecosystem services (Wang et al., 2021), pathways analyses (Hayes et al., 2018, Maltby et al., 2021), and mechanistic modelling (Forbes et al., 2017). However, despite progress, no broadly applicable comparative framework to support chemical prioritisation and chemicals management yet exists. Here we propose a conceptual framework linking ecosystem services to relative Environmental Risks and Impacts of Chemicals (ENRICH), that can be applied to any chemical and enables screening-level and standardised comparative analyses of ecological impacts to support pollution management policies.

The ENRICH framework integrates hazard, exposure, community impacts, ecological logic chains and ecosystem services to characterise and link chemical pollution to ecosystem endpoint changes (as visualised in Figure 1). The ENRICH framework assesses species impacts (proportion of taxonomic groups affected by chemical exposure) using hazard and exposure data, following the central tenet of chemical risk assessment. Unlike traditional risk assessment approaches, our method does not produce binary, absolute risk estimates – acceptable or unacceptable risks. Instead, it ranks chemical hazard and exposure relative to other chemicals and each substance is assigned an eco-potency and an exposure group between 1 and 7.

Substances within the 5th eco-potency percentile (representing the lowest hazard relative to all chemicals assessed) are assigned to Group 1, while those in the 95th percentile (representing the highest hazard) are assigned to Group 7. Exposure groups are assigned in a similar manner, where magnitude and occurrence of exposure to a chemical determines whether it is assigned to a high (Group 7 – 95th percentile) or low (Group 1 - 5th percentile) exposure group (see Figure 1 for the full group assignments). The eco-potency and exposure groupings assign a value to the proportion of species in a community likely to be affected at the prevailing level of exposure for a chemical of a given eco-potency. This extent of overall impact is then apportioned across different taxa based on the available species toxicity data. Ecosystem service logic chains connect these taxa effects to ecosystem service impacts, which can be monetised. The current ENRICH framework is designed to assess impacts at a larger geographical scale – primarily national level - rather than local (e.g., point sources) such as accidental release, unauthorised or inappropriate chemical use. This is due to scope restrictions of the project, and does not prevent future adaptation to local pollution.

We apply the ecosystem service impact assessment framework at UK national scale to three case study chemicals: fipronil, copper, and PFHxA. We use these cases to illustrate how analysis conducted within the ENRICH framework can identify plausible pollution impacts on taxa and link these to plausible consequences on ecosystem processes and services. We also summarise the strengths, weaknesses, data limitations and simplifying assumptions at each step of the ENRICH framework, as well as key research and knowledge gaps requiring further refinement and development to support growing use e.g., by regulators and policy makers.

MATERIALS AND METHODS

Step 1 Hazard Ranking

Hazard ranking compares the eco-potency of the chemical of interest to a distribution of similar values for many other chemicals. The overall chemical eco-potency ranking was created using HC_{50} values from 12,386 SSDs (Posthuma et al., 2019b). These HC_{50}s are ranked from lowest (most eco-potent) to highest (least eco-potent). Eco-potency ranking percentile is determined by placing the most robust HC_{50} available for the chemical of interest within this distribution. The SSD HC_{50} values are used for this eco-potency assessment, as within an SSD, the HC_{50} has the lowest uncertainty and is more robust than using values in the tail of the SSD model, such as the HC_5 value. The SSDs from which we took the HC_{50} to compare to the overall distribution were collected from several sources, with regulatory reviews considered the best and most reliable source, followed by SSD models from the research literature and then bespoke values generated from reported ecotoxicity data. The percentile eco-potency rank generated by comparing the substance specific HC_{50} to the overall distribution is used to assign the chemical to one of seven eco-potency groups, with group 7 (percentile rank 0 to ≤0.05) being that for the most potent substances and group 1 (percentile rank >0.95 to 1) the least potent (Figure 1).

To accommodate data-poor substances, the ecosystem service impact assessment framework allows alternative approaches when SSD generation is not possible, but some toxicity data exists. In such cases, the geometric mean of reported species EC_{50} values for the chemical of interest can substitute an HC_{50} value to assign a eco-potency rank. For chemicals lacking ecotoxicological data, predictive tools like

MoA or quantitative structure-activity relationship (QSAR) models could be used to provide an estimate of eco-potency. For instance, the commonly applied Verhaar classification scheme (Verhaar et al., 1992) could be used and mapped to the eco-potency categories in the ENRICH framework (e.g., Non-polar narcotics = Category 7, Polar narcotics = Category 6, Reactive chemicals = Category 5, Specifically acting chemicals = Categories 4-1, Unknown MoA = Categories 4-1, depending on where MoA specific structural alerts are also present). However, using such simple *in silico* tools introduces greater uncertainty, due to the complexity of predicting MoAs across species. So having at least some measured hazard data or using multiple QSAR approaches is generally desirable to gain a better understanding of ecotoxicity eco-potency for ranking use.

The SSD and HC_{50} catalogue of Posthuma et al. (2019b) was developed using apical toxicity data, such as effects on mortality, growth, reproduction, and population size. However, chemicals can also cause hazards through mechanisms not detected by these bioassays, including endocrine disruption, genotoxicity, and bioaccumulation leading to long-term effects (Baas et al., 2010). These hazards can be predicted using QSAR models to provide “structural alerts” (Pradeep et al., 2021), through mechanistic toxicology studies and *in vitro* assays or through MoA assignments (Kramer et al., 2024). Non-apical mechanisms of effect raise the hazard potential of chemicals. To integrate such hazards into the ecosystem service impact assessment framework, chemicals identified as endocrine disruptors or genotoxic are moved to a higher eco-potency group than indicated by their apical toxicity data alone (Figure 1). Highly bioaccumulative chemicals are also moved up one eco-potency rank due to their greater potential to cause hazard through their potential to cause long-term effects (n.b., we chose to recognise the higher risk potential of bioaccumulative chemicals by raising hazard rather than exposure ranking due to their potential to have greater effects through long-term bioaccumulation leading to higher internal exposure and trophic transfer). For genotoxic chemicals, eco-potency is raised one category for all species (Figure 1). For chemicals with endocrine effects or high bioaccumulation (e.g., bioconcentration factor >2,000), eco-potency for vertebrates is further increased by one category, but not for invertebrates, plants, or microbes due to uncertainties in endocrine effects for these groups and their generally low trophic positions. Chemicals with both genotoxicity and endocrine effects or bioaccumulation, thus, have their eco-potency increased by two levels for vertebrates and one for invertebrates (Figure 1).

Step 2 Exposure Ranking

Exposure ranking follows a similar approach as for eco-potency, where chemicals are ranked relative to others using a frequency distribution (Figure 1). Developing an environmental concentration ranking requires large-scale monitoring datasets. National water quality programs provide inland surface water pollution measurements for England (EA WIMS) and the United Kingdom (UKWIR CIP). European-level data portals (e.g. Water Information System for Europe, NORMAN EXPODAT database) and data-sets for marine waters (European Marine Observation Data Network chemistry portal) are also available. For any national-scale analysis, the use of country-relevant data are preferred where feasible, given how unique chemical use and hydrological/environmental conditions can shape chemical concentrations in different locations.

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The EA WIMS database includes chemicals such as metals, polyaromatic hydrocarbons, pesticides, POPs, pharmaceuticals, industrial chemicals, solvents, PFAS, phthalates, and plastic polymers. Major cations and nutrients are excluded due to their high ecotoxicological thresholds, non-toxic effects (e.g., eutrophication), and role in modifying bioavailability rather than in causing direct toxicity. Using EA WIMS data (a holding that contains ~954,870 measurements between 2017-2022 for ~440 chemicals across ~8,500 sampling sites), chemicals can be ranked by both measured concentration (using 95th percentile values) and detection frequency. We used the 95th percentile exposure concentrations over median concentrations for ranking because the number of non-detects for many chemicals in the data-set limited the reliable calculation of many medians. For emerging chemicals or those with growing use, current monitoring data may not reflect future exposure. In such cases, multi-media fate models could be used as an alternative source of exposure information.

The 95th percentile measurement concentration and detection frequency for the chemical of interest are placed into the relevant frequency distributions for all chemicals derived from the monitoring data (in this case the full EA WIMS data-set). The two percentile ranks are then averaged (Figure 1). This composite percentile ranking is then used to assign the chemical to one of seven exposure groups, with group 7 (percentile rank 0 to ≤0.05) for the highest exposure substances and group 1 (percentile rank >0.95 to 1) the least. A total of 7 percentile groups have been chosen to provide enough granularity and make the ecosystem service impact assessment framework tractable to implement. Chemicals with high persistence and mobility pose particular concern, as they can remain in the environment and be widely transported after release. Therefore, chemicals with high persistence (e.g., half-life >60 days in water, >180 days in sediment, >120 days in soils) and high mobility (e.g., log Koc <3) are considered of additional exposure concern (European Commission, 2022). Chemicals identified as both persistent and mobile are, therefore, raised one exposure class within the assessment (Figure 1).

Step 3 Community and Taxa Impact Assessment

The eco-potency and exposure categories designated in steps 1 and 2 are used to assign a level of expected community effect for the chemical. The impact values in this matrix are defined from evidence on the maximum effect of a chemical on communities at a national scale, with a logarithmic decrease for both lower eco-potency and lower exposure (Table S7). The maximum community effect of 20% at the national level is set based on multiple lines of evidence: 1) a large-scale European study that reported that on average 20% of aquatic species are at risk due to chemical pollution (Posthuma et al., 2019a); 2) Lemm et al. (2021) who found an average 26% impact of chemical exposure on ecological status using a multi-substance Potentially Affected Fraction (msPAF) approach; 3) Posthuma et al. (2020) who concluded that rivers in “bad” ecological status had msPAFs up to ~0.5 for the chemical mixture, of which the most important chemical can be expected to contribute 40-80% of the mixture effect (Spurgeon et al., 2022b). The logarithmic factor of 3 used to calculate proportional effects from lower eco-potency and exposure group combinations is chosen as an intermediate value of concentration response slopes, which typically assumes a value between 0 and 5 (Ritz, 2010). The highest community effect of 20% is assigned to any chemical belonging to the highest eco-potency group 7 (most toxic 5% of chemicals) and highest Exposure Group 7 (top 5% of chemicals for the average of concentration and detection frequency rank). The proportion of species affected decreases with both eco-potency and exposure group.

Ecosystem processes and services are delivered through the functional contributions of key taxa. To allocate the overall chemical effect to taxa, the percentage of species impacted in a community as given from the combination of eco-potency and exposure groupings, apportioned across 17 groups of vertebrates (amphibians, birds, fish, mammals and reptiles), invertebrates (annelids, crustaceans, insects, molluscs, nematodes, rotifers and springtails), plants (algae and higher plants) and microbes (bacterial communities, fungi and protozoa). For the assignment, the available chemical toxicological data (acute EC_{50} values) for species in each group are collected from accessible resources (e.g. US EPA ECOTOX database and the peer-reviewed and grey literature). These data are used to calculate a taxon-specific geomean "sensitivity" value for all of the 17 taxa for which data are available. For unstudied taxa, a read-across approach is proposed to assign a sensitivity value to that group using the geomean for the nearest phylogenetically (for animals and plants) or ecophysiologically (for microbes) related taxa (Table S8). The presence of a phylogenetic signature in the sensitivity of species to toxicants has been reported in both correlative and mechanistic studies (Spurgeon et al., 2020). The presence of this relationship indicates that, although chemicals do not always present a strong phylogenetic signature, phylogenetically close taxa are more likely to reflect the sensitivity of a given taxon than more distant ones, providing a justification for taxa read-across.

The assigned geomean sensitivity, derived either directly or through read-across, is used to assign a relative sensitivity to each taxon calculated as the minimum geomean taxon acute EC_{50} / specific taxon acute EC_{50}; a value of 1 indicating the most sensitive taxon and a value closer to zero the least sensitive. The sensitivity value for each taxon is next used to estimate the proportion of that taxonomic group affected by the chemical exposure, assuming that each species within a given taxonomic group is equally impacted. This proportion is then used to estimate the number of species in each taxon impacted for likely true communities at a national scale. This assessment is done by multiplying the affected proportion by the total number of species in each taxonomic group, using information on species numbers per taxon from the recorded national fauna of the country. The result provides an assessment of numbers (but not the identities) of species affected in each taxonomic group.

Step 4. Ecosystem Service Impacts

Direct impacts from chemicals with a given eco-potency and exposure on taxa identified in steps 1-3 are linked to community and ecosystem service consequences using a set of defined evidence-based logic chains. Each logic chain links one or more taxa to a role in the delivery of ecosystem processes and functions, which are themselves linked to the realisation of provisioning, regulating, cultural, and supporting ecosystem services. Logic chain development followed the approach of Hayes et al. (2018), here expanded to include a wider range of ecosystems and a much wider range of primary impacts to account for the additional taxa potentially affected by the broader range of chemicals the ecosystem service impact assessment framework is intended to cover. A total of eight ecosystem types are included, comprising terrestrial, freshwater and coastal margin systems.

For each taxonomic group within each ecosystem, the consequences of a decline in species abundance and functions, in addition to the potential magnitude of change, were sourced from literature. These changes were then linked via logic chains to secondary and tertiary impacts on ecosystem processes and services. Where literature-based information was not available, expert judgement was used, based on information from similar species and habitats. There were several assumptions and caveats in this process, including that changes were first-order and occurred over a 'snapshot in time'. As such, there was no accounting for any secondary effects or consideration of the time taken for impacts to occur. No prey choice substitutions were made and plant and algal growth were assumed to increase in the absence of herbivory.

Direct human health impacts and direct human welfare effects of ecosystem pollution (e.g. loss of recreation activity) were outside of the ecosystem service impact assessment framework scope, although both could be integrated in a future iteration. Human food impacts are considered as reduced yields, not through quality effects on health. Some ecosystem service impacts directly affect people (e.g., reduced bird populations affecting food provisioning and nature appreciation), while many occur indirectly through trophic networks or altered functions (e.g., decomposition, nutrient cycling).

The list of endpoints linked to taxa through the logic chains is intended to capture meaningful ecosystem features, with potential for extension. The final impacts are linked to the Common International Classification of Ecosystem Services Version

5.1 (Haines-Young and Potschin-Young, 2018). Example endpoints include impacts on bird and mammal populations, wild food, soil and water properties, air quality, and human-relevant services such as pollination and genetic resources (for a full list of endpoints, see Tables S2, S4, S6). The Mapping and Assessment of Ecosystems and their Service (MAES) ecosystem classification (Burkhard et al., 2018) is used to support greater habitat resolution and international applicability. For each habitat, any defined ecosystem endpoint can be reached by multiple logic chains. The values resulting from each chain in conditions unaffected by the chemical hazard, i.e., normal functioning, are summed to give a number (in arbitrary units) for each ecosystem type. Similarly, values from each logic chain are calculated and summed based on the reduction in the functioning linked to the apportioned taxa effects of a chemical of specific eco-potency and exposure as identified in steps 1-3. A percentage reduction in the ecosystem endpoint is calculated based on the ratio of these two numbers. The output values are in terms of the percentage of the ecosystem endpoint remaining, providing values that can be taken forward for further analysis, e.g. economic impact valuation.

Parameterising the Framework for Case Study Chemicals

To test the ecosystem service impact assessment framework, we select three case study chemical pollutants: the insecticide/veterinary medicine fipronil, the metal Cu and the perfluoroalkyl substance PFHxA. These three represent substances from different pollutant classes that have different MoAs, usage profiles and environmental fate, providing different scenarios for ENRICH framework testing. 1) Fipronil (CAS 120068-37-3) is a neurotoxic insecticide with mainly domestic use and low to moderate persistence; Cu (CAS 7440-50-8) is an essential trace metal industrial pollutant and biocide, and PFHxA (307-24-4) is a perfluorinated compound high environmental persistence used in industrial and consumer product applications. All are relatively well studied chemicals, for which some ecotoxicity and chemical measurement data were known to be available.

Fipronil is used mainly as an insecticide in pet flea and household insect control products. Through these distributed uses, fipronil can find its way into the environment through pet swimming, domestic wastewater effluent or biosolid additions to land (Sadaria et al., 2019). Chemical prioritisation and risk assessment studies have identified fipronil as a chemical of concern for its environmental impacts (Spurgeon et al., 2022a).

Cu is a relatively abundant trace element found naturally in the environment. However, Cu can also be toxic at high concentrations (US Environmental Protection Agency, 2007). Cu is widely used in construction, consumer and industrial products, with a niche use as a biocide and pesticide. Current and legacy mining, metal processing, and product use all result in Cu releases to the environment from acid mine drainage, solid wastes, wastewater and process emissions to air.

PFHxA is a per- and polyfluoroalkyl substance (PFAS), a chemical group recognised as being of significant concern for their environmental effects (Ankley et al., 2021). PFHxA has been linked to effects in invertebrate and vertebrate species, including on metabolism and development (Labine et al., 2023). With a growing recognition of the widespread presence of PFAS in the environment and greater knowledge of the potential ecotoxicological effects, there is currently high interest in understanding their risks of PFHxA, and PFAS more generally.

RESULTS

Case Study 1. Fipronil.

Existing information on fipronil hazard and exposure was collected from substance regulatory reviews and documentation, published literature and ecotoxicity and environmental monitoring databases. A regulatory review (Environment Agency, 2022) reports apical endpoint EC_{50} toxicity data for fipronil for 48 species across 7 taxonomic groups. A species sensitivity distribution (SSD) constructed with this data has a hazardous concentration for 50% of species (HC_{50}) of 29.5 μg/L (Figure S1), placing fipronil at the 3rd percentile eco-potency among all chemical HC_{50} values (Figure 2). In the ecosystem service impact assessment framework approach, this relative eco-potency places fipronil into the highest eco-potency Group 7. The OECD Quantitative Structure Activity Relationship (QSAR) toolbox is used to identify any additional hazard mechanisms for fipronil. Available QSAR models identify structural alerts for fipronil for both genotoxicity and bioaccumulation. Within the ENRICH framework, evidence of these additional mechanisms would normally raise the eco-potency group of a chemical. However, as fipronil is already in the highest eco-potency group, its hazard grouping cannot increase further.

Surface water measurements for fipronil in England are not available in the primary data source, the Environment Agency Water Quality Archives dataset (EA WIMS), but are available in an alternative source from the UK Water Industry Research Chemical Investigation Program (UKWIR CIP). The 95th percentile concentration and detection frequency in the UKWIR CIP dataset was used to determine the percentile placement of fipronil compared to the exposure concentrations and detection frequencies of all other EA WIMS reported chemicals. Based on a 95th percentile concentration of 0.08 μg/L and 48% detection frequency

(Figure 2), fipronil is at the 68th percentile for exposure and 62nd percentile for detection frequency of all substances. The average of these percentiles places fipronil in Exposure Group 5. Regulatory chemical mobility and persistence data indicate that in water-sediment systems, fipronil is persistent (DT_{50} between 40-120 days) (Environment Agency, 2022). Within the ENRICH framework, its long environmental half-life moves fipronil up one Exposure Group, ultimately placing it in Exposure Group 6.

The ecosystem service impact assessment framework predicts that a chemical with a eco-potency group 7 and exposure group 6 impacts 12.2% of species in a community. To apportion this percentile effect to specific taxa, the available toxicity data are used to derive geomean EC_{50}s for all of the 7 taxa for which one or more species measurements were available. For the remaining 10 of the 17 total taxa included in the ENRICH framework, we applied 1st, 2nd and 3rd level hierarchical read-across to assign geomean EC_{50}s to 4, 4 and 2 of the untested groups, respectively. The taxa-specific geomean EC_{50}s indicate that arthropods (insects, crustaceans, springtails), nematodes and some microbes are most sensitive to fipronil. By taxa, 31.7% of insects, 31.7% of nematodes, 31.7% of springtails, 7.0% of crustaceans, 6.0% of ciliates, 1.7% of microbes and 1.7% of fungi are predicted to be affected by fipronil (Table S1). Sensitivity of these groups is supported in multiple ecotoxicological studies (Wu et al., 2015).

The predicted effects are used to map fipronil taxon responses to impacts on relevant ecosystem functions for each habitat type compared to the unpolluted state. Through its taxa-specific effects, logic chains indicate that fipronil may affect delivery of functions in each habitat (range 0.12 - 31.7 %) (Figure 3). The greatest effects are on 'pollination', 'food from wild animals (terrestrial) for nutritional purposes' and 'terrestrial game abundance'. These impacts are founded on the role of invertebrates in pollination and provisioning exploitable game species (Figure 3). Ecosystem service reductions are greatest in Forest, Grassland, Heathland and shrub and sparsely vegetated land habitats compared to freshwater and wetland habitats (Figure 3; Table S2).

Case Study 2: Copper (Cu)

There is available EC_{50} toxicity data for apical endpoints (mortality, growth and population size) for 43 species across 8 taxa from a United States Environmental Protection Agency (US EPA) regulatory review (US Environmental Protection Agency, 2007). The HC_{50} (117.1 µg/L) derived from an SSD fitted to these data (Figure S2) compared with the HC_{50}s for all other chemicals from the SSD database (Posthuma et al., 2019b), places Cu in eco-potency group 6 (Figure 2). Neither the regulatory report(US Environmental Protection Agency, 2007) nor OECD QSAR toolbox identify structural alerts for bioaccumulation, genotoxicity or endocrine disruption, retaining Cu in eco-potency group 6.

Surface water measurements for Cu for England are available in EA WIMS. Compared to all chemicals, Cu is ranked at the 85^{th} percentile for concentrations and 84^{th} percentile for detection frequency (Figure 2). The average percentile of these values places Cu in exposure group 6. Cu as a metal, is inherently persistent; however, reported chemical mobility data show that copper is unlikely to be highly mobile (Tipping et al., 2010). As an inorganic substance, Cu does not have a single K_{oc} value, although it is known to bind strongly to organic matter and clay minerals (Tipping et al., 2003). As Cu is only persistent, but not highly mobile, Cu remains in exposure group 6.

Placement in eco-potency group 6 and Exposure Group 6, Cu is predicted to impact 7.5% of species in communities. A national assessment of the risks of Cu to soil organisms across >1,000 UK sites indicated that Cu concentrations exceeded the critical value to impact species at 20.1% of locations, providing support for the plausibility of Cu effects at this scale (Spurgeon et al., 2008). The toxicity data used for the SSD are used to calculate taxa-specific geomean EC_{50} values for 8 directly measured taxa (algae, amphibians, annelids, crustaceans, fish, insects, macrophytes and molluscs) and via level 1, 2 and 3 read-across for 1, 3 and 5 others. This apportionment resulted in a predicted effect of Cu on 33.4% of crustaceans, 22.9% of ciliates, 22.9% of rotifers, 10.9% of molluscs, 9.2% of microbes, 6.8% of amphibians, and 6.3% of algae, these groups contributing 67% of the affected species nationally (Table S3). Consistent with this prediction, studies indicate reductions in amphibian, rotifer and mollusc populations linked to Cu effects on endpoints like juvenile survival and shell physiology (Schanz et al., 2021).

Logic chains are used to indicate taxa effects of Cu linked to changes in the delivery of ecosystem services in habitats compared to the unpolluted state. The potential effects of Cu identified may manifest in impacts on multiple ecosystem services in different focus ecosystems. Most notably, substantive effects in freshwater habitats are identified - particularly via impacts on algae and feedback through direct effects and trophic links through effect on crustaceans and fish, leading to changes in the availability of these taxa for food and recreation (Figure 3; Table S4). The impacts on these taxa can result in changes in water clarity through changes linked to phenomena such as algal blooms frequency.

Case Study 3: Perfluorohexanoic Acid

A regulatory review of the ecotoxicity information on PFHxA identified available acute aquatic toxicity data for 6 species and chronic data for 3 (European Chemicals Agency, 2017). As this analysis contained fewer ecotoxicity data points for PFHxA than for fipronil or Cu, additional searches were carried out in the US EPA ECOTOX database and scientific literature. This effort identified a further 9 acute and 5 chronic effect studies from papers considered reliable and relevant according to CRED (Moermond et al., 2016). The consolidated dataset from the regulatory report and additional published studies provided toxicity data for 11 species from 5 taxa. These data are used to generate an SSD for PFHxA which has an HC_{50} of 208,344 µg/L (Figure S3), placing PFHxA at the 84th percentile for eco-potency and so in eco-potency group 2 (Figure 2). In the OECD QSAR toolbox, PFHxA does not have structural alerts for endocrine activity or genotoxicity, but does have one for bioaccumulation. This alert elevates PFHxA to eco-potency group 3 for vertebrates, while it remained in eco-potency group 2 for non-vertebrates.

UK surface water monitoring data for PFHxA are available in the EA WIMS database, with a 95th percentile concentration of 0.001 µg/L and detection frequency of 67% (Figure 2), placing PFHxA at the 13th percentile for concentration and 78th percentile for detection frequency. The average of these two values places PFHxA in exposure group 4. Typical of many PFAS, PFHxA has a half-life in environmental media that can extend to years or even decades. Further, PFHxA has a reported log K_{oc} < 3 (range of 1.3-3.6) (European Commission, 2023), indicating that PFHxA is persistent and mobile. These characteristics move PFHxA up one level to exposure group 5.

Based on placement in eco-potency groups 3 for vertebrates and 2 for non-vertebrates, and Exposure Group 5, PFHxA is predicted to affect 0.96% of species in communities. To apportion this effect among taxa, the available toxicity data for six algae, one crustacean, one rotifer, two fish, and a bacteria are used to generate geomean EC_{50} values for these 5 taxa, with the remainder generated by level 1 and 2 read-across for 4 and 8 groups, respectively. Based on the available ecotoxicity data, fish are the most sensitive taxa. As the geomean EC_{50} for fish is used to read-across for the remaining untested vertebrates, highest impacts are predicted for these compared to the other groups. Within the five vertebrate taxa (fish, amphibians, reptiles, birds and mammals), 9% of the species are predicted to be impacted by PFHxA exposure (Table S5).

Inputting the predicted species effects into logic chain models indicated minor impacts (<1% reductions) on a range of ecosystem services linked to the roles of vertebrates as food, game and for recreation (e.g. angling) (Figure 3, Table S6). Small effects are also predicted (< 5%) on ecosystem services linked to the emblematic status of vertebrates, which support interest in nature and tourism at protected sites. Because some vertebrates play functional roles in terrestrial ecosystems, very small (~ 1%) effects are predicted for ecosystem services linked to soil functioning and organic carbon sequestration.

DISCUSSION

Evidence-based decisions on chemical management have more credibility if they can be placed into a society-relevant context. There has been a long-standing interest in developing approaches to integrate chemical hazard and exposure information with ecosystem knowledge to generate meaningful regulatory impact assessments. Proposed frameworks have so far only considered pollution costs in generic terms (Maltby et al., 2021) or focused on specific aspects (Hayes et al., 2018, Forbes et al., 2017). Here, we outline a novel ecosystem service impact assessment framework designed to characterise, link and assess chemical eco-potency, exposure, community impacts, ecological pathways and impacts of any chemical pollutant on ecosystem services. Our approach is designed to be usable for any chemical (including data-poor substances), any ecosystem (freshwater, marine, terrestrial), and – with further development - a wider set of geographical areas (country, region, catchment). A key benefit of this standardised approach is that it can be used to assess chemicals for their potential ecosystem service impacts.

It is recognised that this is currently a developing ecosystem service impact assessment framework and that further refinement will be needed for reliable use in regulatory impact assessments. However, the logic and basic structure provides a foundation to build on. To quantify chemical hazard, we draw on the most extensive database of SSDs currently available (Posthuma et al., 2019b). Each of these SSDs provides an HC_{50} value for eco-potency ranking and also a measure of model reliability that could be used in any future uncertainty analysis. To account for effects through other ecotoxicological MoAs, eco-potency ranking initially based on substance HC_{50}

comparison to the overall distribution of values was modified for genotoxic, oestrogen, androgen and thyroid endocrine activity and also for highly bioaccumulative substances given their potential to cause greater ecological impacts through continued uptake and trophic transfer. Additional non-classical MoAs, such as immunotoxicity, neurotoxicity, or nuclear hormone receptor activity identified through QSAR tools such as from the Vega platform, relevant assays or database resources (Kramer et al., 2024) could be incorporated to refine the chemical eco-potency ranking. Although exposure profiling used UK monitoring data, other surface and marine water quality datasets could also serve as alternative sources.

To assess ecosystem impacts, it was necessary to go beyond the unacceptable risk/no unacceptable risk approach of classical risk assessments and identify the scale and nature of potential effects. Effect scaling was based on an assumed increasing relationship of impacts with greater eco-potency and exposure groups up to a maximum of 20% effect (for the most potent chemicals at the highest exposure levels). This maximum effect was set based on the potential for national-level effects, based on evidence from large-scale pollution monitoring studies (Posthuma et al., 2019a, Lemm et al., 2021, Posthuma et al., 2020). Further studies of the relationship between eco-potency, exposure and ecosystem effects are necessary to verify this critical framework aspect - for example, via utilising artificial intelligence and machine learning, analyses of national-scale biodiversity and chemical use/exposure data-sets.

The overall community-level effects attributed to the case study chemicals are apportioned across 17 taxa using any available ecotoxicological data and a phylogenetic read-across approach for unstudied groups. The principle for read-across was based on evidence from both correlative and mechanistic studies based on the assumption that, although not in all cases, closely related taxa are more likely to reflect the sensitivity of a given taxon than more distant ones (Spurgeon et al., 2020). Translation of taxa impacts to effects on functions and services was through logic chain analysis, as a tractable solution to species-ecosystem impact linkage (Hayes et al., 2018, Maltby et al., 2021). Logic chains represent ecosystem complexity in linear and simplified formats. Such simplicity may not reflect reality, as some functions and services depend on contributions from multiple species, and modifications to one may not result in linear change; as is assumed in this framework. Improved ecological models have the potential to better represent the complexity of true taxa to impact connectivity. For example, by incorporating factors such as reduced predation and food requirements due to changing population sizes, interactions such as prey-switching, behavioural plasticity in response to food and habitat availability and non-linearity of response functions, including tipping points could be better integrated.

The geographical scope of the ecosystem service impact assessment framework is currently national with data focussing on the UK, including the use of countrywide monitoring data to define exposure, ascribing the maximum ecosystem effects from large-scale impact assessments, assessing species effects against country inventories, and using logic chains designed for broad habitat applications. Major chemical management decisions (e.g. restriction of a chemical) often take place (pan)-nationally, making this scale of analysis meaningful. However, decisions on chemical management can also be regional or location (e.g., point source) specific. To be useful at such scales, some modifications of the ENRICH framework would be needed. For example, high exposures from point sources could result in community effects well above the maximum 20% attributed at the national scale; specific communities may also be present at such sites that need integration into the ecological impact assessment.

The ecosystem service impact assessment framework is designed for impact assessment of single chemicals. Pollution is, however, often mixtures. Theories in mixture toxicology support additivity for effects based on similar (concentration addition) or dissimilar (independent action) MoAs (Jonker et al., 2005). However, under mechanistic uncertainty, these models can be viewed through their mathematical constructions as combined potencies for concentration addition and event probabilities for independent action. Framework calculations for a chemical of given eco-potency and exposure provide taxon-level effect probabilities, thus allowing mixture effects to be predicted using independent action model principles.

Current parameterisation of the ecosystem service impact assessment framework, by necessity, draws on freshwater data. This focus reflects the bias in ecotoxicology and chemical monitoring towards aquatic, mainly freshwater, studies. A lack of available data currently hampers bespoke terrestrial analysis, marking read across from freshwaters as the only viable approach for any attempt to attribute terrestrial pollution effects. The assumption of similar eco-potency among species from different habitats is supported by comparisons of species sensitivities across habitats (Yanagihara et al., 2022), suggesting that broad rules of taxon sensitivity, based on shared toxicokinetic and toxicodynamic pathways, apply (Spurgeon et al., 2020). Differences in chemical use would be expected to result in variations in the patterns of chemical exposure patterns in terrestrial, marine and freshwater ecosystems. This makes use of freshwater monitoring data for assessing exposure in other ecosystems potentially problematic, potentially leading to misassigned impacts. For example, the focus of fipronil effects on terrestrial ecosystems (e.g. pollination services) may not be replicated if terrestrial rather than aquatic data were used for exposure ranking. Large-scale mandated monitoring of soil, e.g. on the scale of that under the EU Water Framework Directive, would be necessary to provide the needed exposure profiling for terrestrial ecosystems. Until such studies become available, bespoke terrestrial assessments will remain hampered by a lack of data. Ultimately, a large research effort is needed to consolidate the data on terrestrial and marine-specific chemical hazards and exposure building on existing SSD resources (Posthuma et al., 2019b), MoA databases (Kramer et al., 2024) and exposome portals (www.norman-network.net) to better refine terrestrial ecosystem impact assessment.

A future step in ecosystem service impact assessment framework development would be to improve the understanding of uncertainty. In the short term, efforts could focus on validating and refining where research would be beneficial, including integrating broader expert knowledge, ground-truthing assumptions, conducting sensitivity testing, and back-testing outputs. Special attention should be given to the most impactful assumptions, e.g. that of the 20% maximum community impact. Looking forward, supplementing the available data with model outputs could benefit each quantitative step. For example, predictive ecotoxicology based on statistical or mechanistic models could be used to fill gaps on species sensitivity. Multi-media fate modelling can enhance the precision and applicability of the exposure assessment, especially for poorly studied chemicals, including for terrestrial and marine ecosystems. The integration of ecological monitoring approaches may also refine the mapping of taxa effects to ecosystem process and service impacts, potentially allowing the incorporation of second-order and subsequent impacts into the logic chain framework. Application of a spatial modelling approach could also benefit future analyses by including ecological, environmental and ecosystem services information to link the quantitative logic chain changes to area-relevant habitats.

Although there are remaining uncertainties, the ENRICH framework has the potential to underpin the assignment of a monetary values to pollution cases within ecological regulatory impact assessment (Step 5). The current structure can already provide support in decision-making processes such as chemical prioritisation and regulatory management. Thus, the developed approach could become a useful tool to quantify and monetise environmental impacts, ultimately supporting all stages of chemicals policy and regulatory decision-making.

Figure 1: Structure of the conceptual ecosystem service impact assessment framework**:** Step 1 quantifies the ecological hazard (eco-potency) of the chemical of concern relative to that of other chemicals. Step 2 assesses the frequency and severity of environmental exposure relative to other substances. Step 3 combines this relative eco-potency and exposure information to estimate overall community and taxa-specific impacts. Step 4 links taxa effects to ecosystem services using logic chains. Step 5 (not included here) would seek to estimate monetary values for the changes identified in Step 4 using existing evidence on ecosystem service values. Note MoA refers to Mode of Action and SSD refers to Species Sensitivity Distribution.

Figure 2: (A-C) Frequency distribution of HC_{50} values from acute EC_{50} toxicity data for aquatic species for all chemicals in the Species Sensitivity Distribution (SSD) database of Posthuma et al. (2019b), (D-F) Frequency distribution of 95th percentile exposure concentrations and (G-I) Frequency distribution of detection frequency for Fipronil, Copper (Cu) and Perfluorohexanoic acid (PFHxA); the dashed lines in each plot indicate where the HC_{50}, 95th percentile concentration and detection frequency for each chemical falls relative to the value for all other chemicals.

Figure 3: Ecosystem services impact across forest, wetland (bog and fen) and freshwater (river and lake) habitats arising due to pollution by fipronil, copper (Cu) and Perfluorohexanoic acid (PFHxA).

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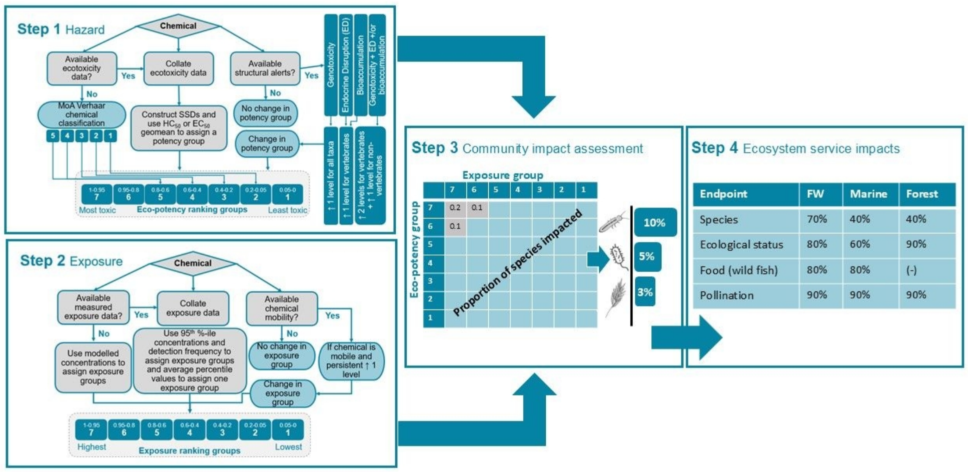

Endpoint	FW	Marine	Forest
Species	70%	40%	40%
Ecological status	80%	60%	90%
Food (wild fish)	80%	80%	(-)
Pollination	90%	90%	90%

Structure of the conceptual ecosystem service impact assessment framework: Step 1 quantifies the ecological hazard (eco-potency) of the chemical of concern relative to that of other chemicals. Step 2 assesses the frequency and severity of environmental exposure relative to other substances. Step 3 combines this relative eco-potency and exposure information to estimate overall community and taxa-specific impacts. Step 4 links taxa effects to ecosystem services using logic chains. Step 5 (not included here) would seek to estimate monetary values for the changes identified in Step 4 using existing evidence on ecosystem service values.

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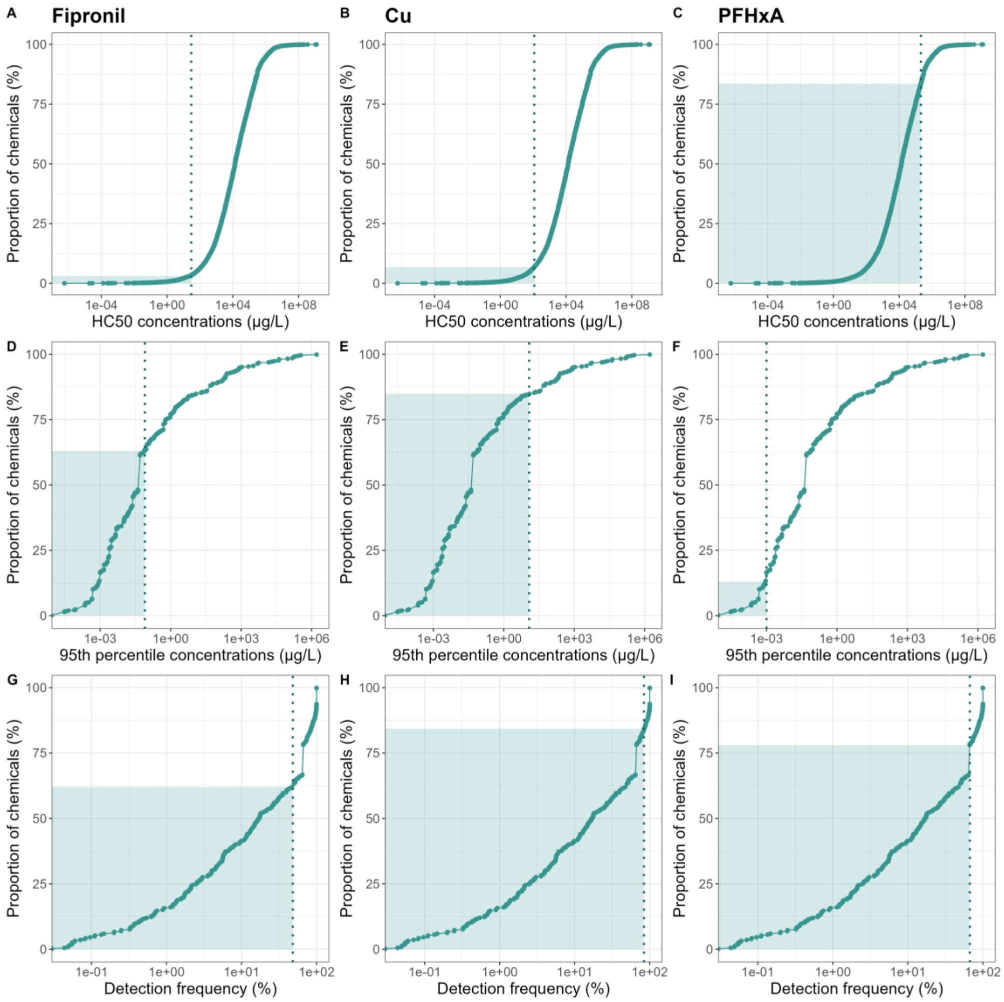

(A-C) Frequency distribution of HC50 values from acute EC50 toxicity data for aquatic species for all chemicals in the SSD database of Posthuma et al. (2019b), (D-F) Frequency distribution of 95th percentile exposure concentrations and (G-I) Frequency distribution of detection frequency for Fipronil, Cu and PFHxA; the dashed lines in each plot indicate where the HC50, 95th percentile concentration and detection frequency for each chemical falls relative to the value for all other chemicals.

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Ecosystem services impact across forest, wetland (bog and fen) and freshwater (river and lake) habitats arising due to pollution by fipronil, copper (Cu) and Perfluorohexanoic acid (PFHxA).

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