Article:

Pistocchi, Alberto, Alygizakis, Nikiforos A, Brack, Werner et al. (2022) European scale assessment of the potential of ozonation and activated carbon treatment to reduce micropollutant emissions with wastewater. Science of the Total Environment. p. 157124. ISSN: 0048-9697

https://doi.org/10.1016/j.scitotenv.2022.157124

Science of the Total Environment 835 (2022) 155101

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Worst-case ranking of organic chemicals detected in groundwaters and surface waters in England

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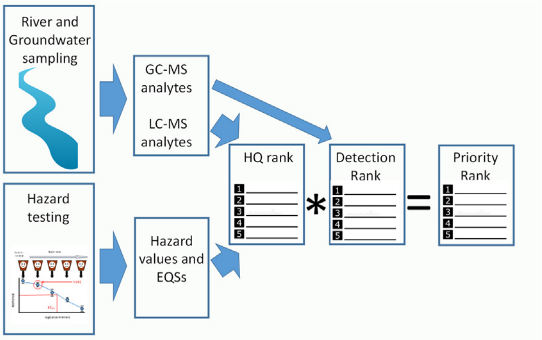
HIGHLIGHTS

- Hazard values and ground/surface water measures were obtained for 1144 chemicals.
- Worst case ranking was conducted by HQ and detection frequency.
- Multiple pesticides and PFAS were highly ranked in both environments.
- More personal care products and pharmaceuticals were highly ranked in surface waters.
- More industrial and plastics additive were highly ranked in groundwater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jay Gan

Keywords:
Hazard ranking
Hazard quotient
Pesticides
Pharmaceuticals
PFAS

ABSTRACT

The Environment Agency has been using Gas Chromatography–Mass Spectrometry (GC–MS) and Accurate-mass Quadrupole Time-of-Flight (Q-TOF) / Liquid Chromatography-Mass Spectrometry (LC-MS) target screen analysis to semi-quantitatively measure organic substances in groundwater and surface water since 2009 for GC–MS and 2014 for LC-MS. Here we use this data to generate a worst-case "risk" ranking of the detected substances. Three sets of hazard values relating to effects on aquatic organisms, namely Water Framework Directive EQSs, NORMAN Network PNECs (hereafter NORMAN PNEC) and chronic Species Sensitivity Distribution (SSD) HC50s from Posthuma et al., (2019) were used for the assessment. These hazard values were compared to the highest measured concentration for each chemical to generate a worst-case hazard quotient (HQ). Calculated HQs for each metric were ranked, averaged and multiplied by rank for detection frequency to generate an overall ordering based on HQ and occurrence. This worst-case approach was then used to generate ranking lists for GC–MS and LC-MS detected substances in groundwater and surface water. Pesticides in the top 30 overall ranked list included more legacy pesticides in groundwater and more current use actives in surface water. Specific uses were linked to some high rankings (e.g. rotenone for invasive species control). A number of industrial and plastics associated chemicals were ranked highly in the groundwater dataset, while more personal care products and pharmaceuticals were highly ranked in surface waters. Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) compounds were commonly highly ranked in both environmental compartments. The approach confirmed high rankings for some substance (e.g. selected pesticides) from previous

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http://dx.doi.org/10.1016/j.scitotenv.2022.155101
Received 13 February 2022; Received in revised form 30 March 2022; Accepted 3 April 2022
Available online 21 April 2022

prioritization exercises, but also identified novel substance for consideration (e.g. some PFAS compounds and pharmaceuticals). Overall our approach provided a simple approach using readily accessible data to identify substances for further and more detailed assessment.

1. Introduction

Direct and indirect releases of organic pollutants to groundwater and surface water bodies can come from a number of sources (Harrison, 2001; Wilson, 2013). In the UK, for example, there has been a circa 50% rise in the average number of different pesticides applied to arable crops in the last two decades (from 11 in 2000 to 17 in 2015 in Pesticide Usage Survey data from FERA (n.d.)). As well as the potential for organic pollutants to arise from agriculture, these pollutants can also enter the environment through a wide range of other sources including: atmospheric deposition, discharges from wastewater treatment works, discharges from industry, landfills leaching, contaminated land and organic and other wastes spread to land. Despite restrictions on the use of some of the most hazardous chemicals, there is a legacy of contamination that results from the persistence of some of these substances (e.g. polychlorinated biphenyls) or as a result of the presence and sustained release of chemicals from long-lived consumer products. The pace at which new chemicals are being developed and released also challenges our regulatory and monitoring response (Schwarzenbach et al., 2006). To address these challenges, surveillance and horizon scanning approaches are needed to identify current and emerging chemicals of concern that may be prioritised for further assessment (Fairbrother et al., 2019; Furley et al., 2018; Van den Brink et al., 2018).

The widespread use of chemicals and the presence of pathways to reach groundwater and surface water has led to an interest in measuring micro-organic pollutants in these environments (Angeles et al., 2021; Burns et al., 2018; Li et al., 2021; Miyawaki et al., 2021). This focus has been reflected in a number of studies conducted in different countries, mainly in surface waters (Altenburger et al., 2019; Hermes et al., 2018; Houtman et al., 2019; Park et al., 2018; Peng et al., 2018). In the UK, the Environment Agency for England has, since 2007, been using the scanning capability of GC–MS to semi-quantitatively measure a wide range of industrial compounds, halogenated solvents and trihalomethanes, plasticisers and pesticides in groundwater and surface water. In 2014, LC-MS analyses were added to the program to provide data on more polar compounds including many pesticides, pharmaceuticals, as well as PFAS compounds. To date these semi-quantitative analyses have been undertaken for ~33,800 GC–MS and ~3600 LC-MS groundwater and surface water samples.

Lapworth et al. (2018) analysed the available groundwater GC–MS and LC-MS target screen data for England to produce summary statistics, detected concentration ranges and spatial concentration distribution maps for the top 50 most frequently detected compounds. Consideration was not, however, given to the potential risk to aquatic species that may result from the presence of the detected chemicals in the environment. Because of the semi-quantitative nature of the GC–MS and LC-MS analysis, it is not possible to comment directly on the absolute risk of these substances. Such an analysis would require a more in-depth assessment of the monitoring data-set, as well as consideration of additional aspects such as routes of exposure, bioavailability, bioaccumulation and food chain transfer potential that would require data that goes beyond the semi-quantitative data available here. Similarly for location specific risk assessments using site specific concentrations, additional effort will be needed to develop a better contextual understanding of the drivers of local concentrations. However, by comparing HQ indicative “risk” for all substances, it is possible to comparatively rank the risk of detected chemicals based on their potential to cause environmental effects (Johnson et al., 2017; Miyawaki et al., 2021). The aim of this study was, thus, to develop and apply an approach to rank substances based on their measured concentrations in the Environment Agency groundwater and surface water data and assess worst-case risk and the extent of exposure, and to use this information to identify substances for further more detailed investigation.

2. Materials and methods

The approach used to rank the substances that have been detected, was based on comparing the highest detected chemical concentrations in groundwater and surface water to a number of ecologically relevant hazard values following the workflow shown in Fig. 1.

2.1. The environment agency groundwater and surface water monitoring data-sets

The groundwater network sites form part of the England-wide Groundwater Monitoring Network, which was designed to provide a picture of the regional quality of the national groundwater resources. However, there are also a relatively small number of other sites represented in the data-set, including some associated with point source pollution monitoring. Almost all of the surface water samples were collected and analysed for statutory monitoring or for studies linked to policy development. Notably, samples for pollution incident investigations were excluded from this data-set, due to their commercial and legal sensitivity. Measurements linked to specific management and regulatory actions are, however, represented. These include measurements of pesticides applied at biocidal levels for invasive species control (e.g. rotenone for invasive fish eradication).

Collection from the England-wide groundwater sampling network generated ~10,800 GC–MS and ~800 LC-MS samples for analysis. Surface water samples for GC–MS analysis were taken from, >600 locations, with >300 of these sites sampled >10 times, and >100 sites >50 times giving ~23,000 sites for GC–MS analysis. Over 100 surface water sites were sampled for LC-MS analysis. These include ten sites sampled >100 times, with the remainder sampled much less frequently. In total this gave ~2800 surface water samples for LC-MS analysis (see Table 1 and Supplementary Table 1 for annual number). The data that is generated by both methods is semi-quantitative.

All chemicals analysis was conducted at the Environment Agency's accredited laboratory in Star Cross, UK, using broad target based semi-quantitative screening methods that are described in detail in Lapworth et al. (2018), Moreau et al. (2019) and White et al. (2019). For brevity a summary of the full method is given below.

For the GC–MS method, due to the wide range of compounds contained within the target database and their variety of chemical characteristics, a liquid-liquid extraction method is utilised. An internal standard (D_{10}-phenanthrene) is added to each sample (1 L) which is extracted using dichloromethane (50 ml). The extraction solvent is removed and the remaining aqueous layer acidified (pH ~ 1–2) using sulphuric acid. The extraction procedure is then repeated on the acidified sample. The combined extracts are then slowly evaporated to avoid any loss of the more volatile compounds to 1 ml using a nitrogen ‘blow down' concentrator. The resultant extract is dried using anhydrous sodium sulphate and transferred to an autosampler vial ready for analysis. The GC–MS target based (multi-residue) screening method allowed for almost all GC-amenable pesticides, as well as hundreds of other organic contaminants to be identified in each sample at concentrations as low as 0.01 μg/l. At the heart of the GC–MS screening capability is the deconvolution reporting software (DRS) application for target compound analysis. This application combines results from the GC–MS Chemstation, the automated mass spectral de-convolution and identification software and the mass spectral search program from the National Institute of Standards and Technology in a single report. Progression of the method over time has added further substances to the analytical suite and also lowered many detection limits. From the suite of potential GC–MS analytes, 491 are found in one or more samples at concentrations above

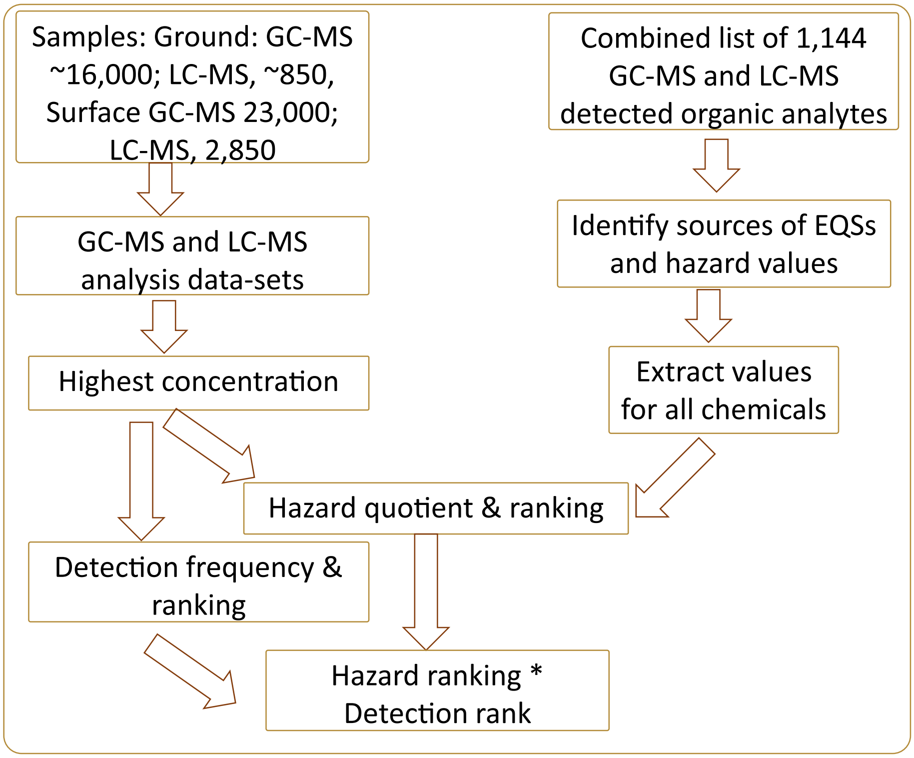

Fig. 1. Schematic of the approach used for chemical “risk” ranking. The exposure term for HQ calculation (left branch of the diagram) is identified as the highest measured concentration and detection frequency from GC–MS and LC-MS measurement made for the groundwater and surface water monitoring data-set. The hazard value (right branch of the diagram) is collected for multiple metric from easily available ecotoxicological resources.

the limit of detection (LOD) in groundwater and 515 in surface water (Table 1).

The LC-MS (Q-TOF) target-based multi-residue screening method allowed for measurement of a large number of LC-amenable pesticides as well as other organic contaminants including many pharmaceutical and perfluorinated chemicals, altogether comprising 620 substances. Waters Oasis HLB SPE cartridges (200 mg) with an automated extraction system are used as described by White et al. (2017). Cartridges were conditioned with methanol (6 ml) followed by Ultra High Purity (UHP) water (6 ml). The water sample (500 ml, flow-rate 10 ml/min) is then loaded onto the cartridge. After loading, the cartridge was washed with UHP water (6 ml) and the sorbent dried fully with high purity nitrogen. The column was then eluted twice, firstly with 6 ml of 0.1% formic acid in methanol: acetonitrile (1:1) and then with 6 ml of dichloromethane (DCM). The eluents were collected in separate vials. The DCM eluent is evaporated to incipient dryness under a gentle stream of nitrogen. The corresponding Methanol: Acetonitrile eluent was then transferred to the dry DCM vials and evaporated to 100 μl. Next 900 μl of UHP water is added to each of the vials containing the 100 μl extract. The sample was vortexed mixed, filtered and transferred to a silanised screw top vial ready for analysis. Target compound identification is made by retention time, accurate mass and by isotope distribution patterns (mass, ratio, spacing). Target compounds for quantification have been analysed in a blank and at a concentration of 0.1 μg/l, the response factor obtained is used to create a single point calibration curve. Estimate of concentration is based on quantification ion response and response of the internal standard. Quantification limits are compound specific and are typically between 0.001 and 0.1 μg/l for the vast majority of compounds. Similar to the GC–MS approach, changes to the method over time have added substances to the suite and also lowered detection limits. From the suite of potential LC-MS analytes, 290 were found above the LOD in groundwater samples and 315 in surface waters, with some overlap between the LC-MS and GC–MS detected analytes.

Table 1
Number of measured substances detected in any sample above the LOD, number of samples with detections above the LOD and maximum concentration ranges for all chemicals measured by GC–MS and LC-MS in the groundwater and surface water monitoring data-sets.

Method	Hazard criteria	Ground water	Surface water
GC–MS	Substances in analytical suite	707	709
	Substance detected >LOD	491	515
	Substance detection frequency	1–2212	1–13,989
	Analysed samples by compound	267–16,631	473–23,030
	Maximum concentration range (μg/l)	0.001–4000	0.004–8700
LC-MS	Substances in analytical suite	619	621
	Substance detected >LOD	290	398
	Substance detection frequency	1–377	1–2612
	Analysed samples by compound	75–858	374–2855
	Maximum concentration range (μg/l)	0.0001–32	0.0001–257
Combined GC–MS & LC-MS	Substances in analytical suite	1144	1144
	Substance detected >LOD	684	769

2.2. CAS number assignment and excluded substances

CAS numbers were assigned to each measured substance to enable searching against databases of hazard values. Any substances lacking CAS numbers or chemical name fields or for which units were not provided, were excluded from the analysis as they could not be unequivocally matched to substance hazard values (the number of such values was always <5% of the total). The sulphur compounds S8 (CAS number 10544-50-0; cyclooctasulphur) and S6 (CAS number 13798-23-7; hexathiane) were excluded as they are not organic and the natural steroid cholesterol and squalene were removed due to their potential endogenous origin. The total number of substances measured is 1144 for the combined GC–MS and LC-MS suite (704 GC–MS and 616 LC-MS analytes with 176 common between suites, see Supplementary File 1 for full lists of analysed substances) with 684 and 769 of these showing positive detects in the groundwater or surface water respectively by one or more method (see Table 1 and Supplementary Table 1 for annual statistics).

2.3. Assignment of use categories

The detected compounds were categorised into broad usage groups (Supplementary Table 2). These categories were based on those of Lapworth et al. (2018), except for the "Pharmaceutical, Personal Care Product, Lifestyle" class which was split between three separate categories: pharmaceuticals (including veterinary medicines); personal care products; and consumer products. An approach based on Lapworth et al. (2018) rather than alternative approaches such as provision of information from the NORMAN List of Emerging Substances was chosen to provide consistency with previous work conducted using the same data-set. For many compounds, allocation to a use category was unambiguous. For example, pesticides were identified from listings in the Pesticide Properties Database (sitem.herts.ac.uk/aeru/ppdb). However, some pesticides can also be used as veterinary medicines, human pharmaceuticals and also in consumer products (e.g. as household biocides). Similar cross overs exist for other usage classes. However, while the use categorisation approach has clear limitations, it still provides a pragmatic approach to cataloguing chemicals by dominant use in a manner that can assist in source identification.

2.4. Choice of concentrations for ranking

For ranking, the highest detected concentration was used as the primary exposure term for each chemical. The highest concentration was chosen rather than a value more embedded in the distribution, such as the mean, median or upper 90th percentile; because for the large majority of chemicals, a high proportion of samples reported values below the detection limit (especially for the GC–MS analytes). For detailed discussion on the problem of calculating summary statistics for these data see Lapworth et al. (2018). To refine the approach, detection frequency data was taken into account so that the overall rank of a substance was based on both hazard the quotient and probability of occurrence. To avoid focussing on rarely detected substances, only substances detected ≥10 times in each monitoring data-set (GC–MS and LC-MS in groundwater and surface water) were included in each hazard ranking list.

Assessment based on the highest recorded concentration is potentially subject to artefacts resulting from the presence of a single anomalous measurement in an individual sample. To partly account for this, we also used the detection frequency of the chemical as a further factor to calculate ranking within our worst-case approach (see below). Further, for specific priority pollutants selected because of their comparatively high frequency of detection or ranking (or both), an analysis of the range of concentrations in the full set of measured samples has been made to assess the extent to which the highest measured value represents an outlier from the remaining levels. The aim was to identify the potential frequency of extreme outlier values from remaining measured concentrations. A highest concentration that was more than an order of magnitude from the next value was used to denote an extreme outlier. This assessment was conducted for 42 of the chemicals detected by GC–MS and LC-MS in groundwater and surface water, namely: groundwater *GC–MS*: strazine, atrazine-desethyl, dimethenamid, benzo[*a*]pyrene, benzo[a[anthracene, benzo[*b*]fluoranthene, benzo[*g*,*h*,*i*]perylene, fluoranthene, pyrene, acetophenone, caffeine, 4-tert-octylphenol, di(2-ethylhexyl) adipate, di(2-ethylhexyl)phthalate, bisphenol A, diisobutyl phthalate, N-butyl-benzenesulfonamide, cyclohexanone, 1,4,-dioxane, tetrachloroethylene, tributyl acetylcitrate, trichloroethylene; *LC-MS*: atrazine, atrazine-desethyl, diuron, isoproturon, PFOS, PFOA; surface water *GC–MS*: benzo[*a*]pyrene, fluoranthene, rotenone; *LC-MS*: fipronil, PFOS, PFOA, perfluorobutane sulfonate, perfluoro pentanoic acid, perfluoro hexanoic acid, perfluorohexane sulfonate, perfluoro heptanoic acid, perfluoroctylsulfonamide, perfluoro nonanoic acid, perfluoro decanoic acid.

2.5. Collate hazard values for each chemical

Three sources of hazard values relevant to surface water receptors were used.

1. *Water Framework Directive (WFD) Environmental Quality Standards (EQS).* Water Framework Directive EQS are statutory standards and, therefore, have a high degree of regulatory acceptance. Values are, however, only available for a small number (61) of organic substances and their close analogues (e.g. differently positioned halogenated hydrocarbons). Where available, WFD EQS Annual Averages, rather than as Maximum Allowable Concentrations were collected. Using the Annual Average to compare with the one-off concentrations measured in the monitoring data-set provides a precautionary aspect to the overall assessment. This choice would not, however, be expected to systematically affect ranking.

2. *NORMAN network database quantitative structure activity relationships (QSARs) predicted PNECs (see https://www.norman-network.com/nds/).* The NORMAN ecotoxicology database collates PNEC values for ≥40,000 substances. The large majority of these PNEC are derived from QSARs for toxicity for four taxonomic groups: protist (*Tetrahymena*), vertebrate (fish), aquatic plant (algae), and invertebrate (*Daphnia*). To generate the QSAR based PNEC values for each substance, the lowest no observed effect concentration (NOEC) from the four taxa is divided by an assessment factor of 1000. The NORMAN PNEC database provides high substance coverage, with >80% of all GC–MS and LC-MS analytes having a reported value. For this study NORMAN PNECs for the relevant compounds were download from the NORMAN Network database on 30 Jan 2020.
3. *Chronic Species Sensitivity Distribution HC_{50} values from* Posthuma et al. *(2019).* Posthuma et al. (2019) used a comprehensive set of ecotoxicity data to derive species sensitivity distribution (SSD) models for 12,386 compounds. The hazardous concentration for 50% of species (HC50) values derived from these SSDs were used here for relative ranking. HC50 values were selected above lower effect threshold values because these are readily available in the supplementary information of the Posthuma et al. (2019) article and also because the HC50 is in the middle of the distribution and so is more robust for hazard ranking applications. Chronic SSD HC50s were used without inclusion of an assessment factor and were used as part of the hazard derivation method for the WFD EQS and NORMAN PNEC values.

2.6. Average HQ calculation for each substance

For each hazard metric the substances were ranked by comparing the highest measured GC–MS and LC-MS concentration in the groundwater and surface water monitoring data-set to each available hazard values within a classic exposure: hazard paradigm. The resulting HQ from these comparisons were placed in rank order for each metric from 1 – X, with 1 being the substance with the highest HQ (i.e. the most "risky" substance detected in the specific environment for that metric) to X being lowest (least "risky" detected), with X being determined by the number of substances in the ranked list. To avoid propagating similar evaluations that would have generated multiple lists, the final ranking was made based on the average substance rank across the three hazard metrics (WFD EQS, NORMAN PNEC, chronic SSD HC50). To calculate this average value, the rank given for that substance for a given metric was first divided by the number of substances with a HQ for that metric (i.e. substances with a detected concentration and an associated hazard value). The available values were then averaged across all metrics and these values ranked from lowest to highest to give the final average worse-case ranking for all substances based on all available HQs.

2.7. Detection frequency correction

Substances to which species are more likely to be exposed at measurable levels are potentially of greater research and regulatory interest than substances that occur more sporadically in the environment (although there are cases where substances that occur sporadically may be of concern). Therefore, a detection frequency correction term was included in the final ranking calculation. For detection frequency correction, all substances with an average ecological value were ordered by their detection frequency, with the relevant analytical method in the sampled environment. Substances were then given a detection frequency rank from 1 – X, with 1 being the substance with the highest percentage detection (i.e. the substance most frequently detected in all analysed samples) to X being the substance detected fewest times (N.B. substances detected <10 times were excluded to avoid focussing on very rarely detected substances). In cases of ties, in the detection frequency of two or more substances, the highest detected concentration was used as a secondary ranking term.

2.8. Calculation of the final detection corrected hazard rank

To calculate the final score for ranking, the average ecological hazard rank for the substance was multiplied by the detection frequency rank. Calculated values were ordered from 1 - X for the final ranking. All substances with ≥10 positive detections in the sample data-set were ranked, although for presentation and discussion purposes the results in this paper focus on the top 30 ranked substances for each of the four data-sets (GC–MS and LC-MS in both groundwater and surface water). The full ranking lists are available in Supplementary File 2 for the GC–MS and LC-MS analytes in groundwater and surface water.

3. Results

3.1. Concentration values and range for substance in the monitoring data-sets

The overall ranking approach was based on a worst-case assessment conducted using the highest measured concentration. This choice to use the highest value was pragmatic given that the limited number of detections for many chemicals precluded the calculation of any distribution-based value. Assessment using the highest concentration is liable to error if this value corresponds to an extreme outlier arising from, for example, a short-term locally intense pollution event or an analytical error. To assess whether there was any evidence of a high frequency of extreme outliers among the highest concentration values, full distributions of measured concentrations of 46 substances had visualisations undertaken to assess whether the highest value would be identified as an extreme outlier (i.e. >10× any other measured concentration).

Across all assessed substances, there was no case in which the highest measured concentration exceeded the next highest value by a factor of >10. The greatest difference between the maximum and next value (6.53 fold) was found for the insecticide fipronil measured by LC-MS in surface waters. The only other substance where the difference from the maximum to the next highest vale was >5 fold was for PFOS in groundwater. A further seven GC–MS measured substances (atrazine-desethyl, dimethenamid, benzo[*a*]anthracene, benzo[*g*,*h*,*i*]perylene, 4-tert-octylphenol, N-butylbenzenesulfonamide, bis(2-ethylhexyl) adipate) in groundwater and two (benzo[*a*]pyrene and fipronil) in surface water had differences between the maximum to next highest concentration of >3. All other substances had a highest measured concentration within 3-fold of the next highest value. The outlier analysis, thus, indicates that while the use of the highest value for assessment is clearly worst-case, extreme outliers are seemingly uncommon in the data-set, supporting the use of the maximum values for worst-case hazard ranking.

3.2. Selection of hazard criteria for use in ranking

The NORMAN PNEC had the greatest number of hazard values for the chemicals detected via the GC–MS and LC-MS screens, followed by the chronic SSD HC50, with the WFD EQS having much lower substance coverage (Table 2). There were 39 chemicals in the GC–MS data-set and 16 in the LC-MS groundwater dataset that had values for all three hazard metrics. In the surface water data-set, 40 chemicals in the GC–MS data-set and 18 in the LC-MS groundwater data-set had values for all metrics. Pesticides and some biocides were the main group of substances with multiple hazard metrics. In contrast there are other chemicals (e.g. some metabolites and intermediates), for which no hazard metrics were available and which, therefore, could not be included in the rankings. Follow up work for these missed chemicals may be warranted to address these knowledge gaps.

Table 2
Number of chemicals measured by GC–MS and LC-MS in the groundwater and surface water monitoring data-sets that have hazard values for the WFD EQS, NORMAN PNEC, Chronic SSD HC50.

Hazard criteria	Yes	No
Water Framework Directive EQS	61	1083
Norman Network Lowest PNEC	979	165
Chronic Species Sensitivity Distribution HC50	719	425
Substance with one or more hazard value	1075	69

The three hazard metrics used are derived using different data and approaches, e.g. experimental data, QSAR model prediction, and with different underlying assumptions, e.g. use of lowest toxicity value or a distribution of values, inclusion, or not of an assessment factor. The implication of these differences can be visualised using scatter plots of hazard metric pairs for individual substances (Supplementary Fig. 2). Where any substance sits on the 1:1 line between the two axes, then that chemical has the same hazard value for each of the metrics. Substances below the line indicate a higher hazard value, and hence lower toxicity, for the X-axis metric, points above the 1:1 line have a higher value, and hence a lower toxicity, for the Y-axis metric. The degree of scatter also indicates the extent of variation in the paired values for chemical between the metrics.

Paired WFD EQS and NORMAN PNEC show a correlation along the 1:1 line reflecting that these values are (largely) derived either from lowest measured or QSAR calculated toxicity values, that is then divided by an assessment factor (Supplementary Fig. 1a). Although predicted from a QSAR model, there is no clear evidence at this scale of investigation that the NORMAN PNEC values are more uncertain (i.e. show greater scatter) than the two metrics that are derived from measured data (e.g. the WFD EQSs and chronic SSD HC50s). Individual WFD EQSs are both lower and higher that the associated NORMAN PNEC, with maximum variation of ~5 orders of magnitude lower for the WFD EQS than the NORMAN PNEC for heptachlor, and ~4 orders of magnitude higher than the NORMAN PNEC for 1,1,2,2-tetrachloroethane. Both the NORMAN PNEC and WFD EQSs are always lower than their chemical-matched chronic SSD HC50s, generally by 1–2 orders of magnitude (Supplementary Fig. 1 b and c). This reflects the use of a median rather than lowest hazard value and also the absence of an assessment factor placed on the HC50 compared to the other two metrics.

3.3. Overall ranking for GC–MS substances in groundwater and surface water

The top 30 overall ranked chemicals detected by GC–MS in each sample type (groundwater, surface water) are shown in Tables 3 and 4 and their usage categories in Fig. 2.

3.3.1. Groundwater

Among the top 30 overall ranked GC–MS substances in groundwater, eight are PAHs (benzo[*ghi*]perylene, benz[*a*]anthracene, indeno[1,2,3-*cd*]pyrene, pyrene, fluoranthene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, dibenz[*a*,*h*]anthracene) (Table 3, Fig. 2). PAHs have a long history of interest for their toxicological effects and widespread occurrence. Multiple plastics-associated chemicals are also in the top 30. Bisphenol A, a well-known plasticiser, is the highest ranked substance, reflecting both its relatively high ranking against especially, the chronic SSD HC50, as well as its comparatively high frequency of detection (present in >1000 samples). The phthalate, bis(2-ethylhexyl)phthalate and phosphate plasticiser

Table 3

Top 30 ranked substances for chemicals in the GC–MS groundwater monitoring data-set (excludes substance detected in <10 samples).

DCWA rank	CAS registry number	compound name	No. positive detects	Detection frequency rank	Maximum conc. (μg/l)	WFD EQS. HQ rank	NORMAN PNEC HQ rank	Chronic SSD HC50 rank	Average HQ rank	Average HQ rank ∗ detection frequency rank
1	80-05-7	Bisphenol A	1191	3	100		45	15	14	42
2	191-24-2	Benzo[*ghi*]perylene	113	68	1.9		5	1	1	68
3	56-55-3	Benz[*a*]anthracene	313	28	2.4		24	2	4	112
4	3622-84-2	Benzenesulfonamide, N-butyl	566	17	4000		21	13	7	119
5	129-00-0	Pyrene	1080	7	2		39	28	18	126
6	1912-24-9	Atrazine	1396	1	0.75	32	87	120	130	130
7	79-01-6	Trichloroethylene	1322	2	184	19	82	96	86	172
8	206-44-0	Fluoranthene	1099	5	3.4	13	40	41	39	195
9	117-81-7	bis(2-ethylhexyl)phthalate (DEHP)	740	12	62	11	3	24	20	240
10	934-34-9	2(3H)-Benzothiazolone	244	34	1000		18		8	272
11	193-39-5	Indeno[1,2,3-*cd*]pyrene	33	154	4.4		4	5	2	308
12	6190-65-4	Atrazine-desethyl (Desethylatrazine)	873	9	1		122	6	36	324
13	77-90-7	Tributyl acetylcitrate	247	33	154		32	30	16	528
14	124-48-1	Chlorodibromomethane	516	19	180		29	70	28	532
15	50-32-8	Benzo[*a*]pyrene	124	64	1.6	3	12	16	9	576
16	106-65-0	Butanedioic acid, dimethyl ester	1107	4	74		213	169	152	608
17	127-18-4	Tetrachloroethylene	913	8	180	20	65	84	79	632
18	205-99-2	Benzo[*b*]fluoranthene	150	53	2.9	7	7	4	12	636
19	53-70-3	Dibenz[*a*,*h*]anthracene	12	224	0.278		16	7	3	672
20	75-25-2	Bromoform	507	20	96		64	57	35	700
21	95-14-7	1H-Benzotriazole	99	77	2000		17	22	11	847
22	333-41-5	Diazinon (Dimpylate)	28	170	25	4	2	3	5	850
23	115-86-6	Triphenyl phosphate (TPPA)	624	16	7.2		31	123	54	864
24	58-08-2	Caffeine	802	11	7.2		216	18	85	935
25	134-62-3	N,N-Diethyl-m-toluamide	1098	6	17		191	199	157	942
26	19,666-30-9	Oxadiazon	68	98	12		23	14	10	980
27	108-94-1	Cyclohexanone	837	10	300		125	134	100	1000
28	75-27-4	Bromodichloromethane	519	18	150		28	131	56	1008
29	67,129-08-2	Metazachlor	349	24	44		89	53	43	1032
30	128-37-0	Butylated hydroxytoluene	236	35	8.7		61	52	31	1085

Table 4

Top 30 ranked substances for chemicals in the GC–MS surface water monitoring data-set (excludes substance detected in <10 samples).

DCWA rank	CAS registry number	Compound name	No. positive detects	Detection frequency rank	Maximum concentraion (μg/l)	WFD EQS. HQ rank	NORMAN PNEC HQ rank	Chronic SSD HC50 rank	Average HQ rank	Average HQ rank ∗ detection frequency rank
1	58-08-2	Caffeine	13,989	1	46		140	15	44	44
2	83-79-4	Rotenone	678	48	2030		1	1	1	48
3	206-44-0	Fluoranthene	9006	3	7	15	44	50	59	177
4	13,674-87-8	Tris (1,3-dichloroisopropyl) phosphate	3887	13	50		10	60	15	195
5	129-00-0	Pyrene	8970	4	1.2		64	55	68	272
6	87,674-68-8	Dimethenamid (SAN 582H)	1091	33	230		60	5	9	297
7	134-62-3	N,N-Diethyl-m-toluamide	11,595	2	19		209	218	170	340
8	115-86-6	Triphenyl phosphate (TPPA)	2147	20	85		23	63	18	360
9	135,319-73-2	Epoxiconazole (BAS 480F)	113	132	770		28		3	396
10	119-61-9	Benzophenone	3244	15	234.7		53	46	28	420
11	142,459-58-3	Flufenacet (Fluthiamide) (BAY FOE 5043)	1182	32	98		37	23	14	448
12	13,684-63-4	Phenmedipham	18	255	3060		6	7	2	510
13	298-46-4	Carbamazepine	6083	6	5.3		158	99	90	540
14	117-81-7	bis(2-ethylhexyl)phthalate (DEHP)	2355	19	170	12	3	28	35	665
15	126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	5415	7	48		162	107	96	672
16	67,129-08-2	Metazachlor	2031	22	340		49	32	31	682
17	80-05-7	Bisphenol A	1426	29	55		72	41	24	696
18	886-50-0	Terbutryn	1014	37	9.3	5	18	29	21	777
19	23,950-58-5	Propyzamide (Pronamide)	2833	16	72		82	62	49	784
20	50-32-8	Benzo[*a*]pyrene	548	57	1.1	1.0	29	40	17	969
21	5915-41-3	Terbuthylazine (TERBA)	96	145	118		11	30	7	1015
22	107,534-96-3	Tebuconazole (Terbuconazole)	300	85	210		31	21	12	1020
23	907,204-31-3	Fluxapyroxad	196	107	190		5	43	10	1070
24	483-63-6	Crotamiton	5195	8	8.8		191		134	1072
25	3622-84-2	Benzenesulfonamide, N-butyl	4554	12	60		147	115	93	1116
26	188,425-85-6	Boscalid (Nicobifen)	294	87	100		14	44	13	1131
27	10,543-57-4	*N*,*N*,*N*′,*N*′-Tetraacetylethylenediamine	6221	5	25		222	320	228	1140
28	115-96-8	Tri-(2-chloroethyl) phosphate	4950	9	16		75	243	127	1143
29	53-70-3	Dibenz[*a*,*h*]anthracene	10	288	21		4	2	4	1152
30	56-55-3	Benz[*a*]anthracene	2049	21	1		55	14	56	1176

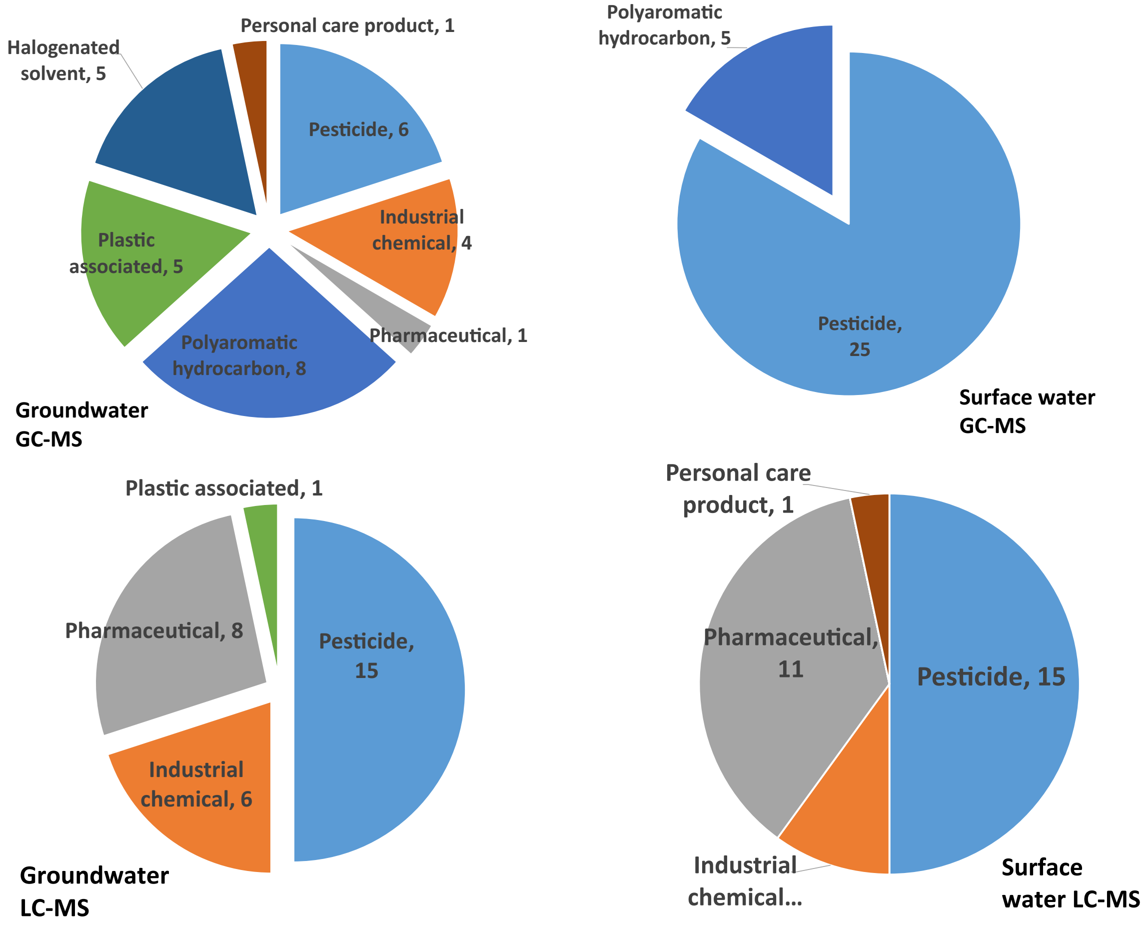

Fig. 2. Main use categories for the top 30 ranked chemicals detected by GC–MS (top) and LC-MS (bottom) in the groundwater (left) and surface water (right) monitoring datasets.

triphenyl phosphate are also in the top 30. N-butyl benzenesulfonamide, a plasticiser used in consumer products (e.g. cosmetics), materials (e.g. polyacetals, polyamides, and polycarbonates) and industrial applications, is also highly ranked (Table 3). The high ranking of phthalates, phosphate plasticisers, bisphenol A and N-butyl benzenesulfonamide is driven by their comparatively high ranking for the NORMAN PNEC and/or chronic SSD HC50 metrics, and also relatively high detection frequency ranks (bisphenol A present in >1000 samples, bis(2-ethylhexyl)phthalate (DEHP), triphenyl phosphate and N-butyl benzenesulfonamide all detected >500 times). N-butyl benzenesulfonamide also has the highest maximum measured concentration of any substances (4000 μg/l).

The remaining substances ranked in the top 30 for GC–MS analysis in groundwater include a number of well-known historic pollutants, including the legacy herbicide atrazine (6th ranked) and its metabolite atrazine-desethyl (12th ranked), the legacy insecticide diazinon (22nd ranked) and the chlorinated solvents trichloroethylene (7th ranked) and tetrachloroethylene (17th ranked). All are detected in >500 samples except diazinon, which despite being present in only 28 samples is still highly ranked based on its high ranking across all three metrics (4th WFD EQS, 2nd NORMAN PNEC, 3rd chronic SSD HC50). Not all of the top 30 GC–MS substances are legacy use substances. Examples include the pesticide metazachlor, pharmaceutical caffeine, plastic-associated chemical tributyl acetylcitrate, halogenated solvent bromoform and industrial chemicals butanedioic acid and 2(3H)-benzothiazolone. In all cases except 2(3H)-benzothiazolone, the average rank for these substances is derived from NORMAN PNEC and/or chronic SSD HC50 values, with no WFD EQS available. For these more current use or emerging substances, case by case assessment may be warranted to establish whether their high ranking is supported by wider substance information held in, for example, REACH registration documents and the wider published literature.

3.3.2. Surface water

The top 30 overall ranked GC–MS detected substances in surface water include eleven substance that are also ranked in the top 30 in groundwater: benzo[*a*]anthracene, N-butyl benzenesulfonamide, benzo[*a*]pyrene, bis(2-ethylhexyl)phthalate, bisphenol A, caffeine, dibenz[*a*,*h*]anthracene, fluoranthene, metazachlor, pyrene and triphenyl phosphate (Tables 3 and 4). Legacy pesticides (e.g. atrazine and its metabolites, dieldrin) are absent from the top 30 ranked list for surface waters. PAHs, common in the groundwater list top 30, are also in the surface water top 30 list, although only five, rather than eight, class members. Top 30 ranked GC–MS substances present only in the surface water GC–MS list include a number of current or recent use pesticides, such as boscalid, epoxiconazole and flufenacet (Table 4).

In surface waters, the highest ranked GC–MS substance is caffeine. This top ranking is based on its frequency of detection (highest for any analyte), as well as moderate to high ranking for multiple hazard metrics. The second highest ranked substance is rotenone. This piscicide is top ranked by both its NORMAN PNEC HQ and chronic SSD HC50 HQ. It is, however, only detected in a moderate number (678) of samples. The high ranking of rotenone in the surface water GC–MS data-set is thought to stem from its operational use as a piscicide in programs to eradicate non-native fish species, such as *Pseudorasbora parva* (top mouth gudgeon), from invaded surface waters. Measurements taken during such limited scale piscicide uses explain the limited frequency of detection of this substance and also why the highest concentrations (measured immediately after addition) exceed the hazard values for aquatic species. Rotenone is widely used for invasive fish control worldwide, so its occurrence could be relevant for other regions and not just the UK. However its application is by its nature targeted and so location specific, so this chemical would not normally be expected to occur at the highest concentrations detected in the surface water dataset outside of areas of active use. This substance, and the samples in which it is found, could have been removed from the analysis. However, it was considered useful to include the samples containing biocidal rotenone, intentionally applied at specific sites in the environment, to gauge the effectiveness of the ranking approach to highlight substances reaching ecological effect levels.

Other pesticides in the top 30 ranked GC–MS detected chemicals include multiple herbicides (dimethenamid, flufenacet, metazachlor, phenmedipham, propyzamide, terbuthylazine, terbutryn) and fungicides (boscalid, fluxapyroxad, epoxiconazole, tetraconazole). The top 30 ranking of many pesticides is driven by their high ranking for their NORMAN PNEC and chronic SSD HC50 metrics (WFD EQSs were not generally available for these pesticides). For both metrics, QSARs used to derived to generate lowest NORMAN PNEC values for substances and toxicity data used to generate the underlying SSD for HC50 derivation are in both cases available for a range of plant and animal species. Hence, the underlying data is able to identify potential hazard of the assessed chemicals on primary producers (e.g. algae), as well as primary (e.g. invertebrate) and secondary (e.g. vertebrate) consumers.

A number of the top 30 GC–MS detected chemicals identified only in surface water are associated with consumer uses. Crotamiton is a pharmaceutical used in over-the-counter medications. Caffeine is also categorised as a pharmaceutical, although is more commonly associated with food and drink. Six plastics associated chemicals are in the top 30 ranked GC–MS detected substances in surface water: bisphenol A, bis(2-ethylhexyl) phthalate, tris (1,3-dichloroisopropyl) phosphate, triphenyl phosphate, tri-(2-chloroethyl) phosphate and benzophenone. All of these plastics associated chemicals are comparatively commonly detected (detected in >2000 samples in all cases), indicating that both older plasticisers (e.g. bisphenol A and phthalates) and also alternatives and chemicals used in other aspects of plastic production, widely reach surface waters. Consumer products likely to reach surface waters via sewage effluent are also top 30 ranked, such as *N*,*N*,*N′*,*N′*-tetraacetylethylenediamine and 2,4,7,9-tetramethyl-5-decyne-4,7-diol, which are both present in products such as detergents and coating treatments.

3.4. Overall ranking of LC-MS detected substances in groundwater and surface water

The top 30 ranked LC-MS detected chemicals in groundwater and surface water are shown in Tables 5 and 6 respectively and their usage categories in Fig. 2.

3.4.1. Groundwater

The top 30 overall ranked LC-MS detected substance in groundwater are dominated by pesticides, human and veterinary pharmaceuticals and industrial chemicals (Table 5, Fig. 2). The three highest ranked substances are the herbicide metabolite atrazine-desethyl, fungicide boscalid (also top 30 ranked in the GC–MS groundwater and surface water data-sets) and the herbicide trietazine. For boscalid, high placement is based on high ranking for multiple hazard metrics (NORMAN PNEC 1st ranked, chronic SSD HC50 7th ranked). Trietazine is 4th ranked against the NORMAN PNEC value, while atrazine-desethyl has a high rank for its chronic SSD HC50 (1st ranked) and to a lesser extent NORMAN PNEC (26th ranked). Atrazine-desethyl has a relatively high level of detection (377 of 822 samples) and boscalid a moderate level of detection (105 of 853 sample). Trietazine is, by contrast, rarely detected (26 of 839 samples), indicating that high ranking of any given hazard metric is sufficient to give a high overall rank.

Table 5

Top 30 ranked substances for chemicals in the LC-MS groundwater monitoring data-set (excludes substance detected in <10 samples).

DCWA rank	CAS registry number	Compound name	No. positive detects	Detection frequency rank	Maximum concentraion (μg/l)	WFD EQS. HQ rank	NORMAN PNEC HQ rank	Chronic SSD HC50 rank	Average HQ rank	Average HQ rank ∗ detection frequency rank
1	6190-65-4	Atrazine-desethyl (Desethylatrazine)	377	1	0.28		26	1	5	5
2	188,425-85-6	Boscalid (Nicobifen)	105	27	2.4		1	7	2	54
3	1912-26-1	Trietazine	26	69	0.18		4		1	69
4	1763-23-1	Perfluorooctane sulfonate (PFOS)	227	12	0.71	1	18	13	6	72
5	1007-28-9	Atrazine-desisopropyl (Deisopropylatrazine)	370	2	0.048		64		38	76
6	56,038-13-2	Sucralose	306	5	19		32		16	80
7	1912-24-9	Atrazine	339	4	0.31	8	11	15	30	120
8	50-36-2	Cocaine	38	58	32		7		3	174
9	25,057-89-0	Bentazone	195	15	1.9		45	6	12	180
10	122-34-9	Simazine	362	3	0.033	15	43	59	73	219
11	2971-90-6	Clopidol	245	10	3.5		41		22	220
12	2303-17-5	Triallate	17	85	1.7		15	2	4	340
13	375-73-5	Perfluorobutane sulfonate	196	14	1.1		47		25	350
14	120,068-37-3	Fipronil	105	28	0.0095		40	11	13	364
15	142,459-58-3	Flufenacet (Fluthiamide)	69	40	0.2		29	19	10	400
16	330-54-1	Diuron	254	6	0.028	12	118	23	70	420
17	335-67-1	Perfluoro Octanoic Acid	246	9	0.12		39	104	50	450
18	298-46-4	Carbamazepine	229	11	0.1		93	47	46	506
19	210,880-92-5	Clothianidin	215	13	0.15		78	51	42	546
20	131,860-33-8	Azoxystrobin	90	30	0.052		37	36	19	570
21	307-24-4	Perfluoro Hexanoic Acid	178	18	0.16		60		36	648
22	65,277-42-1	Ketoconazole	14	95	0.12		5	27	7	665
23	886-50-0	Terbutryn	17	86	0.067	2	6	14	8	688
24	6339-19-1	Chloridazon-desphenyl	111	26	6.3		49		27	702
25	115-28-6	1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dicarboxylic acid	64	44	2.1		35		17	748
26	84,057-84-1	Lamotrigine	168	20	0.13		10	107	39	780
27	2706-90-3	Perfluoro Pentanoic Acid	182	17	0.25		79		51	867
28	375-85-9	Perfluoro Heptanoic Acid	151	22	0.053		66		40	880
29	120,067-83-6	Fipronil Sulfide	12	105	0.006			21	9	945
30	60,207-90-1	Propiconazole	87	34	0.12		52	43	28	952

Table 6
Top 30 ranked substances for chemicals in the LC-MS surface water monitoring data-set (excludes substance detected in <10 samples).

DCWA Rank	CAS Registry Number	Compound Name	No. positive detects	Detection frequency rank	Maximum concentraion (μg/l)	WFD EQS. HQ rank	NORMAN PNEC HQ rank	Chronic SSD HC50 rank	Average HQ rank	Average HQ rank ∗ detection frequency rank
1	120,068-37-3	Fipronil	2603	2	0.98		12	2	6	12
2	25,057-89-0	Bentazone	2377	13	51		28	5	4	52
3	83,881-51-0	Cetirizine	1820	31	53		5		2	62
4	84,057-84-1	Lamotrigine	2612	1	1.6		11	116	65	65
5	144,701-48-4	Telmisartan	826	67	0.082		4		1	67
6	298-46-4	Carbamazepine	2578	3	1.5		91	34	43	129
7	188,425-85-6	Boscalid (Nicobifen)	2522	5	0.63		20	60	31	155
8	3380-34-5	Triclosan	874	61	58	1	3	1	3	183
9	15,307-86-5	Diclofenac	2360	14	0.76		35	28	14	196
10	330-54-1	Diuron	2522	6	0.48	7	110	14	46	276
11	142,459-58-3	Flufenacet (Fluthiamide)	2111	25	1.5		33	19	13	325
12	23,950-58-5	Propyzamide (Pronamide)	2400	10	2.2		94	44	33	330
13	131,860-33-8	Azoxystrobin	2405	8	0.76		31	25	45	360
14	56,038-13-2	Sucralose	2352	15	257		27		34	510
15	335-67-1	Perfluoro Octanoic Acid	2444	7	0.16		95	177	87	609
16	29,122-68-7	Atenolol	2383	11	1			59	57	627
17	81,103-11-9	Clarithromycin	2025	29	1.1		44	38	29	841
19	66,108-95-0	Iohexol	422	98	1.4		25		9	882
20	2971-90-6	Clopidol	2551	4	0.077		265		227	908
21	1763-23-1	Perfluorooctane sulfonate (PFOS)	2252	21	0.088	2.0	118	83	44	924
22	2303-17-5	Triallate	1158	47	0.98		54	18	20	940
23	83,905-01-5	Azithromycin	450	96	0.87		37	10	10	960
24	54-31-9	Furosemide	654	82	1.8		48	6	12	984
18	41,859-67-0	Bezafibrate	215	124	39		9	27	8	992
25	135,319-73-2	Epoxiconazole (BAS 480F)	2380	12	0.2		142		86	1032
26	198,904-31-3	Atazanavir	12	227	0.23		13		5	1135
27	60,207-90-1	Propiconazole	2404	9	0.082		146	114	139	1251
28	375-73-5	Perfluorobutane sulfonate	1028	51	14		46		25	1275
29	1912-24-9	Atrazine	813	68	1.7	6	18	16	19	1292
30	15,687-27-1	Ibuprofen	1585	38	1.1		71	36	37	1406

Several LC-MS detected pesticides, including insecticides, herbicides and fungicides are ranked in the top 30 for groundwater. These include legacy compounds (e.g. atrazine, clothianidin, diuron, simazine, trietazine) and their metabolites (atrazine-desethyl, atrazine-desisopropyl), as well as products currently approved for use (e.g. bentazone, chloridazon-desphenyl, azoxystrobin, fipronil, flufenacet, triallate, boscalid). High ranking for these pesticides draws on their inherent toxicity, resulting in high NORMAN PNECs and/or chronic SSD HC50 HQ based rankings. Many of these substances, especially some of the herbicides, such as atrazine (and its metabolites), bentazone, and chloridazon-desphenyl, are also relatively frequently detected (all found in >100 out of ~850 samples).

A number of pharmaceuticals are in the top 30 ranked groundwater list (Table 5). In addition to the recreational drug cocaine, veterinary drugs such as clopidol and human medicines, such as carbamazepine, are highly ranked. For the two pharmaceuticals, detection frequency is relatively high (245 and 229 of ~850 samples respectively). This is not the case for cocaine, which is detected in only 38 of 822 samples. Further work is needed to confirm the high placing identified for these pharmaceuticals, especially as for two (cocaine, clopidol) hazard is based only on a NORMAN PNEC.

There are six PFAS chemicals among the top 30 ranked LC-MS detected substances in groundwater (Table 5). Each has moderate to high ecotoxicological hazards based on their NORMAN PNEC and chronic SSD HC50 (where available). For all six, detection frequency is relatively high, with all being present in >150 samples. In addition to these six PFAS compounds, further PFASs are also found in groundwater (and surface water) including some at high detection frequency. Limited hazard information is available for these substances (e.g. NORMAN PNECs only or no values) indicating that these chemicals may warrant further investigation. Further studies should include targeted analysis for full quantitative measurement and a wider collection of hazard information from the available literature and risk assessment documents.

3.4.2. Surface water

The top 30 ranked LC-MS detected substances in surface water are dominated by pesticides, human and veterinary pharmaceuticals and some industrial chemicals (Table 6, Fig. 2). The insecticide fipronil and herbicide bentazone are the top two ranked chemicals. For fipronil, high placement is based on high ranking against both the NORMAN PNEC (12th ranked) and chronic SSD HC50 (2nd ranked), while for bentazone, high ranking is found for the chronic SSD HC50 (5th ranked) and to a lesser extent, the NORMAN PNEC (28th ranked). Both of these pesticides were high ranked for their detection frequency (2nd and 13th ranked respectively), with each detection in >2000 samples indicating widespread presence in surface waters.

In addition to fipronil and its degradation products fipronil sulfon and bentazone, herbicides such as propyzamide, flufenacet, triallate and multiple fungicides including boscalid, epoxiconazole, propiconazole and azoxystrobin are also highly ranked. Many of these in-use active ingredients have a high detection frequency, being found in >2000 (>75%) of the surface water samples. This high detection frequency contributes to the substances high ranks. Thus, while some of these pesticides may rank relatively low for one or more hazard metrics (e.g. propiconazole 145th for NORMAN PNEC, 114th for chronic SSD HC50), these substances make the top 30 rank, in large part, because of their high detection frequency (e.g. propiconazole 9th ranked based on detection in 2404 of 2702 samples).

A range of pharmaceuticals are in the top 30. These include well known and widely used human drugs such as diclofenac and carbamazepine, as well as less familiar human and veterinary medicines. High ranking for these pharmaceuticals is due to a number of factors. Some, such as atazanavir have a high ranking (only for the NOMAN PNEC), but are relatively rarely detected (12 of 1109 samples) (Table 6). In other cases, the primary driver for high ranking is a moderate hazard rank coupled with a high detection frequency rank. This is the case for diclofenac, which is NORMAN

PNEC 35th and 28th chronic SSD HC50 ranked, but is 14th ranked for detection frequency (2360 of 2850 samples); atenolol, which is 59th chronic SSD HC50 ranked, but 11th ranked for detection frequency (2383 of 2850 samples) and clopidol which is 265th NORMAN PNEC ranked, but 4th ranked for detection frequency (2551of 2702 samples).

Three perfluorinated chemicals PFOS, PFOA and perfluorobutane sulfonate are in the top 30 ranked LC-MS chemicals in surface waters. All score moderately against the available hazard metrics, N.B. the metric all cover direct freshwater toxicity and will not include hazard for potential for bioaccumulation. Additionally, all of the PFAS compounds are commonly detected (PFOS 21st ranked based on detection in 2252 of 2824 samples, PFOA 11th ranked based on detection in 2444 of 2702 samples, perfluorobutane sulfonate 51st ranked based on detection in 1028 of 2708 samples), indicating the widespread presence in surface waters. Other perfluorinated substances are also widely detected in surface waters indicating that these substances may require further investigation due to their high detection frequency and more limited hazard data, which in some cases did not allow a ranking by average HQ as no metric was available.

4. Discussion

4.1. Appropriateness of the approach used for ranking

The ability to conduct large-scale semi-quantitative analysis of samples for an extensive range of chemicals on a national scale can provide insight into the types and concentrations of organic substances present in groundwater and surface water (Houtman et al., 2019; Kruve, 2019). In this work, a simple approach for ranking was developed that compares the highest concentration of substances detected using a semi-quantitative GC–MS and LC-MS screening analysis to a set of readily available hazard metric value (WFD EQS, NORMAN PNEC, chronic SSD HC50). The approach adopted provides a way to use exposure and hazard data for a large range of substances to undertake a high-level screen to flag substances for further consideration for research and risk assessment. The average rank derived for the three metrics considered was used in combination with a detection frequency ranking to calculate the final rank for all substances detected by GC–MS and LC-MS in national scale groundwater and surface water monitoring programs. In developing the overall approach, a number of decisions and assumptions were made, each with the potential to affect the ranking outcomes.

4.2. Choice of hazard metrics

The hazard metrics selected for this study are only some of those that could have been chosen. Hence, there remains the potential to add further metrics to the assessment. As an example, the ecotoxicological hazard values reported under the EU (& UK) Classification Labelling and Packaging (CLP) regulation could potentially be used. These values are accessible in downloadable formats from the European Chemical Agency (http://echa.europa.eu/), although full assessment requires expert knowledge and would be resource intensive to conduct. Addition of values relevant for human health, such as Drinking Water Standards, Acceptable/Tolerable Daily Intakes or Benchmark Dose value, could also be included alongside the ecotoxicological hazard metrics.

4.3. Weighting of metrics for average ecological ranking

To derive the average ecological rank position, the ranking for all three hazard metric (WFD EQA, NORMAN PNEC, Chronic SSD HC50) were average. Averaging reduces the number of ranking lists to produce a single consolidate ranking for each detection method and environment. For averaging, an equal weighting was given to each hazard metric, even though the three hazard metrics differ in their input data (e.g. measured toxicity data, QSAR model predicted toxicity), level of regulatory acceptance (high for WFD EQS, none as yet for the other two metrics) and application of assessment factor (included for WFD EQS and NORMAN PNEC, not included for the chronic SSD HC50). Greater weighting could, for example, have been given to the rank for the regulatory accepted value (e.g. WFD EQSs). However, WFD EQS values are available for only a small proportion of substances. Hence, greater weighting to those regulatory approved values could have skewed the analysis to already assessed substances above emerging chemicals. Equal weighting, in contrast, retains the possibility for emerging substances that are not yet the focus of regulatory value setting to have equal potential to be ranked highly.

4.4. Inclusion of detection frequency in ranking

The final ranking was generated by ordering the product of the average rank and detection frequency rank. Detection frequency correction raised the overall ranking of substances commonly detected and reduced the ranking of substances rarely found. This meant that inherent substance hazard and also the potential for that hazard to occur were both considered in the assessment. For inherent substance hazard assessment and ranking, the inclusion of detection frequency correction may not be appropriate. However, as the focus here was on identifying substances for their potential to cause ecological effects, some consideration of likelihood of exposure in groundwater and surface water was deemed appropriate.

4.5. Choice of maximum concentration

The highest measured concentration was used throughout as the exposure term for ranking, and a means to conduct a quick high level worst-case screen to flag substances for further consideration. Use of the highest value clearly has pitfalls in its interpretation. However as previously outlined, the use of values embedded in the distribution of concentrations (e.g. mean, median, 90th percentile) was possible only for a small number of chemicals, mainly in surface waters. Hence, use of a distribution-based value would have precluded ranking for a high proportion of the detected substances. Analysis of the distribution of measured concentrations indicated that in all assessed cases, the highest measured value was not an extreme outlier (Supplementary Fig. 1 a-xx). This supports the validity of the generic use of the maximum value for worst case ranking. For any wider assessment, a more complete analysis of concentrations in time and space, and their relationship with different hazard metrics would be warranted.

4.6. Identified (top 30 ranked) substance patterns and trends

Separate rankings for groundwater and surface water allowed the identification or substances for further investigation relevant for both environments and also distinct for each. Further, by considering potential use category, it was possible to gain an overview of the potential sources and routes of release of the highest ranked substances (Fig. 2). Although attribution to a single use class was sometimes difficult, clear patterns did emerge.

In both environments and for both detection methods, legacy or current use pesticides contribute a major fraction of the top 30 ranked chemicals (Fig. 2). There was a greater representation of legacy pesticides (e.g. triazines, phenylureas, diazinon) in groundwater. The presence of legacy pesticides in the environment is consistent with the results from other monitoring programs (Manamsa et al., 2016; McKnight et al., 2015; Shishaye et al., 2021). Given the long time-span that has elapsed since authorisation was removed for the widespread use for these pesticides in England (e.g. since 2004 for triazines), their continued presence in groundwater indicates a lower degradation potential and consequently longer retention times in the sub-surface than the surface water environment. This is consistent with the previous finding of longer triazine persistence in groundwater than predicted, based on half-lives due to limits on bioavailability or the energetic constraints of microbial growth in the sub-surface (Rodriguez et al., 2021) that can result in the reduced degradation for some (Navarro et al., 2004), but not all (Di et al., 1998) pesticides.

Current use active ingredients were more common in the surface water top 30 ranked list compared to in groundwater. The prevalence of current use pesticides in surface water indicates both the relatively widespread nature of land to surface transport of pesticides under the agricultural management and climate conditions prevailing in England. Except for rotenone, which is detected here through its piscicide use for invasive fish species, pesticides reach groundwater and surface water following soil application through percolation, run-off and sub-surface flow (FOCUS, 2001). Among the ranked, currently approved for use pesticides in surface waters, herbicides and fungicides were the main classes identified. Presence of the active ingredients is likely to be due to their high usage amounts (http://pusstats.fera.co.uk/home/) leading to high occurrence and also to high detectable levels in some cases. In almost all examples, current use pesticides are ranked based on NORMAN PNEC and/or chronic SSD HC50 values. In cases of the highest ranked substances, further work may be warranted to identify vulnerable taxa, especially fungicides given that fungal taxa are not covered by the modelled NORMAN PNECS are rarely tested in experimental studies and that they may also have biocidal action against a range of taxa (Maltby et al., 2009).

In groundwater, a greater proportion of the high ranked chemicals are associated with industrial processes and products, such as PAHs, industrial chemicals, solvents and plasticisers (Table 3). The role of contaminated land and urban areas such as reservoirs for such pollutants, is widely recognised and could partly account for the presence of such chemicals in groundwater, for example, the persistence and leaching of PAHs has been demonstrated in industrial and urban settings (Hankard et al., 2004; Schiedek et al., 2007; Zhang et al., 2013). Potential sources include: fossil fuel processing, storage, distribution and retail facilities, diffuse pollution, industrial sites and contaminated land sites. The presence of plasticisers in groundwater also points to a potential role of industrial and domestic landfill as a pollution source, especially from older unlined landfills that lack impermeable layer to limit downward flows. Other potential sources of plasticisers in groundwater include treated effluent discharges and materials spread on land. Although plasticisers have been shown to have laboratory half-lives typically of a few weeks, they have been found to remain in natural soils across a range of land uses for longer timescales, from where they may enter groundwater (Billings et al., 2021).

A greater number of pharmaceuticals are top 30 ranked in surface waters than in groundwater (11 surface water, 8 groundwater) (Fig. 2). This high ranking for multiple pharmaceuticals is based both on the hazard rank (especially against the NORMAN PNEC value) and also their higher detection frequency ranking in surface water than groundwater. The presence of pharmaceuticals in surface waters may be linked to releases from wastewater treatment work discharges following human use (Gardner et al., 2013; Heffley et al., 2014). These represent pharmaceuticals ingested and excreted without biotransformation by patients that subsequently enter and pass through the sewage treatment system to be released in effluent (Boxall et al., 2003; Nikolaou et al., 2007). However, in addition to these human pharmaceutical uses, a number of the high ranked substances are also used as veterinary medicines. Entry of these chemicals into surface water, and even groundwater, following direct outdoor excretion to land and surface waters or after leaching from manures, may provide entry routes for these substances (Kemper, 2008). Veterinary medicines that are used on pets may also enter the water environment through treated effluent discharges.

4.7. Comparing ranking outcomes with other prioritization studies

The need to focus research and regulatory action on the chemicals of greatest concern has prompted an interest in chemical ranking. The selection of substances for inclusion within the main WFD substance list (and the associated watch list) prioritises substances of regulatory concern for which sufficient data is available for generation of environmental quality standard. In groundwater, there are 13 substances in the top 30 GC–MS and/or LC-MS substance ranked lists that have a WFD-EQS (or value for a close analogue). This corresponds to 21% of substances with an EQS compared to ~5% of the combined total of 1144 analytes. The higher proportion of substances with a WFD EQS in the top 30 ranked list demonstrates the potential of the approach to identify high priority substances and also the relevance of some, but not the majority, of the WFD substances to groundwater and surface waters in England.

In addition to substances currently regulated under the WFD, the EU also maintain separate watch lists of substances of regulatory concern for both surface water and groundwater. The recently revised 3rd WFD watch list for surface water includes pesticides (azole fungicides), antibiotics (sulfamethoxazole, trimethoprim), antifungal (clotrimazole, fluconazole, miconazole) and other pharmaceuticals (venlafaxine) (Gomez Cortes et al., 2020). None of these watch list substances, however, appear in any of the top 30 ranked lists despite being included in the GC–MS or LC-MS suite and being measured in all cases in >1000 samples and in some cases in many more. The absence of the priority chemicals may be linked to the different protection goals of this study relevant to some of the drivers for inclusion of the WFD watch list. For example, the antimicrobial and antifungal chemicals may be identified for their potential to induce antimicrobial resistance (Assress et al., 2021; Stanton et al., 2020), rather than their toxicity for aquatic plants of animals; while antidepressants may be highlighted for their behavioural, rather than apical, toxic effects (Bossus et al., 2014; Ford et al., 2018; Saaristo et al., 2017).

Within a research context, other authors have developed approaches to chemical assessment and ranking for aquatic ecosystems. Generally these studies have followed the approach applied here of using measured or modelled environmental concentrations and databases of openly available toxicity data as input for comparative ranking (Guillen et al., 2012). These ranking studies have focussed on different geographical regions and aquatic habitats including substances in Europe (Donnachie et al., 2014; Donnachie et al., 2016; Johnson et al., 2017), North American (Maruya et al., 2014) and Chinese (Johnson et al., 2018) freshwaters and marine systems (Barbosa et al., 2021).

Johnson et al. (2017) conducted a chemical "risk" ranking study for UK freshwaters that used a composite set of literature and monitoring data (e.g. from the Forum of European Geological Surveys and Environment Agency data from 2010 to 2012) for the exposure term and lethal and sub-lethal toxicity data (including LC50, LOEC, EC50) as the hazard term. "Risk" was calculated by dividing the median water concentration by the median effect concentration. Use of median value for the exposure term is less conservative than the highest value approach used here; while use of the median effect concentration is consistent with the use of chronic SSD HC50s, but less conservative than in the use of the WFD EQS and NORMAN PNEC values. Using this median based approach, metals, which were not assessed in the current study, were found to represent 5 of the top 10 and 12 of the top 30 ranked substances. Of the organics, ethinylestradiol, triclosan, methomyl, chlorpyrifos, benzo[*a*]pyrene and nonylphenol were all in the top 15 rank. Of these six organic chemicals, ethinylestradiol, methomyl and 4-nonylphenol are not detected in any groundwater or surface water samples (despite measurement in >1000 samples) and chlorpyrifos in <60 samples across the two monitoring data-sets analysed here. Benzo[*a*]pyrene in both groundwater and surface water and triclosan in surface water are, however, included in top 30 the ranked chemicals. Johnson et al. (2018) also applied the same median value based ranking approach to two Chinese catchments. Again, inorganic chemicals dominated the top ranked substances (10 of the top 15). Organic chemicals in this top ranked set included benzo[*a*]pyrene and bis(2-ethylhexyl) phthalate that were also both top 30 ranked in groundwater and surface water in this study.

Maruya et al. (2014) used the maximum concentrations of organic chemicals detected in wastewater effluent and published toxicity benchmarks (e.g. NOECs or PNECs) for survival, growth, and reproduction in aquatic species to prioritise potential chemicals for further monitoring. Of 61 chemicals assessed, 15 were identified as candidates for monitoring. Six of these candidates are in the top 30 ranked substances in surface water, i.e. bis(2-ethylhexyl), bisphenol A, ibuprofen, diclofenac, PFOS and triclosan. Other substances identified by Maruya et al. (2014) included steroid hormones and chlorpyrios, also identified by Johnson et al. (2017), pyrethroid insecticides and PBDEs. A further study by Barbosa et al. (2021) used in vitro experimental data from the TOXCAST project to assign a "concern index" from which to prioritise classes of chemicals for further assessment. PBDEs, phthalates, herbicides and phenol had the highest average rank through this approach. PAHs in contrast had an intermediate average "concern index" and PFAS a low value. The high average ranking of phthalates and some herbicides is consistent with the ranking generated here; but not the intermediate and low ranking of PAHs and PFAS, multiple class members of which are highly ranked in groundwater and/or surface water. The different ranking results between these studies for PAHs and PFASs may relate to the difference in hazard metric used, which we based on whole organism endpoint in the current work compared to the in vitro mechanistic endpoints used by Barbosa et al. (2021).

4.8. Overall conclusion and future use of the developed rankings

A novel approach for ranking of substance detected by GC–MS and LC-MS in water samples is presented. The aim of the work was to do a high-level worst-case screen of the available scan data to identify substances for further consideration as part of an assessment of environmental fate and effects. Of the GC–MS and LC-MS detected substances in groundwater and surface water in England, only a relatively small proportion (≤20%) have a WFD EQS (the major regulatory values used for surface water quality assessment). Among the remaining high ranked chemicals there are a significant number for which Posthuma et al. (2019) were able to assemble sufficient ecotoxicological data to parameterise a chronic SSD. Substances highly ranked with a chronic SSD HC50, but not a WFD EQS, represent both substances of potential concern and also chemicals for which sufficient data could be accessible for a more detailed assessment. Highly ranked substances of this nature include a number of current use pesticides, industrial chemicals (notably PFASs), plastics-associated chemicals (notably phthalates and phosphate plasticisers) consumer products and human and veterinary pharmaceuticals. Detailed assessment of these substances for their ecological effects would require significant efforts depending on the approaches to chemical management in place at a given time. Substances that are high ranked based only on a NORMAN PNEC (i.e. with no WFD EQS or chronic SSD HC50) should be given further consideration for more detailed assessment. For these substances, the absence of a chronic SSD HC50 suggests there is a lack of available toxicity data to conduct any such analysis. Hence, such substances may be a priority for consideration for further assessment and, if necessary, research to address any gaps in ecotoxicological knowledge.

Funding sources

This work was supported by the Environment Agency under a collaborative research agreement, with co-funding from NERC National Capability Funding through an Individual Merit Award (06896) to DJS.

Availability of supporting data

The authors are grateful to numerous Environment Agency staff for managing groundwater and surface water monitoring programmes, sample collection and laboratory analysis, without whom this project would not have been possible.

Data-sets relating to these meta-analyses are available on request from the corresponding author (as Microsoft Excel or comma separated text). The Environment Agency's GC–MS and LC-MS target screen data-sets are available for download here: https://data.gov.uk/dataset/0c63b33e-0e34-45bb-a779-16a8c3a4b3f7/water-quality-monitoring-data-gc-ms-and-lc-ms-semi-quantitative-screen.

CRediT authorship contribution statement

The views expressed in this paper are those of the authors and not the organisations for which they work. The study was conceived and designed by DJS and TB. Data analysis was conducted by DJS, who prepared the manuscript and figures. WC led the generation and management of the GC–MS and LC-MS data. LH, EA, NK, KS and TB contributed to the development of the overall ranking method, the interpretation of the results and the finalisation of the manuscript.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

David Spurgeon reports financial support was provided by Environment Agency. David Spurgeon reports financial support was provided by National Capability IMP project 06896.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155101.

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