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Prioritizing toxic shock threats to sewage treatment plants from down-the-drain industrial chemical spills: the RAVEN STREAM online tool†

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Down-the-drain chemical spills that reach a sewage treatment plant (STP) can cause a biological "toxic shock" that may reduce or eliminate the capability of STP microorganisms to remove organic matter and nutrients for weeks to months. Thus, chemical spills are a threat to water quality. Here, we present a case study of toxic shock threat prioritization for chemicals used at industrial facilities connected to the Käppala STP in Stockholm, Sweden. We surveyed 60 facilities, collected information on the use and storage of bulk chemical products, and documented 8676 uses of constituent chemicals. *In situ* chemical tracer experiments were conducted in the primary sewer tunnel leading to Käppala to measure chemical spill dilution during transit to the plant. To assess chemical risks to the plant, we extracted data on toxicity to STP microorganisms for 6168 chemicals from European Chemicals Agency brief profiles and estimated exposure concentrations in the plant using conservative assumptions. Under a high-end spill scenario, the majority of chemicals in the survey posed a negligible risk for adverse effects on plant microorganisms, however 28 chemicals were identified as posing a potential risk and were prioritized for additional information gathering to refine our conservative assumptions. The analysis framework was built into an online tool (RAVEN STREAM) provided as free, open-source software for STP operators to screen for threats posed by possible chemical spills at connected facilities. The threat identification framework can facilitate communication between STPs and their upstream industrial clients to mitigate possible high-risk chemical spills before they happen.

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Environmental significance

Down-the-drain chemical spills at industrial facilities can contaminate a receiving sewage treatment plant and damage the microbial community's ability to remove environmentally harmful material from wastewater. To help identify and prevent such chemical spills from happening, we developed an open-access online tool that helps identify chemicals used upstream that could harm a treatment plant if spilled down the drain, and informs the need for supplementary spill mitigation measures. The output of the chemical spill threat identification framework facilitates improved management of industrial chemical storage, reduces risk to the proper operation of the receiving sewage treatment plant, and thus helps mitigate environmental pollution.

1 Introduction

Sewage treatment plants (STPs) play a crucial role in maintaining water quality by removing nutrients such as nitrogen and phosphorus, as well as organic matter, from wastewater prior to its release to the environment. Depending on clarification requirements, sewage treatment can involve a primary (mechanical), secondary (biological), and advanced (or tertiary) step.[1] In a well-functioning STP with a secondary biological treatment step, microbial activity (*e.g.*, respiration, nitrification, denitrification) along with chemical precipitation of phosphorus can result in near-complete nutrient removal (on the order of 80% for total nitrogen and >95% for phosphorus) and near complete biological oxygen demand removal (>99%) from the influent wastewater.[2]

The capacity of STP microorganisms for nutrient removal can be degraded or even destroyed during so called "toxic shock" events, in which a large-volume chemical spill reaches the plant in influent water. One example of such an event was the release of a chemical used in adhesives upstream of the Syvab STP near

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Stockholm, Sweden in the fall of 2013.[3,4] The toxic shock event caused by that chemical spill resulted in complete termination of the nitrification ability of microorganisms in the activated sludge, and a roughly 5-fold increase in the outgoing ammonium levels from the plant. Proper nitrogen removal capacity was not fully restored for over 6 months after the event. In another case, Topalova *et al.*, 2018 (ref. 5) documented the impacts of an upstream spill of mazut that impacted functioning of activated sludge at an STP in Sofia, Bulgaria for a period of over 3 weeks. Another incident was recorded in the city of Borås, Sweden, where a spill of roughly 17 m^3 of diesel oil at a hospital contaminated the municipal STP and disrupted the nitrogen processes of the biological stage, causing ammonium levels to be above acceptable levels for roughly one month.[6]

STP operators can work to avoid toxic shock events caused by chemical spills through communication and cooperation with their upstream clients. Ettala and Rossi, 1994,[7] for example, conducted on-site surveys of 11 industrial facilities across two STP service areas. Based on chemicals stored on-site, chemical inhibition concentrations, and STP operational details, they calculated threshold amounts of chemicals that would have to be spilled to impair methanogenesis, carbonaceous material removal, and nitrification capabilities of the plant, as well as the possibilities for sludge contamination or exceedance of the plant's aeration capacity.[7]

A number of modelling frameworks have been developed for planning responses to contamination of wastewater, such as the modelling framework by Amstutz *et al.*, 2008 (ref. 8) and the US EPA's Wastewater Response Protocol Toolbox (WRPT).[9] One of the recommended risk assessment tools in the WRPT is the Water Contaminant Information Tool (WCIT), which is a secure tool that can be used to assess risk to water from contamination by accidental spills or terrorist activity.[10] The WCIT contains information on more than 800 drinking water and wastewater contaminants, including industrial chemicals and pathogens. The source code for the WCIT is, however, not publicly available, and use of the tool is limited to US-based drinking water and wastewater facilities, state and federal officials, and EPA partners.[10] Furthermore, risk for disruption to the proper operation of STPs are not calculated by this tool, but rather only estimates for how a chemical may physically contaminate STP infrastructure. The integrated modelling framework by Amstutz *et al.*[8] combines simulations of contaminant transport through source water, drinking water, and wastewater to plan for and respond to the impacts and risks from deliberate or accidental toxic chemical contamination events. This modelling framework, however, utilises computationally-intensive hydraulic simulations in a geospatially-explicit representation of the urban water infrastructure domain, making it poorly suited for rapid analysis of risks posed by a large number of industrial chemicals used upstream from an STP. Thus, there is currently a lack of an open source, high-throughput, upstream chemical risk assessment tool that can be used by STPs to rapidly screen for and prioritize threats from spills of a large number of industrial chemicals that may be used upstream.

Here, we present a novel upstream chemical threat prioritization framework, and demonstrate its use with a case study conducted at Sweden's third largest STP which is operated by Käppalaförbundet (*i.e.*, "The Käppala Association", hereafter referred to as "Käppala"). The framework addresses a key question of upstream chemical management: which industrial chemicals at which upstream facilities could result in adverse impacts on the STP if they are spilled? In our case study, we combined a survey of industrial chemical products used by upstream clients, data on chemical toxicity towards activated sludge microorganisms, *in situ* measurements of simulated chemical spills in the STP tunnel system, and modelling of hypothetical high-end chemical spill scenarios to produce a screening assessment of threats to the Käppala STP from possible upstream chemical spills.

The output of the threat prioritization framework is a ranked list of industrial chemical products and the constituent chemicals used upstream that, if spilled, pose the highest risk to the proper functioning of the receiving STP. The chemical risk values generated by our approach are not 'true' risks posed to an STP, because a number of factors that are not considered at the industrial facilities, in the sewer tunnel system, and in the plant may affect the actual risk. Rather, the outcome is a prioritization list that can facilitate communication between STPs and their upstream clients by identifying potential threats to the plant and providing a list of chemicals for which additional information gathering is needed regarding the likelihood and potential severity of a down-the-drain spill (*e.g.*, storage locations, refined inventory information, existing safety protocols, *etc.*). Such information gathering may elucidate the need for additional mitigation measures to reduce the likelihood of down-the-drain spills of chemicals that pose a high potential risk. The chemical datasets and risk modelling framework behind our threat identification methodology are provided as freely available, open-source, online software: The Rapid Assessment of Vulnerability from Emissions Upstream (RAVEN STREAM) tool (**https://raven-stream.shinyapps.io/raven_stream/**).

2 Methods

To address the overarching question of which industrial chemical products used at upstream facilities pose a risk to an STP's microorganisms in the event of a spill, answers to three sub-questions are required:

(1) What industrial chemical products are used, what are their chemical compositions, and in what quantities are these products stored on-site at upstream facilities at any given time?

(2) How toxic are these industrial chemical products and/or their constituent chemical ingredients to the microorganisms in the receiving STP?

(3) How much of the industrial chemical product, if spilled, will reach the biological treatment regions of the STP?

Here, we use the Käppala sewage treatment plant, located on the island of Lidingö in the Stockholm Archipelago, as a case study. Käppala is owned and operated by a partnership of 11 suburban governments in the greater metropolitan area of Stockholm, Sweden (see Fig. S1 in the ESI†). It treats wastewater from ~567 000 person-equivalents, and a wide variety of

industrial facilities (2200 registered) are connected to the waste stream, including energy plants, hospitals, chemical industries, food processing facilities, and car washes (see Table 1).

Käppala employs a mix of mechanical, chemical, and biological treatment steps to treat influent wastewater (see Fig. S2†). The first step in the treatment process screens out large material and employs a grit settling chamber. Influent is then split into 11 separate treatment lines. The initial phase of these treatment lines is the primary sedimentation stage, with a residence time of 4–6 hours, where approximately 66% of the suspended solids in the wastewater influent are removed and diverted to an anaerobic digestor. After primary sedimentation, wastewater is treated in activated sludge tanks. Here, the wastewater is passed through anoxic, aerated, and non-aerated parts of the tank over a period of roughly 24 hours. The wastewater is then passed to secondary sedimentation tanks, where return activated sludge is recycled back into the activated sludge region at half of the inflow rate as well as diverted to the STP's anaerobic digestor (whose median residence time is roughly 20 days). On all of the treatment lines, ferrous sulphate is added to the return activated sludge from the secondary sedimentation to remove phosphorus. Finally, the remaining wastewater is passed through a sand filtration step, and the effluent is released at a rate of approximately 140 000 m^3 day^{-1} into the Baltic Sea at a depth of 45 meters, having removed roughly 80% of the total nitrogen, 97% of the phosphorus, and 99% of the organic matter (expressed as biological oxygen demand BOD) from the influent wastewater.[2,11] Sludge processed in the anaerobic digestor is used on agricultural fields, and biogas generated by the plant is processed for use in city buses.[11]

Our approach to answering each of the three sub-questions for the Käppala sewage treatment plant, and synthesizing the answers into the RAVEN-STREAM threat identification framework that can be applied to other STPs, is described in the following sections. All analysis was conducted using the R programming language, version 3.6.0 (ref. 12).

2.1 Upstream industrial chemical usage data

2.1.1 Survey of upstream industrial chemical usage. Käppala is a member of Revaq, a Swedish sludge certification organization that oversees the production of sludge for application to agricultural fields.[13] Certification by Revaq requires, among other demands, that member STPs collect information from upstream industrial facilities about chemicals that can be expected to be released into the sewer lines, and potentially contaminate sludge. In order to fulfil Revaq certification requirements, information about purchases of chemical products was collected by Käppala, and this information from 60 upstream facilities was used in this analysis. The upstream chemical inventory is updated annually, and the data used here

Table 1 Meta-data associated with the survey of upstream industrial products and constituent chemicals

Facility category	Total # products	# products only M_R reported	# products only Y_R reported	# products M_R & Y_R reported	Total # constituent chemicals	# chemicals with valid STP PNEC values	# chemicals with no toxicity likely/ expected	# chemicals with STP PNEC information missing
Airport	45	0	45	0	108	42	19	47
Buses 01	144	0	61	83	507	238	74	195
Automotive 01	22	0	22	0	72	21	6	45
Automotive 02	5	0	5	0	16	3	2	11
Automotive 03	118	0	118	0	441	140	73	228
Buses 02	33	0	0	33	192	132	22	38
Waste disposal	46	0	0	46	194	87	27	80
Chemical industries 01	160	4	125	31	261	103	52	106
Automotive 04	7	0	7	0	18	8	4	6
Disposal plants	167	0	145	22	576	246	75	255
Energy plants	164	52	30	82	476	185	48	243
Food industry	57	0	24	33	139	57	23	59
Hospitals	33	0	33	0	41	27	2	12
Buses 03	102	9	1	92	357	153	34	170
Laundry	116	7	38	71	345	163	60	122
Automotive 05	69	0	60	9	359	167	83	109
Chemical industries 02	493	0	493	0	3600	2342	136	1122
Surface treatment	13	0	4	9	50	30	6	14
Train washes	97	0	61	36	335	150	45	140
Vehicles other	195	1	145	49	589	299	89	201
All industries	2086	73	1417	596	8676	4593	880	3203[a]

[a] Of the 3203 constituent chemical uses that do not have STP PNEC information, 1293 (15% of total) have CAS numbers that match chemicals in the ECHA database, 1613 (19% of total) have valid CAS numbers but do not have matching chemicals in the ECHA STP PNEC database, and 297 (3% of total) have invalid CAS numbers reported from the upstream industries. Abbreviations: M_R: maximum mass of chemical product in stock directly reported by facilities. Y_R: reported yearly usage of chemical product (see Section 2.1.2). STP PNEC: sewage treatment plant predicted no-effect concentration.

were mostly reported for the year 2018. Information on the product mass or volume used throughout the year, the maximum mass or volume of product held in stock at one time, the constituent chemical ingredients of the products (identified by their CAS numbers), and the fraction contribution of the constituent chemicals to the product was requested.

In cases where a range of fraction contributions to the overall product is provided for a constituent chemical, the higher-end of this range was selected and used in our analysis to maintain a conservative estimate of chemical risk (the sensitivity of the results to this assumption is explored in Section 3.5.1). For product usage and/or storage amounts that were provided on a volume basis, a density of 1 kg L^{-1} was assumed to convert volume to mass.

2.1.2 Estimating 'max-in-stock' amounts. In response to the survey, chemical product usage data was reported by facilities as either the amount used on an annual basis (referred to as "yearly usage" amounts) and/or the maximum amount of product that is held in stock at a given time (referred to as "max-in-stock" amounts). At any given time, the max-in-stock amount of a chemical product is the largest potential down-the-drain spill, and we sought to model such a worst-case spill.

Max-in-stock values (M_R, kg, where the subscript R denotes reported values) were directly reported for 669 (32%) of the upstream chemical products, while for 2013 products (~97%) yearly usage data (Y_R, kg $year^{-1}$) were reported. For 596 products (~29%), both Y_R and M_R values were reported. To estimate max-in-stock values for chemical products for which only Y_R was reported, we developed an extrapolation algorithm based on the relationship between max-in-stock values and yearly usage values for the 596 chemical products for which both were reported. For products where both Y_R and M_R values were reported, the maximum number of months of inventory of a product in stock (t_{max}, months) was calculated using eqn (1):

$$t_{max} = \frac{M_R}{Y_R} \times \frac{12 \text{ months}}{\text{year}} \quad (1)$$

The distribution of t_{max} across the 596 chemical products is shown in Fig. S3.† For chemical products where only yearly usage values are provided, an estimated (denoted by subscript E) max-in-stock value, M_E, is then derived using eqn (2):

$$M_E = t_{max}(P) \times Y_R \times \frac{\text{year}}{12 \text{ months}} \quad (2)$$

where P is a selected percentile of the distribution shown in Fig. S3.† For most of the results discussed in this study, a value of $t_{max}(50) = 4.8$ months is used to estimate M_E from reported annual usage Y_R. The impact on the results of employing different values of P to estimate M_E (and ultimately chemical risk to the STP) is discussed in Section 3.5.1.

2.2 ECHA sewage treatment plant predicted no effect concentration (STP PNEC) values

The European Chemicals Agency (ECHA) collects chemical property and toxicity data on chemicals registered for use in Europe under the REACH regulation. Toxicity information collated from dossiers submitted by companies applying for use authorization for chemicals within Europe are available on the ECHA website organized by CAS number onto individual web pages (or "Brief Profiles", see for example this Brief Profile for peracetic acid, CAS no. 79-21-0: **https://echa.europa.eu/brief-profile/-/briefprofile/100.001.079**). If the registered chemicals meet the volume threshold of 10 tonnes per year, a sewage treatment plant predicted no effect concentration (referred to as an STP PNEC) is generally required to be provided by the registrants for the chemical.[14] The STP PNEC values can be derived through a variety of methods, including extrapolation from biodegradation data, an activated sludge respiration inhibition test, or a nitrification inhibition test (see ECHA 2008 (ref. 15) for a full list of possible STP PNEC derivation methods). STP PNEC values are not required to be provided for a registered chemical if the chemical does not meet the 10 tonnes per year reporting threshold.

We developed a web scraping algorithm to extract STP PNEC values from across CAS number-specific Brief Profile webpages provided by ECHA. To do this, we downloaded the full list of registered chemicals within the ECHA database, which contains a mapping between the CAS number and the chemical's Infocard number.[16] This Infocard number is the primary identifier within the CAS number-specific URL for the Brief Profile webpage where the chemical's property and toxicity data can be accessed. A total of 18 280 CAS number-URL matches were established. Using the R programming language packages 'rvest'[17] and 'xml2',[18] along with information on the structure of the HTML code for the Brief Profile webpages, the available STP PNEC information was scraped from the Brief Profile of each chemical. Because we collected STP PNEC values directly from the ECHA Brief Profiles and not the underlying dossiers, we did not collect information on the type of test used to derive each STP PNEC value, or the assessment factors applied in deriving the final displayed STP PNEC value. The STP PNEC values are used 'as-is' from the data provided on the ECHA webpage, and any possible errors made in the transfer of toxicity information in the chemical dossiers to the values provided on the ECHA webpage are not considered.

Using the above web scraping procedure, STP PNEC values for 4496 unique CAS numbers were extracted, along with 1672 chemicals being identified as having either no or no expected toxicity towards STP microorganisms. 217 of the 4496 STP PNEC values that were identified in the ECHA database have a range of values provided. In our default assessment scenario, the lowest available STP PNEC value (*i.e.*, highest toxicity) for a given chemical was employed to maintain a conservative estimate of risk. The impact on the results of using the full range of STP PNEC toxicity values when deriving chemical risks is explored in Section 3.5.1.

2.3 Influent wastewater contamination

2.3.1 *In situ* measurements of a simulated chemical spill. We conducted a series of chemical tracer emission and measurement tests along Käppala's northern sewer system line to estimate the transport and dilution characteristics of

a theoretical chemical spill through the sewer network. Slug injections of uranine, a conservative fluorescent tracer, were used to simulate a chemical spill at distances of 9.1 km, 21.7 km, and 45.9 km from the STP's inlet (see Fig. S4 and Table S1†). The injections were carried out either directly into or close to the primary sewage transport tunnel, rather than within the municipal sewer networks, due to accessibility, ease of replicating a slug injection, and to minimise losses of tracer during injection. We measured concentrations of the tracer in sewage at the inlet of the STP to determine the time time-varying dilution patterns of the simulated chemical spills upon entry into the plant. For more details, see the "*In situ* measurements of a simulated chemical spill" section in the ESI,† and Scullin, 2021 (ref. 19) for a comprehensive presentation of the tracer study.

2.3.2 Spill scenarios for industrial chemical products and calculation of risk. In our conservative, high-end scenario for possible down-the-drain spills of upstream industrial chemical products and their subsequent contamination of the Käppala STP, the max-in-stock amount (*i.e.*, either M_R or M_E) of each chemical product in our inventory is assumed to be spilled down the drain (see Fig. 1). The fate of chemicals in the plant as a function of chemical properties is not considered when assessing exposure of microorganisms in the sewage treatment plant. Rather, our spill scenario considers two different situations to estimate the worst-case scenario risk to different regions of interest in the plant under two bounding scenarios for chemical fate: (1) the constituent chemicals in the spilled chemical product are fully partitioned to the influent liquids and contaminate the activated sludge reactors, and (2) the chemicals are fully sorbed to influent solids and contaminate the anaerobic digestors. Further, we conservatively assumed that the primary sedimentation tank solids are all diverted to the anaerobic digestors, and all liquids are diverted to the activated sludge reactors. In reality, only about 66% of the solids are removed to the anaerobic digestors at this step, with the remainder coming in from the secondary sedimentation step after the activated sludge (see Fig. S2†). However, if equilibrium partitioning is assumed in the primary sedimentation tank, and chemical is assumed to only be bioavailable in the liquid phase in the activated sludge tank and only in the solid phase in the anaerobic digestors, then this simplifying assumption would have little effect. For the scenario where chemicals fully partition to the liquid phase of the influent, the risk to the activated sludge is estimated by assuming the chemical mass is divided according to the influent flow splitting between the smaller (36% of flow) and larger (64% of flow) activated sludge regions of the plant (Fig. 1). For the scenario where chemicals are fully partitioned to the solid phase of the sewage, the full mass of the spilled chemical is assumed to contaminate the anaerobic digestors for estimating risk to this part of the STP.

We calculated the masses of the constituent chemicals from their reported fraction contribution in the bulk chemical products, and we used these chemical masses along with corresponding STP PNEC values as the basis of the risk calculation. The risk R_i for a given constituent chemical (i) posed to a specific region of the plant (*i.e.*, the smaller activated sludge region, the larger activated sludge region, or the anaerobic digestors region) is calculated using eqn (3):

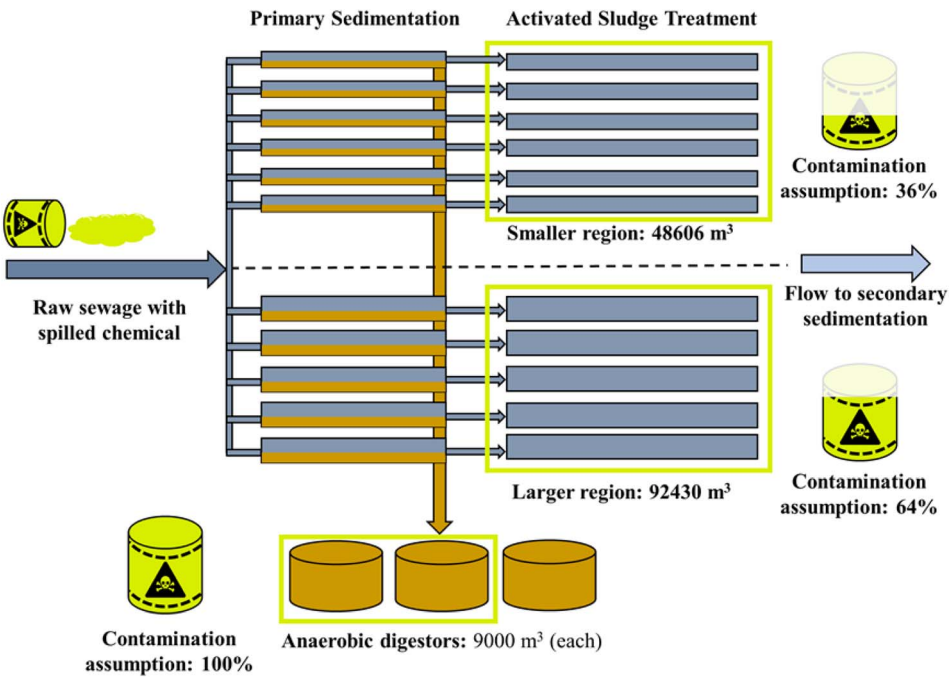

Fig. 1 Schematic illustrating assumptions for the high-end contamination scenarios assessed for potential down-the-drain spills of industrial chemical products and their constituent chemicals that are used upstream of the Käppala sewage treatment plant. While there are 3 anaerobic digestors on site at Käppala, at the time of the analysis only 2 were operational, and so the volume of these two is used in the chemical risk calculations. The different regions of the plant are not drawn to scale. See Fig. S2† for a schematic of the full-scale treatment process at Käppala.

$$R_i = \frac{M_X \times \text{frac}_i}{V_{Reg} \times \text{PNEC}_i} \times \frac{10^6\ \text{mg}}{\text{kg}} \quad (3)$$

where M_X can be either M_R or M_E (see Section 2.1.2), frac_i is the fraction contribution of the constituent chemical to the chemical product, V_{Reg} is the volume of the given region of the STP (litres), PNEC_i is the STP PNEC value of the chemical $\left(\frac{\text{mg}}{\text{litre}}\right)$, $\frac{10^6\ \text{mg}}{\text{kg}}$ is a conversion factor from kg to mg, and the subscript i corresponds to values for a specific constituent chemical. The risk R_P that a given bulk chemical product poses to the region of the STP is then obtained by assuming additive toxicity of the constituent chemicals and summing the risks from each of the constituent chemicals in the product using eqn (4):

$$R_P = \sum_{i=1}^{n} R_i \quad (4)$$

where n is the number of constituent chemicals in the industrial chemical product for which risk values could be calculated.

The anaerobic digestor is the region of the plant where the lowest chemical dilution potential exists, *i.e.*, the region where the combination of the fraction of diverted influent and the volume of the region results in the highest concentration of chemical (see Fig. 1). However, the focus of the STP PNEC values is on quantifying the impact of chemicals on nutrient removal (particularly using the respiration inhibition test), rather than on processes occurring in an anaerobic digestor (*e.g.*, biogas production), so it is unclear how the toxicities provided by ECHA relate to toxicity towards anaerobic digestor microorganisms.[14,15] In the absence of toxicity values directly applicable to anaerobic systems, we present risks for the second-most exposed region of the plant, *i.e.*, the smaller activated sludge region, in Fig. 3 and 5. Risk quotients for the larger activated sludge region are a constant factor of 1.1 lower than the risk quotients for the smaller activated sludge region, reflecting differences in dilution of chemicals (see Table S2†). If STP PNECs are assumed to also apply to the anaerobic digestor, then risk quotients are highest there, a constant factor of 7.5 higher than in the smaller activated sludge region.

3 Results and discussion

3.1 Upstream industrial chemical usage survey and corresponding STP PNEC data

A total of 60 facilities, 2086 uses of chemical products, and a corresponding 8676 uses of constituent chemical ingredients are reported in the upstream usage data, with the unique number of products and constituent chemicals across the dataset being 1818 and 1361, respectively. A synthesis of the available upstream industrial chemical use data is provided in Table 1. Some of the information gathered from the facilities is considered proprietary, and for this reason facility-specific chemical use information cannot be provided here. 4593 of the constituent chemicals in the upstream industrial chemical use inventory (53%) have STP PNEC values, 880 (10%) chemicals exhibit no or no expected toxicity, and 3203 (37%) either do not have STP PNEC information provided from ECHA or are invalid CAS numbers (and so cannot have risk estimates generated). Statistics on the availability of STP PNEC values on the basis of constituent chemicals used within each facility category are provided in Table 1.

3.2 Chemical tracer experiments

Fig. 2 shows the concentration of the uranine tracer at the STP inlet as a function of time after emission into the sewer lines for each of the three tracer experiments. As a measure of the duration of the breakthrough curve of the tracer, the length of time between which at least 5% of the peak concentration was

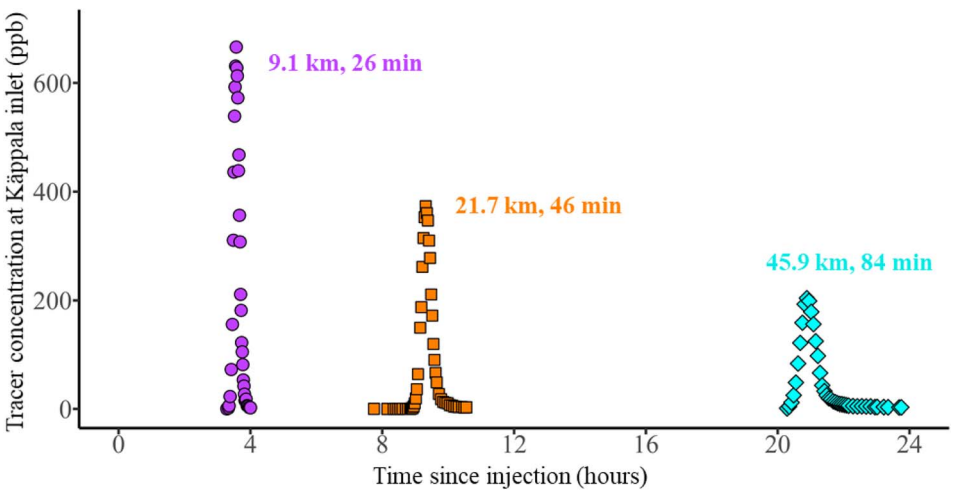

Fig. 2 Results of the uranine tracer chemical spill dilution experiments showing the breakthrough curves of the three spill experiments as measured at the inlet to Käppala (normalized to an injected mass of 1 kg uranine). For each experiment, the distance between the injection point and Käppala is noted, along with the duration of the breakthrough curve, measured as the amount of time that at least 5% of the maximum tracer concentration was measured in the influent sewage stream. See ESI† for more details. Figure generated using the R programming language package 'ggplot2'.[30]

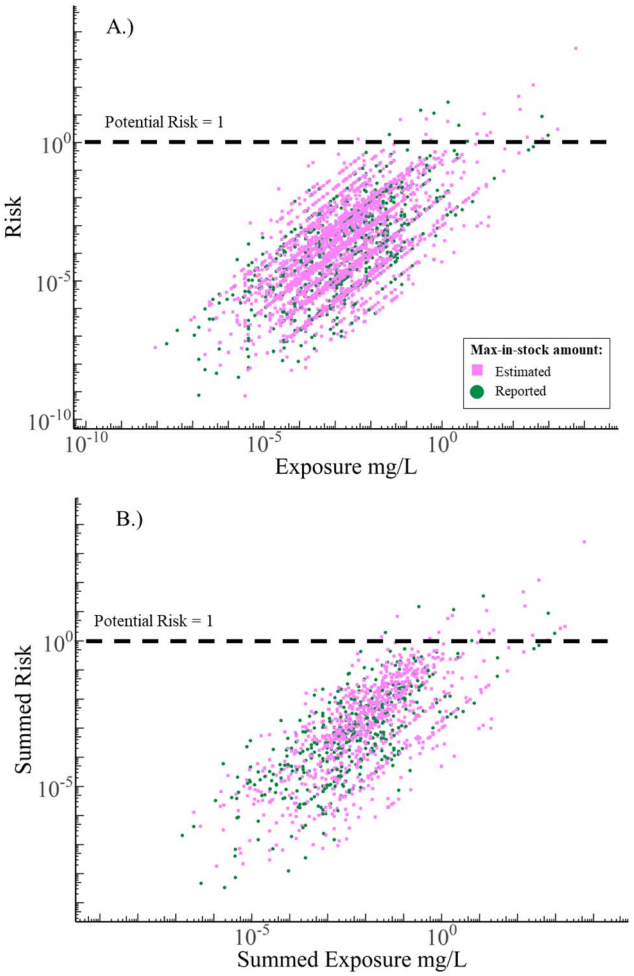

Fig. 3 Scatterplots of the constituent chemical ($n = 4593$, panel A) and bulk industrial chemical product ($n = 2086$, panel B) exposure concentrations and associated risks posed to the smaller activated sludge region of Käppala using the high-end spill scenario. Pink-coloured squares correspond to values for which the maximum mass of industrial chemical product held in stock at a given time was extrapolated based on the annual usage of that product using a value of $t_{max}(P = 50)$ (using eqn (1) and (2); see Section 2.1.2). Green circles correspond to values for which the max-in-stock value was directly reported by the facility. In panel A, risk values are shown for all constituent chemicals present in the upstream industrial chemical usage survey for which sewage treatment plant predicted no effect concentration (STP PNEC) values were available from the European Chemicals Agency. In panel B, risk values are shown for the industrial chemical products corresponding to the constituent chemicals in panel A, assuming additive toxicity of the risks from the constituent chemicals (calculated using eqn (4)). See Fig. 1 for an explanation of the regions of the sewage treatment plant. Figures generated using the R programming language package 'ggplot2'.[30]

measured is also displayed for each experiment. The results show that the duration of the breakthrough curve is short (maximum of 84 minutes) in comparison to the residence time of wastewater in the activated sludge reactors of Käppala (~24 hours) and the anaerobic digestors (median of ~20 days). Even at the farthest injection point (45.9 km from Käppala) where dilution and spreading of the injected tracer was highest, the majority of the simulated spill (roughly 95% of the total recovered mass) arrived at the STP over a period of just 84 minutes (Fig. 2; see also Scullin, 2021 (ref. 19)). Thus, the observed dilution behaviour of the chemical tracer upon release at different locations along or near the main sewer line supports our assumption that an industrial chemical spill in the STP's service area can be treated as equivalent to the full mass of the chemical being spilled directly into the treatment regions of the Käppala STP.

3.3 Risks posed by industrial chemicals used upstream from Käppala

Fig. 3, panel A shows the potential risks posed to the smaller activated sludge region of Käppala from constituent chemicals used at the surveyed industries upstream under the high-end spill scenario. 28 out of 8676, or 0.3% of chemicals have a potential risk value above 1, indicating toxic shock in the activated sludge process is possible under our high-end spill scenario assumptions.

Using the risk values presented in Fig. 3, an upstream chemical risk prioritization list was developed for all constituent chemicals that exhibit a risk value >1 for the activated sludge regions of the plant (Table S2†). This ranking identifies the constituent chemicals (and their parent products) that should be prioritized by the upstream chemical managers at Käppala. For example, the two highest risk constituent chemicals, namely 1305-78-8 (calcium oxide) and 1305-62-0 (calcium dihydroxide) exhibit risk values over 100 to the smaller activated sludge region. Additional investigation is needed regarding the actual masses of the parent industrial chemical product that is in stock at the upstream facilities, the feasibility of a down-the-drain spill occurring, and other factors to determine if additional spill mitigation measures are needed. Table S2† provides risk values for all three regions of the plant.

Fig. 3, panel B shows the potential risk that industrial chemical products used upstream pose to the smaller activated sludge region of Käppala assuming additive toxicity of the constituent chemicals in a given product. While a slight upward shift in risks is seen compared to the risks from constituent chemicals in panel A, most products still pose a risk value less than 1, indicating an adverse outcome in the smaller activated sludge region is unlikely from exposure to these industrial chemical products under the high-end spill scenario. As in Table S2, Table S3† displays the risk prioritization list for all upstream industrial chemical products that pose an additive risk of >1 to the activated sludge regions. For almost all of the industrial products, the ranking of risk does not change from the ranking based on the single constituent chemical risks in Table S2.† The minimal shifting of industrial chemical product prioritization relative to the constituent chemical prioritization indicates that for these high-risk industrial products, the risk is generally being driven by a single constituent chemical.

3.4 The Rapid Assessment of Vulnerability from Emissions Upstream (RAVEN STREAM) online tool

To enable the use of the upstream chemical threat identification framework developed here by other STPs, an open source

online tool has been developed using the R Shiny web application framework.[20] The Rapid Assessment of Vulnerability from Emissions Upstream (RAVEN STREAM) tool provides an easy-to-use interface for upstream chemical management operators at STPs to assess the potential for chemical contamination and toxic shock episodes at their plant (see Fig. 4). Users upload a .csv file containing information on the upstream industrial facilities, amounts of industrial products held in stock at the facilities, and the constituent chemicals of the products, along with a few basic operating parameters of the STP (*e.g.*, volumes of the biological treatment regions of the plant). RAVEN STREAM then applies the risk assessment framework outlined above to the user input data to generate estimates of risk to either the highest-risk region of the plant or a particular region of interest to the user. Graphical visualizations of the risks are provided to the user, along with downloadable risk prioritization lists of the constituent chemicals and industrial chemical products. A summary report on the data analysis can also be downloaded, which includes an enumeration of the number of constituent chemicals in each industrial facility category that did and did not have corresponding STP PNEC information available to enable risk prioritization. The RAVEN STREAM tool, along with a template input data file, is available at **https://raven-stream.shinyapps.io/raven_stream/**. Potential users of the tool may include the 44 sewage treatment plants in Sweden that are part of the Revaq certification system and would thus already collect information on the chemical products used at industries connected to their receiving waste streams (see Revaq, 2022 (ref. 21)), STPs that have collected or have access to information on the chemical products used at connected industries, or STPs interested in exploring hypothetical chemical storage and spill scenarios that would pose a risk to their operations.

3.5 Uncertainties, limitations, and areas for future work

3.5.1 Uncertainties. There are several points of uncertainty associated with the analysis of potential toxic shock risks presented here, namely that the fraction contribution of some constituent chemicals within the industrial chemical products were reported by the facilities as a range of values, some constituent chemicals have STP PNEC values from ECHA provided as a range of values, and the max-in-stock values of the majority of products are estimated from their yearly usage amounts (see Section 2.1.2). For the generally high-end chemical risk screening we present here, the maximum fraction contribution for each constituent chemical in a chemical product was employed, along with the lowest (*i.e.*, most toxic) STP PNEC value, and a value of $t_{max}(P = 50)$ was used to estimate max-in-stock values from yearly usage data where necessary. Fig. 5, panel A shows the estimated constituent chemical exposure and risk values to the smaller activated sludge region of Käppala with error bars that reflect the reported range in fraction contribution of the constituent chemicals to the parent chemical product, the range of STP PNEC values, and values of $t_{max}(P = 25)$ to $t_{max}(P = 75)$ for constituent chemicals whose parent chemical product mass was estimated from yearly usage amounts (see Section 2.1.2). Many of the constituent chemicals displayed in Fig. 5 exhibit a range in risk values that is one order of magnitude or less. Furthermore, while there is substantial overlap in the range of risk values between chemicals, which would indicate uncertainties surrounding the rank-order prioritization of chemicals that warrant additional investigation (see Table S2†), prioritizing chemicals with a risk value >1

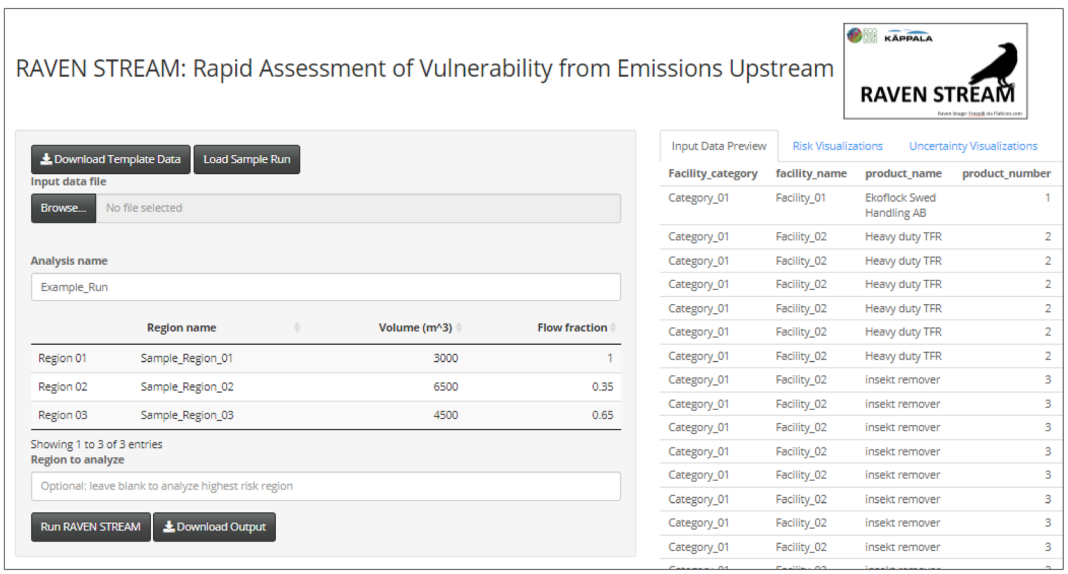

Fig. 4 Part of the graphical user interface of the Rapid Assessment of Vulnerability from Emissions Upstream (RAVEN STREAM) online tool. User input file paths and sewage treatment plant operating properties are input on the left-hand side, while a partial display of the input data is shown on the right. Chemical risk and uncertainty visualizations and prioritization lists are generated as output upon running the tool. The tool can be found at the following web address: https://raven-stream.shinyapps.io/raven_stream/. Raven icon from Freepik *via* Flaticon.com. Graphical user interface generated using the R programming language package 'shiny'.[20]

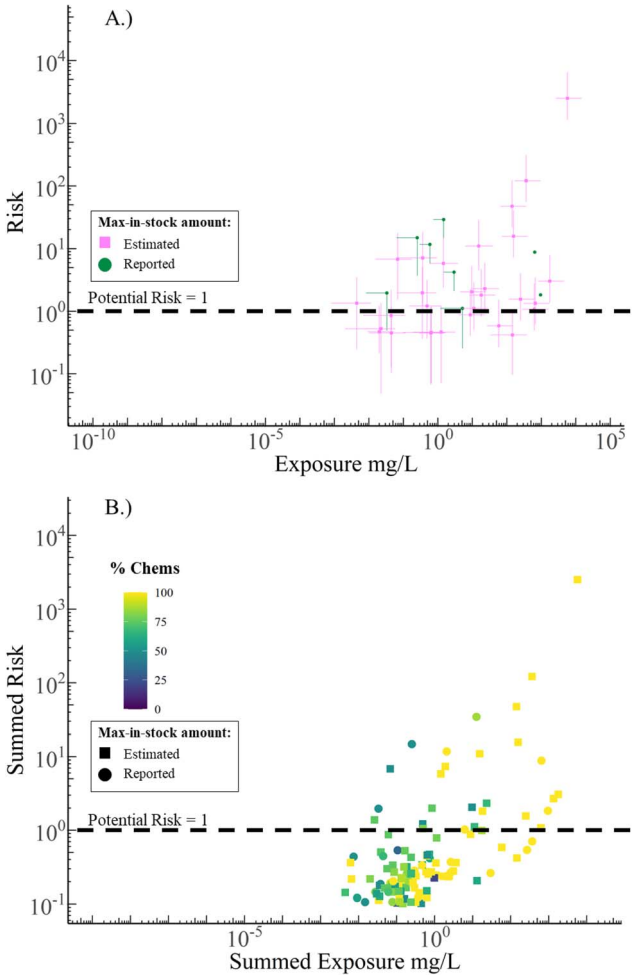

Fig. 5 Panel A: scatterplot of the constituent chemical exposure concentrations and associated potential risks posed to the smaller activated sludge region of Käppala using the high-end industrial chemical product spill scenario. Uncertainty associated with the exposure and risk values is illustrated using error bars and accounts for the possible range of STP PNEC values, the range of fraction contribution of constituent chemicals within the industrial product, and values of $t_{max}(P = 25)$ to $t_{max}(P = 75)$ for estimating max-in-stock chemical product masses from yearly usage data (using eqn (1) and (2); Section 2.1.2). For ease of viewing, points are only plotted if their uncertainty risk range exceeds the threshold of 1. Pink-coloured squares and lines correspond to chemicals for which the max-in-stock amount of the parent industrial chemical product was estimated (see Section 2.1.2), while green circles correspond to products for which the max-in-stock amount of the product was directly reported by the facility. Panel B: scatterplot of the chemical product exposure concentrations and associated potential risks posed to the smaller activated sludge region of Käppala using the high-end spill scenarios and assuming additivity of the exposures and risks from constituent chemicals in the products. Shading corresponds to the percent of the constituent chemicals in a product for which STP PNEC values were available. Squares correspond to products for which the max-in-stock amount of the industrial chemical product was estimated based on the annual usage of that product using a value of $t_{max}(P = 50)$, while circles correspond to products for which the max-in-stock amount was directly reported by the facility. In both panels, the y-axis is focused to risk values above 0.1 to enable easier interpretation of the figure. Figures generated using the R programming language package 'ggplot2'.[30]

using the deterministic, generally high-end assumptions (*i.e.*, the maximum fraction contribution of constituent chemicals, the lowest STP PNEC value, and a value of $t_{max}(P = 50) = 4.8$ months) captures 28 of 38 chemicals for which the range of possible risk values exceeds 1 in Fig. 5. Upstream chemicals managers can use the primary risk ranking, along with information about the uncertainties surrounding these risk values, to determine where to allocate resources for additional investigation and communication with upstream industrial facilities.

For industrial chemical product risks, the additive risk estimates may only reflect the risk from a subset of the full number of constituent chemicals in the bulk product, since risk values can only be calculated for constituent chemicals for which corresponding STP PNEC values are available from ECHA. As an illustration of this uncertainty, Fig. 5 panel B displays potential risks to the smaller activated sludge region from industrial chemical products with the shading of the data points corresponding to the fraction of the constituent chemicals in the product for which STP PNEC values were available. This analysis indicates that of the 1350 products for which any risk values were able to be calculated from their constituent chemicals, 715 products have STP PNEC values for 75 to 100% of their constituent chemicals, while 635 of the products have STP PNEC values for fewer than 75% of their constituent chemicals. Furthermore, 52 products exhibit additive risk values between 0.1 and 1 where STP PNEC values for less than 100% of their constituent chemicals are available. It is possible that the risk value of 1 could be exceeded for these products if toxicity information were available for all of the constituent chemicals. Upstream chemical managers at the STP should take such uncertainty surrounding the toxicity of chemical products into consideration when allocating resources for additional investigation with upstream industrial facilities, particularly for products that have moderate risk values (*e.g.*, 0.1–1) but a low availability of the constituent chemical STP PNECs.

3.5.2 Limitations. The upstream chemical threat prioritization approach developed here is a screening approach. The potential risks calculated here are generally high-end estimates that leave out processes that may have a large impact on the concentrations of the contaminating chemicals, and ultimately the adverse outcomes at the sewage treatment plant. For example, the max-in-stock chemical product masses that are provided by the upstream facilities are used as-is, with the full chemical product mass assumed to be released for the spill scenario. Variability in the amount of stored chemical mass at any given time, as well as the actual feasibility of the full stored chemical product mass being involved in a down-the-drain spill at one time, are not considered. Furthermore, as the upstream chemical survey is based on chemical purchase information at the facilities, data on the storage patterns of any chemicals synthesized at the facilities (and any chemical intermediates) are not available for inclusion in the screening.

While the *in situ* measurements of simulated chemical spills outlined in Section 2.3.1 indicate that the assumption that spilled chemical reaches the biological treatment process as a single dose is valid, these measurements were limited to spills along a few locations on or near the primary sewer tunnels,

rather than within the individual municipal sewer networks (see Fig. S1 and S4†). Municipal sewer networks are more likely to increase the dilution and spreading of down-the-drain spills due to increased tortuosity, non-uniformity, and number of connections in such networks compared to the primary sewer tunnels. Such non-uniform reaches of the sewer network may have dispersion coefficients substantially larger (potentially by a factor of 100) than reaches with uniform geometry and stable flow.[22] Furthermore, some in-stream losses of the chemical tracer were observed in the chemical spill simulations (between ~26% and ~33%, see Table S1†), however we did not consider this process in our risk screening. Additionally, neither degradation nor the formation of transformation products of the spilled chemicals were considered in the risk screening.

As indicated in Section 3.1, STP PNEC information was only available for 63% of the constituent chemicals present in the upstream industrial product use survey. For the remaining 37% of constituent chemicals, no risk values could be calculated, highlighting a key limitation of this study. Furthermore, the STP PNEC values obtained from the ECHA database of chemical properties are used as-is, and any uncertainties or errors associated with their reported values are not considered (other than when a range of values is reported by ECHA; see Section 3.5.1). Additionally, the assumption of additive toxicity of the constituent chemicals when estimating the risk of the full chemical products ignores possible synergistic or antagonistic effects of chemical mixtures. This is, however, an assumption commonly used in toxicology and is generally a good assumption for chemical risk screening.[23]

Furthermore, prolonged exposure to some chemicals can modify microorganism communities within activated sludge.[24,25] Käppala may have had previous exposures to industrial products that have been used upstream for some time due to regular use and disposal patterns of these products, but in small enough quantities that have not resulted in a toxic shock. The impact of such previous exposures on the actual toxicity of a spilled product to the specific microorganism community at Käppala is, however, beyond the scope of this study. Similarly, microorganism communities can adapt such that previously harmful concentrations of chemicals are no longer damaging to the nutrient removal capabilities of the plant,[26] and this potential for the microorganism community to be adapted to contamination of a previously-spilled industrial chemical is not captured in this screening framework. It is also possible that background levels of industrial chemicals present in the influent wastewater could exacerbate the effects of a chemical spill on the treatment plants' microorganisms, however our analysis and online tool do not consider these possible background effects when generating the upstream chemical prioritization list.

Additionally, only potential chemical spills from permanent, known locations of stored chemicals can be analysed within the RAVEN STREAM framework. Sewage treatment plants can be threatened by spills from releases of chemicals down the drain from other entities, such as from spills during the transport of chemicals[9] or from dumping of chemicals used in illicit drug manufacturing.[27] Such potential upstream chemical risks are not assessed in the current version of RAVEN STREAM.

While STPs are limited by the data they are able to collect on the mass and constituents of chemical products used at upstream facilities, the RAVEN STREAM online tool offers the opportunity to rapidly prioritize which facilities and chemical products should be investigated for additional information related to specific storage patterns, existing infrastructure that may attenuate the mass of a spilled chemical that reaches the main sewer lines (*e.g.*, on-site sewage treatment at the industry), or other information that could further refine possible spill and contamination scenarios of high-risk chemical products. This risk screening and additional information gathering would inform spill mitigation measures that may be needed at a given facility to reduce the risk of adverse outcomes at the receiving STP.

3.5.3 Generation and adoption of robust, widely applicable STP toxicity QSARs. Expanding the number of constituent chemicals for which STP PNEC values are available is a key area for future work. 1293 of the upstream constituent chemical uses (or 15%) had CAS numbers that matched chemicals in the ECHA database but did not have STP PNEC data available, while 1613 (19%) had valid CAS numbers reported but did not match any CAS numbers in the ECHA STP PNEC database (and could thus not have risk estimates derived; see Table 1). In the absence of large-scale, high throughput toxicity testing of industrial chemicals, an *in silico* method for estimating toxicity towards STP microorganism communities would help fill this data gap. *In silico* prediction of chemical toxicity for a wide range of chemical classes exists, but for toxicity towards more complex single species such as mice and fish as part of the U.S. EPA's CompTox dashboard (**https://comptox.epa.gov/dashboard/**). Furthermore, some quantitative structure activity relationships (QSARs) have been developed to predict toxicity of chemicals towards activated sludge microorganisms,[28,29] but the applicability domain for these models often covers a limited number of chemicals or a narrow range of chemical classes. ECHA currently does not generally accept in silico-based predictions of chemical toxicity towards STP microorganisms, however ECHA indicates that if future, robust QSARs for this endpoint were developed they could be incorporated into data reporting requirements.[14] The development of such a tool for a wide range of chemical classes, and its acceptance as a source of STP PNEC value estimation by ECHA, would likely enable the screening of risk for a much larger number of industrial chemicals used upstream of STPs. The ability to estimate risk for the different microorganism communities expected in activated sludge *versus* anaerobic digestors would also help constrain potential risks posed to different regions of the plant from upstream chemical spills.

4 Conclusion

Down-the-drain spills of industrial chemicals have been known to cause severe damage to their receiving sewage treatment plants, in some cases causing a long-duration reduction or elimination of the plant's ability to remove organic material and

nutrient pollutants from the sewage before release to the environment. We developed a novel framework for upstream threat identification and prioritization of potential down-the-drain chemical spills, which we have organized into an open-source online tool called RAVEN STREAM (**https://raven-stream.shinyapps.io/raven_stream/**). This easy-to-use tool aims to enable real world application of the risk screening framework by sewage treatment plants with access to (or interest in collecting) inventories of chemical products used and stored at industries connected to their waste streams. Application of RAVEN STREAM and subsequent communication with upstream clients can help identify and prevent potentially damaging down-the-drain spills of chemical products, avoiding toxic shock episodes and keeping STPs operating properly, helping to support the sustainable use of water bodies receiving treated wastewater.

Code availability

The processing code used for the web scraping of sewage treatment plant predicted no effect concentration values from the ECHA webpages, along with all of the source code associated with the RAVEN STREAM online tool, can be accessed *via* the following GitHub repository: **https://github.com/John-D-Hader/RAVEN_STREAM**.

Conflicts of interest

There are no conflicts to declare.

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