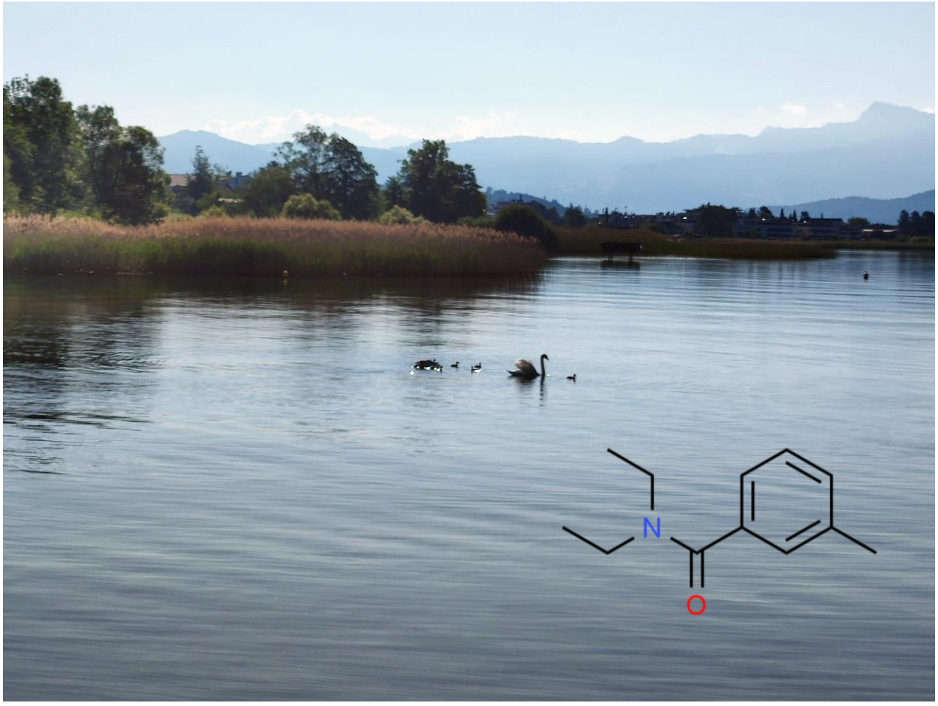
Mass Balance of Diethyltoluamide (DEET) in the Environment



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Summary

The biocide diethyltoluamide (DEET) is used worldwide as an insect repellent on human and animal skin and is among the most frequently detected organic chemicals in surface waters. The ubiquitous detection of DEET in Swiss waters, even during winter months, despite its apparent seasonal use as an insect repellent, has led to question the sources and fate of DEET in the environment and the validity of previous risk assessments for Switzerland. This study summarizes the occurrence, fate and emission dynamic of DEET in Swiss aquatic systems and attempts to clarify its sources in the Swiss aquatic environment.

Existing monitoring data for DEET in the aquatic environment and WWTPs were collected from Swiss institutions, cantonal and federal authorities and aggregated to estimate the consumption of DEET in Switzerland. In addition, the main actors of DEET's supply chain in Switzerland (manufacturers, formulators and distributors) were surveyed to determine the production and distribution volumes of DEET-containing products. The findings from both approaches were then compared to provide a first mass balance for DEET in Switzerland. Analysis of Swiss monitoring data, particularly from the Rhine River, indicates an annual Swiss consumption of 2 tons of DEET, which is consistent with the estimate of 2 to 12 tons of DEET estimated from production data provided by the DEET supply chain. These values provide a first indicative mass balance for DEET in Switzerland and demonstrate that, from a mass balance perspective, the widespread detection of DEET in Swiss waters can be corroborated by its consumption as an insect repellent alone. Although DEET is classified as an inherently biodegradable substance, the evaluation and aggregation of Swiss monitoring data indicates that its degradation in Swiss surface waters is not as high as expected from literature.

The Biocidal Products Regulation (BPR, (EU) 528/2012) regulates the authorisation of biocidal products in the European Union. In Switzerland the authorisation of biocidal products is regulated by the Ordinance on Biocidal Products (OBP,RS 813.12) and a Mutual Recognition Agreement with the European Union (MRA, RS 0.946.526.81) ensuring the agreed technical equivalence with the BPR. The authorization is based on established models for environmental risk assessments: the emission scenario documents (ESD). The ESD pertinent to DEET (Product Type 19 – Repellents and attractants, ECHA, ESD PT19) were evaluated in this study and compared to the aggregated monitoring data and newly obtained mass balance of DEET for Switzerland. The ESD-based environmental risk assessment significantly overestimates the release and occurrence of DEET in Swiss surface waters and provides a worst-case scenario that is consistent with the precautionary principle.

In summary, this study provides a characterization of DEET occurrence in Swiss waters as well as DEET Swiss consumption to extrapolate a first indicative mass balance of DEET for Switzerland and compare this to established models for environmental risk assessment. This approach could be exemplary for other biocidal products whose emissions and occurrence are unclear and which are characterized by higher ecotoxicity than DEET.

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1 Introduction

The biocide diethyltoluamide (DEET) is widely used as an insect repellent on human and animal skin and is among the most frequently detected organic chemical contaminants in environmental water samples (Marques dos Santos et al., 2019; Merel et al., 2016; Merel et al., 2015; Loos et al., 2010; Sandstrom et al., 2005; Sun et al., 2015). In Switzerland, DEET is repeatedly detected in wastewater treatment plants (WWTPs), rivers, lakes and groundwater. DEET is classified as a readily biodegradable substance and is mostly measured below critical concentrations for aquatic organisms. However, the ubiquitous detection of DEET, has led to question the sources and fate of DEET in the environment and the validity of previous risk assessments for Switzerland. In particular, the occurrence of DEET in Swiss aquatic systems is poorly understood due to a lack of production and consumption data.

This report attempts to clarify these aspects by systematically evaluating the occurrence, fate and emission dynamic of DEET in Swiss waters and comparing these to the Swiss consumption of DEET. Existing results from monitoring campaigns in the aquatic environment and WWTPs are collected and aggregated to estimate the consumption of DEET in Switzerland (bottom-up approach). Furthermore, DEET production, import and distribution amounts in Switzerland are explored (top-down approach). The findings from both approaches are compared to provide a first mass balance for DEET in Switzerland.

The established risk assessment methodology of the European Union and Switzerland under the Biocidal Products Regulation (BPR) following the emission scenario documents for product type 19 (ECHA, ESD PT19) is evaluated for DEET and compared with the results of this study. Possible modifications to input parameters of the ESD are discussed.

2 Background

2.1 Legal Basis

The BPR regulates the market commercialization and use of biocidal products in the European Union and Switzerland. These products are used to protect humans, animals, materials or articles against harmful organisms like pests or bacteria, by the action of the active substances contained in the biocidal product. All biocidal products require an authorization. The approval of active substances takes place at European Union level and the subsequent authorization of the biocidal products at Member State level incl. EFT states (CH) or European Union level.

DEET (N, N-diethyl-m-toluamide; CAS: 134-62-3) is used in many different formulations such as sprays and lotions as a biocide of product type 19 (PT19). These biocidal products are typically used as personal insect repellents applied on uncovered human skin or clothing, and as insect repellents for animals (mainly horses). Products containing DEET are expected to be used both indoors and outdoors (ECHA ESD PT19, 2015). The active substance is authorized for use in repellent products in the EU and Switzerland until 2025 and is currently undergoing an authorization renewal process.

2.2 Anthropogenic Sources of DEET

DEET is primarily used as an insect repellent. For human and animal use it is mostly applied as a spray or lotion directly on the skin to avoid mosquito bites. Studies have also reported the incorporation of DEET in clothes and nets (Kitchen et al., 2009; Pennetier et al., 2010; Sibanda et al., 2018; Di Lorenzo et al., 2019). However, an explorative online search for treated textile products available in Switzerland revealed that manufacturers rarely impregnate textiles with DEET, likely since DEET can damage some synthetic fabrics (Brown & Hebert, 1997). In particular, army uniforms are sometimes treated with DEET or permethrin (e.g. in France and Germany), however the procurement division of the Swiss army confirmed this is not the case for Switzerland.

Other identified potential uses of DEET include its application as a resin solvent, dye carrier, surface plasticizer, film former and as a pharmaceutical dermal penetration enhancer (Holsten & Neely, 1993; Larranaga et al., 2016; Weeks et al., 2011). A more recent study proposes DEET as a synthesis solvent for meta-organic frameworks (Dodson et al., 2020). However, little to no information could be found on the extent of these applications and their relevance for the emission of DEET to the environment in the EU and Switzerland. Also no actual product containing DEET for other reasons than its insect repellent proprieties was identified or authorized under the BPR.

DEET is not used in large-scale commercial applications (Weeks et al., 2011). If DEET were used as an industrial chemical in quantities exceeding 1 ton per year in the EU and Switzerland, a registration dossier in accordance with the REACH regulation should have been submitted, which did not occur. Moreover, Clariant, one of the major manufacturers of DEET, assured us that all DEET they produce is sold exclusively for use as an insect repellent.

2.3 Natural Sources of DEET

Natural production of DEET has been observed in female pink bollworm moths (*Pectinophora gossypiella*) in concentrations ranging from 30 µg to 605 µg per insect (Jones & Jacobson, 1968). The highest concentrations of DEET were found in female adults followed by female pupae. No DEET has been detected in female larvae or in male moths at any stage of development (Jones & Jacobson, 1968). Surprisingly, no further link to naturally produced DEET was found in recent literature. Other natural sources of DEET, other than the pink bollworm, were not reported.

The pink bollworm moth is a well-known pest in cotton farming, native to Asia (Figure 1). It is present in many cotton-producing areas of the world, where it causes great damages to cotton fields. The female moths lays eggs on the cotton balls, where the larvae, once hatched, enter the bulb, eat the seeds and damage the cotton fibers (Henneberry, & Naranjo, 1998).

No reports of the presence of the pink bollworm moths in Switzerland could be found. This is to be expected, as Switzerland does not possess any significant amount of cotton plants to sustain the pink bollworm life cycle. Still the question is raised, whether cotton imported from regions where the pink bollworm is present could be contaminated with DEET originating from dead female moths or pupae. No information was found in this regard, however such contamination, if present, is expected to be small compared to other sources of DEET in Switzerland.

Figure 1: Pink bollworm larvae on a cotton bulb [Wikipedia; https://en.wikipedia.org/wiki/Pink_bollworm#/media/File:Pinkbollworm.jpg]

2.4 Pathways into the Environment

The main pathways of DEET to the environment are presented in this chapter. It is assumed that the primary pathway into the environment is indirect through domestic use, where after showering, laundry and disposal of unused products down the drain, DEET reaches the water compartment via WWTP effluents (Marques dos Santos et al., 2019; Chen et al., 2012; Merel et al., 2015) (Figure 2). Another emission to WWTPs is the loss of DEET from industrial processes such as blending of products by formulating companies. Through recreational activities (e.g. swimming in lakes), DEET can also enter the aquatic environment directly (Merel and Snyder, 2016). Used as an insect repellent on animals, especially horses, a fraction of DEET is washed off and might enter the environment by stormwater runoff. A combination of these different emission pathways lead to the varying concentrations measured in Swiss waters. Direct emissions of DEET to soil are expected to be localized and negligible (ECHA, CAR 2010), whereas indirect emissions to soil via WWTP sludge application are not relevant for Switzerland, as the application of sewage sludge to fields is prohibited in Switzerland since 2006 according to the Chemical Risk Reduction Ordinance (ORRChem).

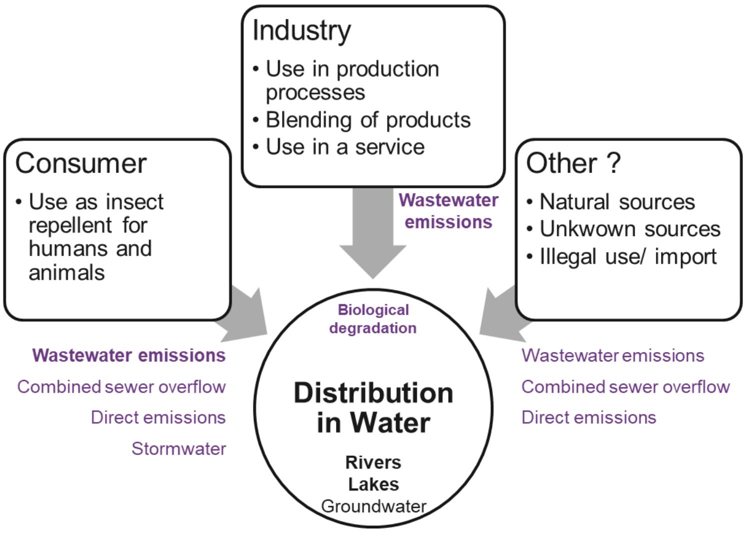

Figure 2: Main pathways of DEET into the aquatic environment.

2.5 Environmental Fate and Ecotoxicity

A substance emitted into the environment will distribute among the different environmental compartments based on its chemical formula, physiochemical proprieties, and emission dynamic. Consequently, the fate of DEET in the receiving environmental media is determined by its partitioning and by biological, chemical transformation and transport processes.

According to level III fugacity models, DEET will primarily partition to the water compartment (ca. 80 %). DEET is not very volatile in water as indicated by its Henry's law constant of $3.4E^{-8}$ $atm{\cdot}m^3{\cdot}mol^{-1}$, meaning that DEET is considered to be less volatile than water (ECHA, CAR 2010). The low average log k_d of 1.91 (Hyland et al., 2012) and low log K_{ow} of 2.5 (Chiaia-Hernandez et al., 2020) predicts that little of the DEET fraction will end up in wastewater sludge, soil and sediments. Bioaccumulation potential of DEET in aquatic organisms is also low (ECHA, CAR 2010). The bioconcentration factor for DEET is estimated to be 22 in the aquatic environment and 3.85 to 63.1 in the terrestrial environment based on QSAR modelling (ECHA, CAR 2010).

The assessment of the environmental fate and behavior of chemicals in the environment is a critical part in the classification of chemicals in the regulatory evaluation process. Based on the chemical assessment report (CAR), DEET is categorized as "readily biodegradable" and causing only minor inhibitory effects on WWTP microbial activity (ECHA, CAR 2010).

Removal of DEET in the environment is mainly governed by biological processes as abiotic degradation of DEET in water is limited due to low hydrolysis and photolysis (Weeks et al., 2011). Biodegradation studies of DEET have found it to be inherently to readily biodegradable (Weeks et al., 2011). The half-life of DEET (DT_{50}) in surface water is estimated to range between 5 and 15 days due to its readily biodegradable classification (Weeks et al., 2011). Nevertheless, DEET is measured ubiquitously in high concentrations in different surface and ground waters in many countries (see Chapter 4.1). This raises the question about how well DEET degrades in the natural environment.

Several environmental threshold values are defined for DEET for different matrices (Table 1). It is noted that the PNEC value from the CAR (ECHA, CAR 2010) differs from the acute and chronic environmental quality criteria defined by the Ökotoxzentrum. Such differences are usually due to small differences in literature basis, methodology and expert judgment used to derive these values (Junghans et al., 2011). However, in the case of DEET, the general limit value for organic pesticides (biocidal products and plant protection products) set in the Swiss Waters Protection Ordinance (WPO, RS 814.201) of 0.1 µg/l legally applies to DEET in Switzerland. According to the Classification, Labelling and Packaging (CLP) legislation DEET is a skin and eye irritant of category 2 and has an acute toxicity of category 4 (moderately hazardous).

Table 1: Threshold values of DEET based on the ECHA final CAR for DEET and Swiss Ökotoxzentrum and CLP Classification. [1]ECHA, CAR 2010; [2]Ökotoxzentrum 2016; [3]Swiss Waters Protection Ordinance (WPO). [4]ECHA, Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).

Ecotoxicity Threshold Values	Compartment	Concentration
PNEC[1]	surface water	43 µg/L
PNEC[1]	wastewater	10'000 µg/L
PNEC[1]	sediment	74.1 µg/kg
PNEC[1]	soil	37.9 µg/kg
Acute Quality Criteria (CH)[2]	surface water	410 µg/L
Chronic Quality Criteria (CH)[2]	surface water	88 µg/L
Legislative Threshold Values		
Swiss Water Quality Standard[3]	surface water and groundwater	0.1 µg/L
Legislative Threshold Value, ECHA[1]	groundwater	0.1 µg/L
CLP Classification		
Acute Tox. 4[4]	H302	
Skin Irrit. 2[4]	H315	
Eye Irrit. 2[4]	H319	

2.6 Monitoring Data and Analytical Challenges

The detection of DEET in aqueous environments in winter despite seasonal use and reports of DEET sample contamination and detections in laboratory and field blanks have led to concerns of analytical bias (Merel & Snyder 2016; Brumovsky et al., 2017; Lapworth et al., 2018; Wieck et al., 2018) with DEET being sometimes excluded from studies (Feguson et al., 2013). Moreover, possible overestimation of DEET concentrations due to co-eluting compounds and contamination of LC-MS solvents with DEET have been reported (Merel et at., 2015). Further doubts about the accurate quantification of DEET result from significant differences in DEET concentrations measured using GC-MS and LC-MS (Merel et at., 2015; Trenholm et al., 2008) supporting the hypothesis of analytical interferences.

Following these numerous claims of potential analytical interferences, this topic was discussed with Swiss national and cantonal laboratories. The Intercantonal Laboratory (IKL, laboratory of the cantons of Appenzell Ausserrhoden, Innerrhoden and Schaffhausen) confirmed the detection of DEET or a DEET mimic (same retention time and 2 MS/MS fragments) in samples analyzed by LC-MS during the development of their analytical method for DEET. They determined the source of this detection to be from plastic materials commonly used in several laboratories. By the help of a pre-column, this potential analytical interference could be excluded. This observation raises two questions. First, could the plastics lead to contamination of samples with DEET or DEET mimics in other Swiss laboratories? Second, could widespread use of these plastics lead to DEET or DEET mimics from this source entering the environment?

The first question was discussed with the Agency for Environment and Energy of the Swiss canton Basel-Stadt (AUE), which performs the measurements at the Rheinüberwachungsstation (RÜS, Chapter 4.1.1.1), the Environmental Chemistry Department at Eawag, which operates the MS2Field (see Chapter 4.1.1.2 & 4.2.3) and the IKL. For all three institutions, the risk of erroneous DEET measurements due to laboratory contamination was estimated to be negligible thanks to strict quality control. Laboratory contamination is identified by the use of blanks and thus taken into account. Detection of DEET in blanks are limited and mostly below LOQ. Furthermore, the RÜS analyzed samples over a long period of time by both LC-MS and GC-MS with close to identical results in contrast to some literature reports (Merel et at., 2015; Trenholm et al., 2008).

The question remains whether the substance from plastics (DEET or a mimic) measured by the IKL can also be found in the environment and thus in the Rhine. Based on a thorough search (interviews with producers of plastics, material scientists etc.), no industrial-scale use of DEET in plastics was identified, but references to potential applications are given in literature (Chapter 2.2). A recent study showed that only one potential substance N-tert-butyl-4-methyl-benzamide, could possibly interfere with DEET determination using LC-MS/MS, however rigorous quality assurance and quality control (QA/QC) procedures should prevent significant interferences that would lead to false positive DEET detections. Moreover, NMR spectroscopy analysis of environmental samples did not suggest the presence of DEET mimics in real samples (Marques dos Santos et al., 2019). In summary, common quality assurance procedures such as blank and blank analyses, determination of analyte recoveries, and sufficiently selective analytical methods (GC-MS, LC-MSMS) currently prevalent in Swiss analytical laboratories should ensure reliable measurement of DEET.

3 DEET Supply Chain

The Swiss supply chain for DEET products includes manufacturers, formulators, distributors and the final consumer/customer (Figure 3).

Manufacturers

Manufacturers synthetize DEET which is sold as a pure substance to distributors. Based on the BPR (Article 95 List), there are two manufacturers of the active substance DEET, namely Clariant and Vertellus Chemicals both located outside of the EU. This means that DEET is neither manufactured in Switzerland nor in the EU. According to consultation with Clariant the total import in Europe is estimated to be about 400 tons per year. If this quantity is distributed evenly among all European citizens, a total consumption of approx. 4 tons of DEET can be expected for a Swiss population of 8.6 million inhabitants. It is noted that the amount of DEET consumed in Switzerland is not equivalent to the amount of DEET imported/exported, which as described in Chapter 3.1.2, is certainly larger.

Distributors

Distributors purchase DEET as an active ingredient from manufacturers and mandate the formulation of DEET containing products to third parties, so called formulators. Distributors then place their products on the Swiss market by distributing them to retail stores or selling it directly to the final consumer. Distributors can import DEET into Switzerland as an active substance or as part of blended products. A search in the Swiss register of chemicals products (Swiss RPC) indicated the presence of 27 distributors of DEET relevant for the Swiss market, of which 22 are based in Switzerland and six abroad (see Appendix Table A1; status Nov 2020).

Formulators

Formulators blend DEET as an active ingredient into a final product for the consumer on behalf of distributors. In Switzerland, five formulators professionally blend DEET products for different distributors based on a search in the Swiss RPC.

DEET containing products

The list of biocidal products authorized in accordance with the BPR contains 162 biocidal DEET products of PT 19 "Repellents and Attractants" (PT19) (29.03.2021). According to the search in the Swiss RPC, there are currently 41 authorized DEET containing products on the Swiss market. Of these 41 products, 15 (37 %) are imported directly from the distributors and 9 (22 %) are formulated in Switzerland prior to distribution. No information on production sites was gained for the remaining 17 products. About half of them are intended for human use with an average DEET content of 30 % and the other half for animal use with an average DEET content of 5 %.

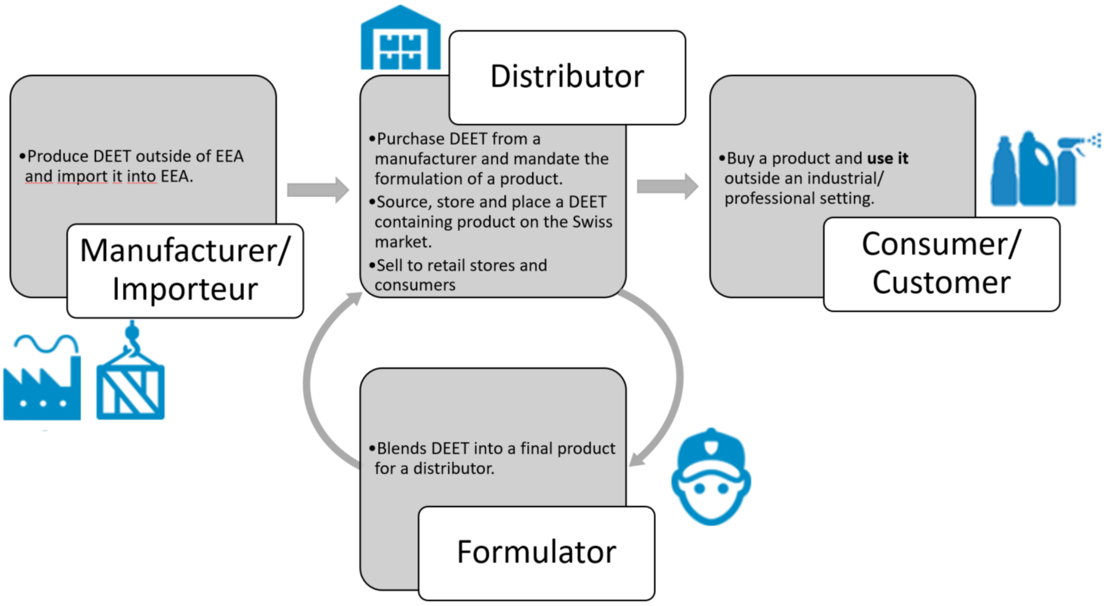

Figure 3: Scheme of DEET supply chain for Switzerland. No Manufacturers of DEET are present in Switzerland.

3.1 DEET Use by Distributors/Formulators of DEET

In a survey, the production data (formulation/distribution location, production/distribution amount, production/distribution period, etc.) of DEET distributors and formulators was reviewed. Feedback was obtained for all five formulators and ten of the 27 distributors. Figure 4 gives an overview of the findings of this survey and a mass balance for DEET based on production data is provided in Chapter 5.

3.1.1 Distributors

Twelve distributors disclosed the amount of products sold, totaling approximately 13 tons of DEET active ingredient distributed per year. This includes the largest Swiss DEET distributors, which together cover at least 75% of the Swiss DEET distribution market, according to the information provided in the survey. The majority of the reported amount is intended for human use, while less than 5% is included in products for animal use. Seven distributors also confirmed that the majority of sales occur during summer months. Unfortunately, for several distributors (15 of 27) the amount of DEET distributed is not available, either because it was not disclosed, was unknown, or because the company did not respond to the survey or contact information was missing. Since distributors simply trade DEET containing products, no emissions to the environment are expected to take place until application from the consumer.

3.1.2 Formulators

All five formulators in Switzerland replied to the survey. For one of them additional information was provided by cantonal authorities.

Two formulators, owned by the same contract manufacturing group, formulated products containing between 30 and 80 tons of DEET per year. This amount is produced in 50 to

200 batches and is equivalent to ca. 0.7 to 1.8 million bottles of a typical DEET containing product (150 mL, 30 % DEET). Production takes place mostly between November and Mai and the products are sold in Switzerland (30 %) and abroad (70 %). These two companies are by far the largest formulators of DEET in Switzerland, likely accounting for over 90 % of DEET formulation in the country. In fact, the amount of DEET formulated per year in their facilities accounts for 7 to 20 % of the 400 tons estimated to be imported in Europe by the two producers of DEET (Clariant and Vertellus Chemicals), likely placing them between the largest formulators of DEET in Europe as well. According to both formulators, no wastewater is generated at these facilities during the processing of DEET since 2019, resulting in no emissions to the WWTP.

A third formulator uses about 400 kg DEET per year for a total of 8.5 tons of DEET containing products per year. The company blends the products in a batch reactor (< 1 m^3). Any wastewater for cleaning is collected and treated with an internal plant consisting of an oil separator, settling tank, neutralization, biological treatment and ultrafiltration before being discharged to the municipal WWTP. Production occurs depending on the distributors requests, usually from March to September.

Another formulator blended DEET containing products in the last couple of years, in quantities < 1 ton DEET per year. They formulated DEET in 2 - 3 batches a year based on client's demands. Wastewater resulting from washing of equipment using for blending and bottle filling was discharged to the WWTP after adjusting the pH and eventual dilution in cases of high chemical oxygen demand (COD).

The fifth formulator indicated that they dismissed the use of DEET in their facility since 2019. This formulator assured that well below 1 ton per year were used in the past.

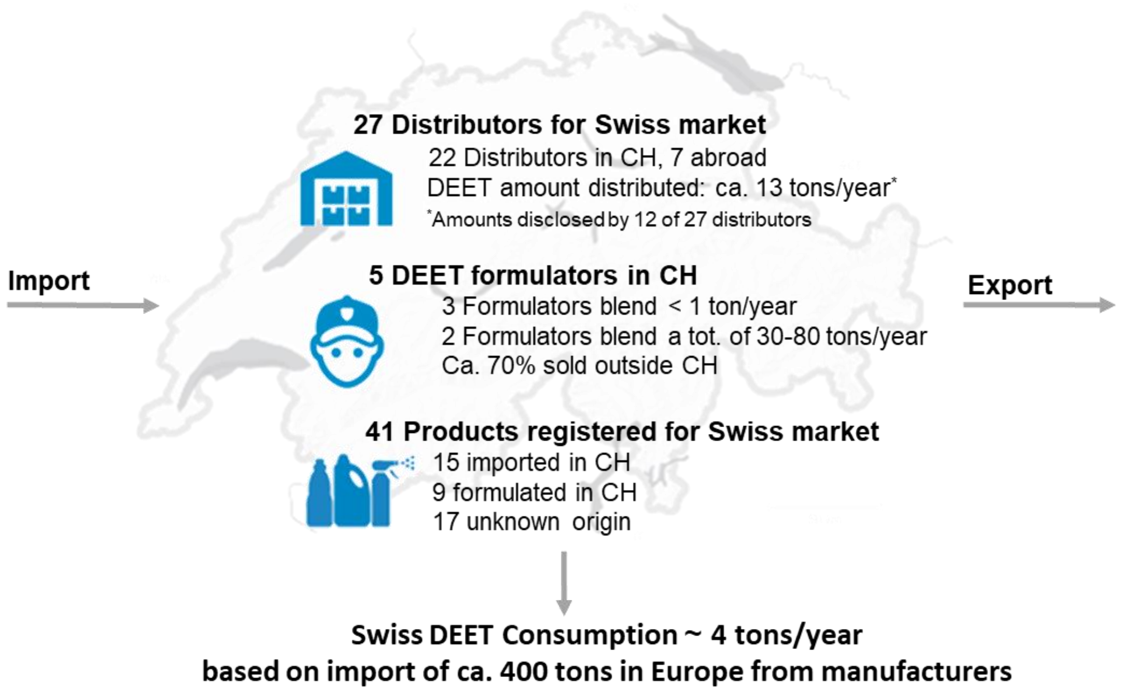

Figure 4: Swiss DEET consumption estimate and results of the survey regarding the use of DEET by distributors and formulators.

4 Monitoring Data

4.1 Occurrence of DEET in Swiss Aquatic Systems

The first published detection of DEET in surface water dates back to 1993 in the Mississippi river (Pereira and Hostettler, 1993). Since then reported concentrations are among the highest for trace organic contaminants with concentrations as high as 24 µg/L for surface water samples (Merel and Synder, 2016). Monitoring studies show that DEET is found ubiquitously in groundwater and surface water samples in many countries (Merel and Synder, 2016). In fact, the hydrophilic nature of DEET results in a widespread contamination of waters, including groundwater (Merel and Synder, 2016; Marques dos Santos et al., 2019). In Sweden for example, in the main drinking water reservoir lake Mälaren, DEET was found in all 69 sampling points, at different depths in concentrations around 3 ng/L (Rehrl et al., 2020).

The following sections summarize existing measurement data for Swiss waters (lakes, rivers, and groundwater) and additionally, soils, sediments, rain and air to better understand the current occurrence of DEET in Swiss aquatic systems.

4.1.1 Swiss Rivers

Most WWTPs discharge their effluent in rivers. As a result, DEET often accumulates along the river course if multiple WWTPs are present. Furthermore, during rain events potentially contaminated stormwater is also discharged to surface waters.

For this project, DEET measurements from several Swiss streams and rivers were retrieved (summarized in Annex Table A2, A3, A4). The obtained dataset is composed of 2887 samples from 91 different sampling sites. Figure 5 illustrates the distribution of the sampling sites in Switzerland for the data provided by the National Surface Water Quality Monitoring Programm (NAWA), the Office for Waste, Water, Energy and Air of the Canton of Zürich (AWEL) and the Office for Water and Energy of the Canton of St.Gallen (AWE). DEET was found above the limit of quantification (LOQ) in 71 % samples (2066 of 2887 samples), with an average concentration of 70 ng/L and a median of 36 ng/L, and concentrations above 1 µg/L in only ca. 0.5 % of the total sample number (15 samples). The highest concentration measured was 8.0 µg/L DEET. Additionally, more than 4000 daily DEET measurements with a mean value of 14 ng/L and a maximum value of 250 ng/L were obtained from the Rhine at the RÜS monitoring station in Weil a.R.

DEET concentrations above the recommended Swiss water quality standard for biocides in surface waters of 0.1 µg/L (Swiss Waters Protection Ordinance, WPO) were measured in 7% of the samples (204 out of 2887) and at 40 different monitoring sites (not including the RÜS). At the RÜS the water quality standard of 0.1 µg/L was exceeded during 28 days from 2010 to 2020. Having this said, no samples exceeded the acute (410 µg/L) or chronic (88 µg/L) quality criteria set by the Ökotoxzentrum (2016) nor the Predicted No Effect Concentration (PNEC) of 43 µg/L specified in the chemical assessment report for DEET (ECHA, CAR 2010).

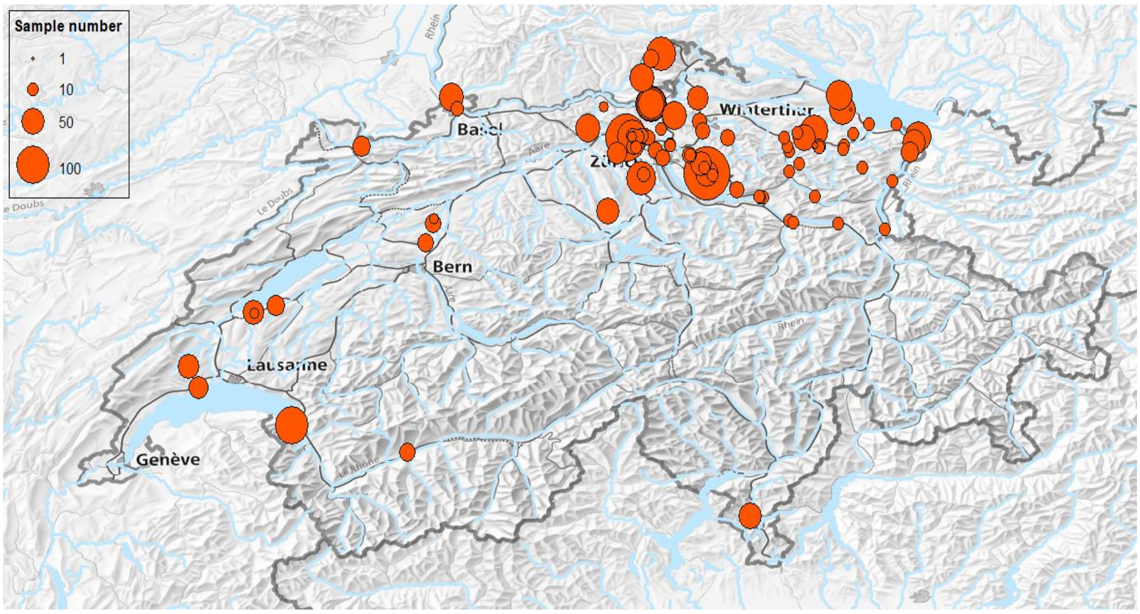

Figure 5: Spatial distribution of the sampling sites of the NAWA, AWEL and AWE sampling campaigns reported in this study where DEET was analyzed. The size of the points is proportional to the number of samples taken. Not included in this figure is the RÜS monitoring station in Weil a.R. with over 4000 samples. Details in Annex Table A2, A3, A4.

In order to give an overview of the DEET concentrations found in Swiss rivers and streams, the results of the above mentioned sampling campaigns are classified and summarized in Table 2 by the average water flow at the sampling site. It can be noticed that the average DEET concentration does not correlate with the water flow at the sampling sites and remains in a narrow range (0.01-0.12 µg/L). The highest average concentration was observed in rivers with an average flow of 0.5-5 m^3/s, mostly due to some peak emissions.

Table 2: Summary of the average and maximum concentration of DEET in Swiss rivers and streams according to the water flow at the sampling site (AWEL, FOEN, RÜS, AWE, details in Annex Table A2-A4). LOQs: 0.002 µg/L – 0.05 µg/L. [1]Mean concentration of samples with positive detection (con. > LOQ).

Water flow river class at sampling [m^3/s]	Nr. samples	Nr. samples > LOQ	Mean con.[1] [ug/L]	Max conc. [ug/L]
Not available	615	452	0.06	3.17
0-0.5	811	551	0.05	0.58
0.5-5	803	579	0.12	7.92
5-10	321	222	0.06	0.99
10-100	130	55	0.05	0.16
100+	4223	4210	0.01	0.25

4.1.1.1 River Rhine

About 80 % of Switzerland's rivers enter at some point the river Rhine before the water leaves Switzerland in Basel with an average flow rate of 1'000 m^3/s transporting about 60'000 t dissolved organic compounds (DOC) and 48'000 t nutrients (Ruff et al., 2013). In order to monitor the water quality in this important drinking water source, the countries along the Rhine operate a network of monitoring stations. The first such station, the RÜS, was built in Weil a. R. (Germany) in 1993. This station and the associated laboratory are operated by the AUE. At the RÜS, the river Rhine drains a catchment of about 36'500 km^2, which is home to approximately 6.7 million people, of which ca. 5.6 million live in Switzerland and the rest in Germany and Austria (Mazacek et al., 2016). All five formulators of DEET present in Switzerland as well as over 700 WWTPs are also located in the catchment (map.geo.admin.ch, 2021). Any potential DEET emissions from all Swiss formulators of DEET would enter the Rhine between Lake Constance and the RÜS.

At the RÜS daily time proportional 24h-composite samples are screened for more than 380 target substances. In addition, non-target analysis is combined with an innovative trend-detection software for suspicious temporal trends or unusually high intensities (Mazacek et al., 2016; Ruppe et al., 2018). The RÜS measurements provide, therefore, very valuable data for assessing the occurrence of long-lived chemicals in Swiss rivers and for documenting their inputs over time. Further, the effect of water protection measures to reduce such substances can be evaluated. One of the target compounds is DEET, for which the data set goes back to 1992, showing a high temporal variability of concentrations over the last 11 years (Figure 6).

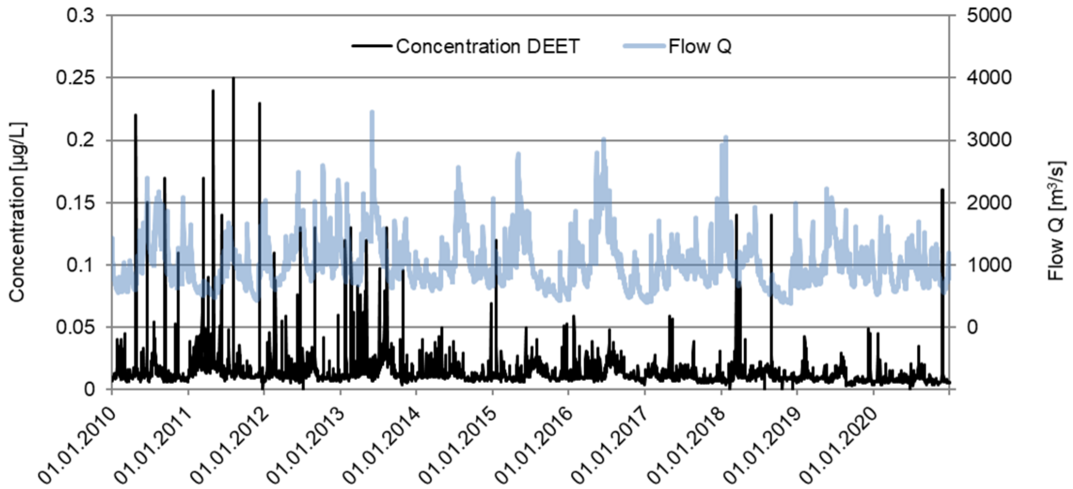

Figure 6: Daily variability of DEET concentrations 2010-2020 in the river Rhine at sampling point RÜS, where time proportional 24h-composite samples are analyzed daily. Number of samples: 4017. LOQ: 0.003 ug/L.

The monitoring of DEET at the RÜS over the last 11 years shows a decrease in yearly loads as well as a seasonal trend with higher loads being detected in the warmer months (April – September) compared to the colder months of the year (October-March) (Figure 7). During the warm season, the load of DEET in the river Rhine is on average about

60 % higher compared to the load in the cold months of the year (even when peak emissions > 0.03 µg/L are excluded). This is likely due to the higher use of DEET at times of the year when mosquitos/insects are more present. These findings are in line with scientific literature, which also report a clear seasonal pattern of DEET emissions and occurence (Bernot et al., 2013; Hope et al., 2012; Marques dos Santos et al., 2019; Loos et al., 2013; Sui et al., 2011; Yang et al., 2011). It should be noted that the seasonal pattern described for DEET loads in the Rhine is less pronounced for DEET concentrations due to the higher water flows in the summer.

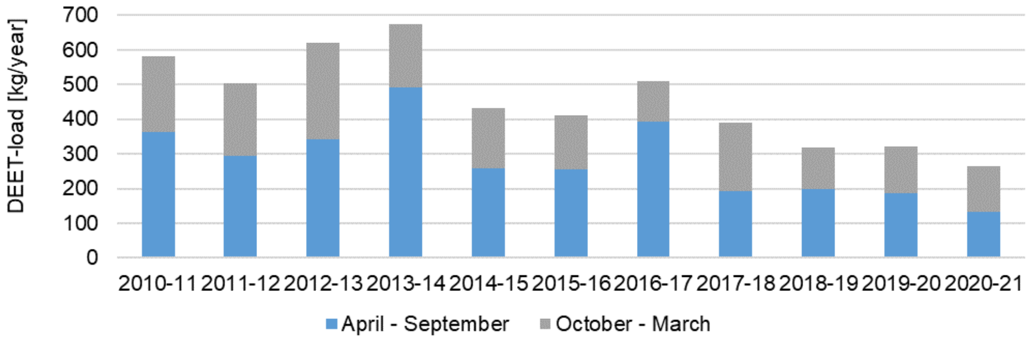

Figure 7: Seasonal variability of DEET loads in the river Rhine at sampling point RÜS.

Over a single year, about 350 kg of DEET pass the river Rhine monitoring station RÜS, with strong daily fluctuations, which can lead to an abrupt increase in the cumulative load as shown in Figure 8 for 2018. Such peaks occurred multiple times in the last 11 years, with concentrations reaching up to 250 ng/L and a corresponding daily load of ca. 25 kg/d (Aug 2011, Figure 6). There appears to be no correlation between these peaks and flow or precipitation amounts (Annex, Figure A2 and A3).

To better describe the emission dynamics of DEET in the Rhine, the data was divided into base and peak emissions (as exemplified in the Annex, Figure A4). The cutoff was set at 0.03 µg/L with observations below this threshold being categorized as base emissions and values above as peak emissions. Figure 9 illustrates the evolution of the base and peak load over the past 11 years.

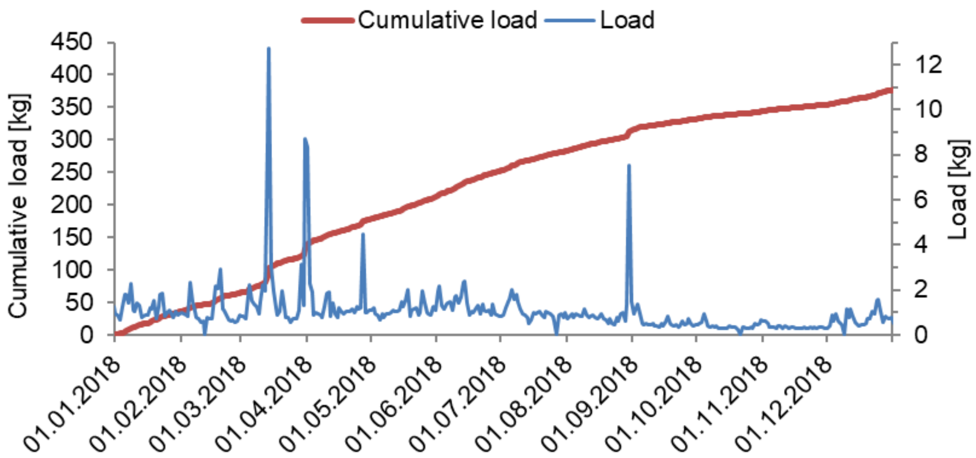

Figure 8: Variability of DEET loads as well as the cumulative load for 2018 in the river Rhine at the RÜS.

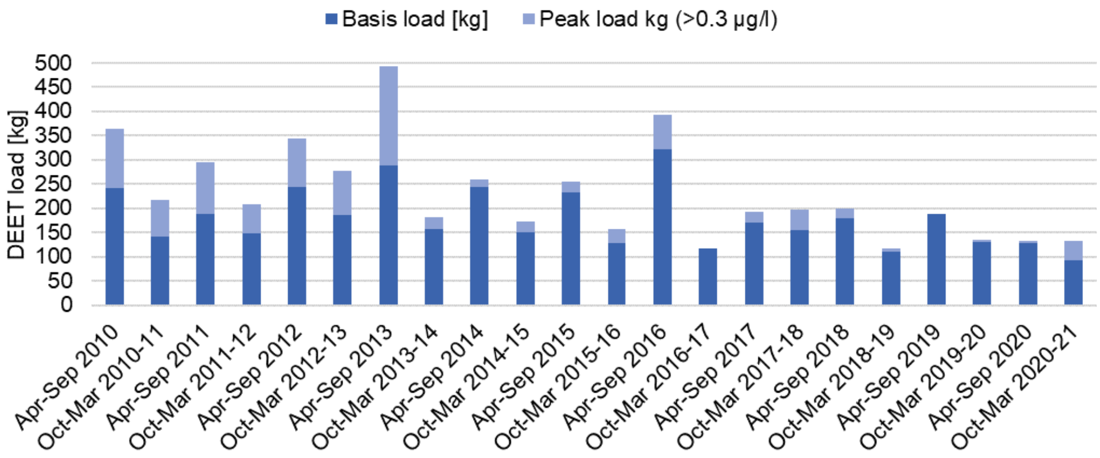

Figure 9: Seasonal variability of DEET loads as well as base and peak load in the river Rhine at the RÜS (threshold between base and peak emissions set at 0.03 µg/L).

As can be seen in Figure 9 the occurrence of peak emissions appears to have decrease over the last decade with almost none occurring in 2018 and 2019, resulting in concentration mostly below 50 ng/L. This observation may be the success of efforts by cantonal and federal authorities to reduce point source emissions to Swiss streams (see Chapter 4.2.4). Overall, Peak emission have accounted for about 25 % of DEET load over the last decade compared to ca. 10 % in the last 4 years. Table 3 summarizes the average concentrations and loads of DEET measured at the RÜS from 2017 to 2020 based on the yearly season and base or peak emission.

Table 3: Summarized average DEET concentrations, loads and normalized loads per person at RÜS for 2017-2020. LOQ: 0.003 ug/L. [1]April to September. [2]October to March.

Average 2017-2020	**Sample Nr.**	**Ø Conc. [µg/L]**	**Ø Q [m³/s]**	**Ø Load [kg/year]**	**Ø Load [kg/d]**	**Ø Load [µg/pers/d]**
RÜS Warm season[1]	732	0.01	995	178	0.98	146
RÜS Cold season[2]	729	0.01	896	120	0.84	126
RÜS basis (conc. <0.03 µg/L)	1424	0.01	951	302	0.90	134
RÜS peak (conc. >=0.03 µg/L)	33	0.06	890	38	4.65	693

4.1.1.2 In a creek

Peak concentrations of pesticides and biocides in surface waters can be of great biological and regulatory significance, but are rarely detected and only at great expense. The MS2field platform (online sample preparation coupled with LC-MS/MS) is one of the first mobile measurement infrastructures that allows continuous and temporally highly resolved measurements of micropollutants in environmentally relevant concentrations directly in the field (Stravs et al., 2021). The MS2field has been especially helpful in elucidating pesticide concentration dynamics and showing to what extent peak concentration in streams have so far been underestimated with conventional sampling and measurement techniques.

During a measuring campaign in a creek in summer 2019, two peak emissions of DEET have been registered (Figure 10). The catchment is composed of mainly agricultural land with some forest and no discharge from WWTPs. Also no animal husbandry is present, however, a small amount of animals (cows, goats) have been observed on the fields. The high temporal resolution (analysis of a sample every 20 min) identified two events with DEET concentrations above the limit of quantification (LOQ = 8 ng/L) during the measurement campaign in 2019. These peaks correlated directly with rain events and the concentrations were far below the quality criteria. The question remains open what the source of these peaks is. This could be due, for example, to a small amount of DEET being spilled in the catchment during an application and entering the stream through stormwater runoff. Another hypothesis could be that DEET was washed off by rain from a riding horse on which DEET was applied.

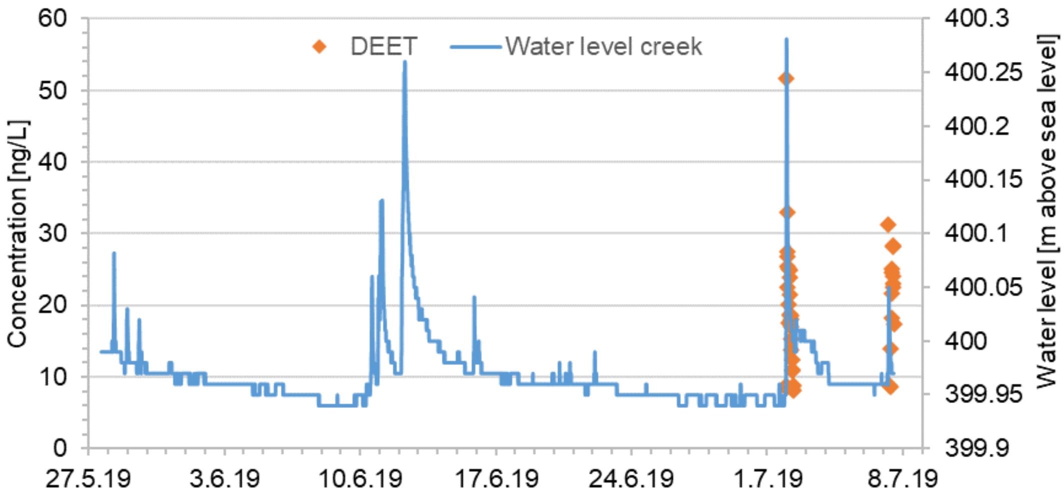

Figure 10: MS2field measurements of DEET with 20 min resolution in a little creek in Switzerland over 6 weeks (Eawag, Environmental Chemistry Dept.) plotted with water level data. LOQ: 8 ng/L - no data points mean that DEET could have been nonetheless present below LOQ.

4.1.2 Swiss Lakes

Existing measurement campaigns were searched for DEET concentrations in Swiss lakes. Lakes can play an important role as a "buffer" of DEET loads, as the hydraulic residence time typically covers years. In fact, DEET accumulates in lakes and a certain amount of DEET is continuously released from the lake into outflowing rivers. This leads to relatively constant emissions throughout the year in rivers connected to large lakes.

In 2015, a comprehensive study identified concentrations of micropollutants including DEET in five Swiss lakes (Götz et al., 2015). In the Alpnachersee 19 ng/L (n=1), in the Zugersee an average of 11 ng/L (n=6), in the Urnersee 3 ng/L (n=1) and in the Luzernersee 4 ng/L (n=1) DEET were measured.

In the Bodensee, DEET concentrations were measured at nine different locations and depths resulting in an average concentration of 7.5 ng/L (Götz et al., 2015; Singer et al., 2009). The residence time of the water volume of 48.4 km^3 in Lake Bodensee is on average 4.3 years. In the catchment of the Bodensee nearly 150 WWTPs are discharging effluent water (Figure 11). It seems plausible that the treated wastewater is contributing to the measured 7.5 ng/L and corresponding with an estimated amount of 360 kg DEET in Lake Bodensee. On average, an outflow of 370 m^3/s is typical for the Bodensee in Stein am Rhine corresponding to an amount of 240 g DEET per day or about 90 kg per year.

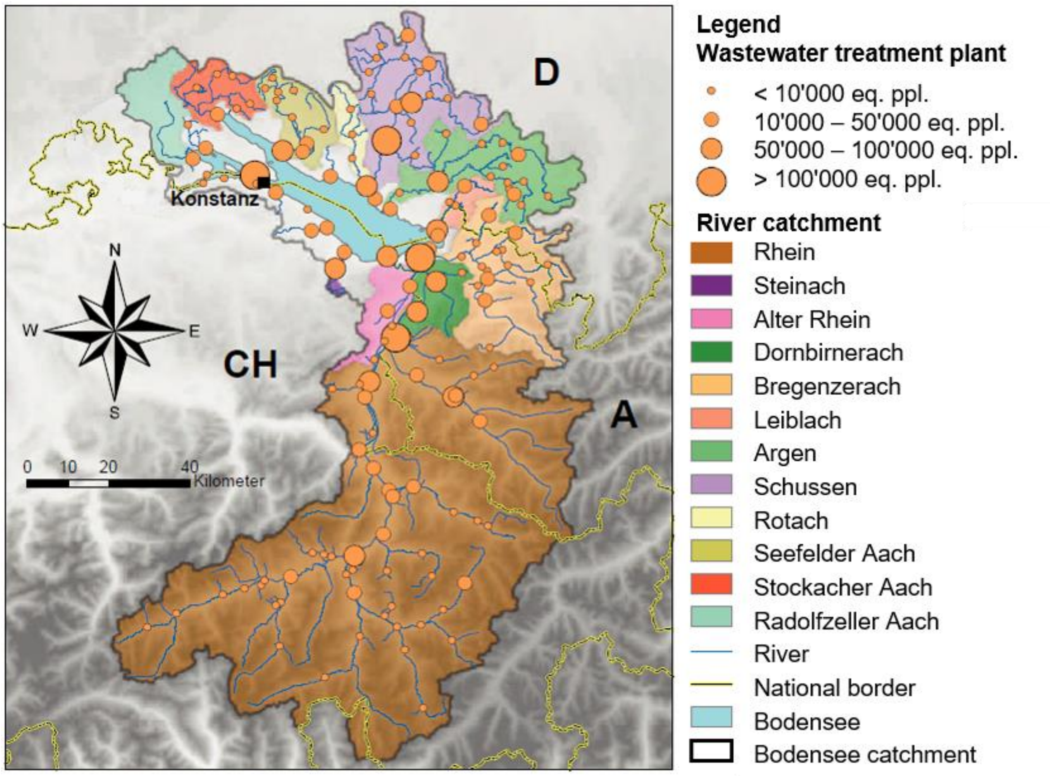

Figure 11: Catchment area of Bodensee and its 12 main sub-catchments (in color) with rivers. Wastewater treatment plants (orange circles) with inhabitant equivalents (modified Abb. 2 from Longrée 2011).

4.1.3 Groundwater

A dataset of groundwater measurements was obtained from AWEL. This dataset is composed of 1416 samples from 116 sampling sites in the canton of Zürich. DEET was found in 18 of the 1416 samples and in 7 different sampling sites at a concentration ranging from 10 ng/L to 90 ng/L. The concentration limit of 0.1 µg/L set by the Swiss Water Protection Ordinance was never exceeded in any of the 1416 groundwater samples. Table 4 summarizes the results for those sampling sites where DEET was detected. The spatial distribution of these sampling sites is shown in Figure A5, Annex. Although DEET was detected in only ca. 1 % of the samples and often at concentrations close to the LOQ, the presence of DEET in groundwater could still be a reason of concern as long as the sources are not well known, especially since DEET removal from drinking water is technically challenging (Pai et al., 2020; Golovko et al., 2020)

Table 4: Positive detection of DEET in Groundwater samples of the canton of Zürich (AWEL). [1]Mean concentration of positive detections.

Municipality	Sampling site	Sampling period	No. DEET detections / No. samples	Mean conc[1] [ng/L]	LOQ [ng/L]
Regensdorf	Altburg	2011-2019	1 / 20	10	10
Laufen-Uhwiesen	Chressen	2011-2019	8 / 16	20	10
Rorbas	Geissberg	2010-2019	1 / 9	10	10
Embrach	Kellersacker	2011-2019	1 / 16	10	10
Küsnacht	Schmalzgrueb	2010-2019	1 / 18	10	10
Andelfingen	Seelenstall	2011-2019	6 / 16	50	10
Elgg	See	2010-2019	1 / 14	40	10

4.1.4 Soil and Sediments

A study by Chiaia *et al.* (2020) analyzed 13 soil samples from the Swiss National Soil Monitoring Network (NABO) collected from 2005 to 2009 and three sediment cores of the lake Greifensee sampled in 2014. DEET was detected in two soil samples in suburban and urban forest sites at a maximum soil concentration of 12 $\mu g/kg_{oc}$ and in 2 of the 3 sediment cores. Based on these results, DEET occurrence in soils seems to be limited and specific to locations with human outdoor activities or animal application as well as mosquito presence. Accordingly, the same can be assumed for leaching of DEET from soils during rain events. This observation is, however, based on a limited number of samples in the canton of Zürich and may not be representative for all of Switzerland.
Apart from the sediment measurements mentioned above (Chiaia et al., 2020), measurement of DEET in sediments in Switzerland are scarce and not further discussed in this report.

4.2 Wastewater Treatment Plants

4.2.1 WWTP Influents

Few measuring campaigns analyzed the DEET concentrations of WWTPs influents. For this project, DEET measurements of eight WWTP influents in Switzerland (Otto et al., 2014) and five WWTP influents in Germany (UBA 2020) were studied. This data was used to calculate the DEET elimination rates (Chapter 4.2.5) and to verify the consumer usage discussed in Chapter 5.

The measured concentrations in the influents varied from LOQ to 8 µg/L DEET with an average of ca. 2.6 µg/L (Figure 12). The boxplots from the WWTPs in Germany show relatively little variation of influent concentrations. A larger variation between WWTPs is observed in the smaller Swiss WWTPs, for which however only one influent sample is available per WWTP. In general, influent WWTP concentrations are generally a factor of 100 to 1000 higher than in surface waters. The PNEC value of 10 mg/L for WWTPs (ECHA CAR, 2010) was never exceeded in any of the influent samples.

Average influent loads per capita resulted in 690 µg DEET per person a day (Figure 13). These daily loads per capita are calculated by dividing the total daily load in each WWTP by the resident equivalents. The normalization of loads in "µg/per/d" is useful for the comparison of data from different WWTPs and scenarios, which can help identify specific patterns that might indicate for example a point source emission. This aspect is further discussed in Chapter 4.2.4.

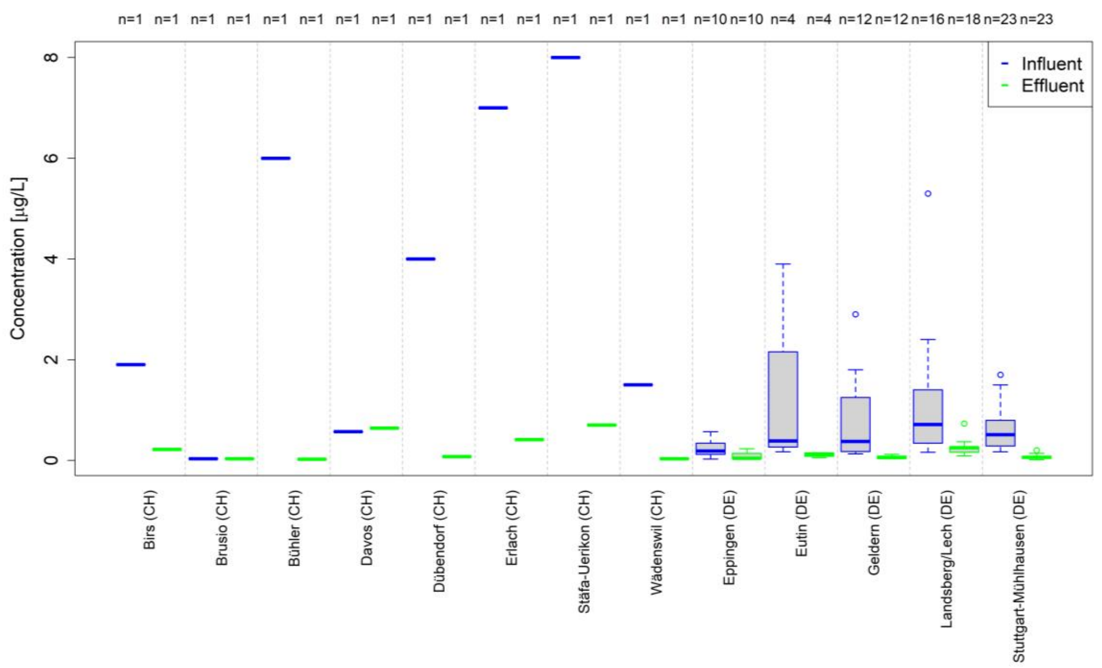

Figure 12: Measured DEET concentrations for eight WWTPs in Switzerland (Otto et al., 2014) and as boxplots for five WWTPs in Germany (UBA 2020). LOQs: 0.02-0.05 µg/L. The number of samples is indicated with "n=". The detection rate for all sites is 100 %.

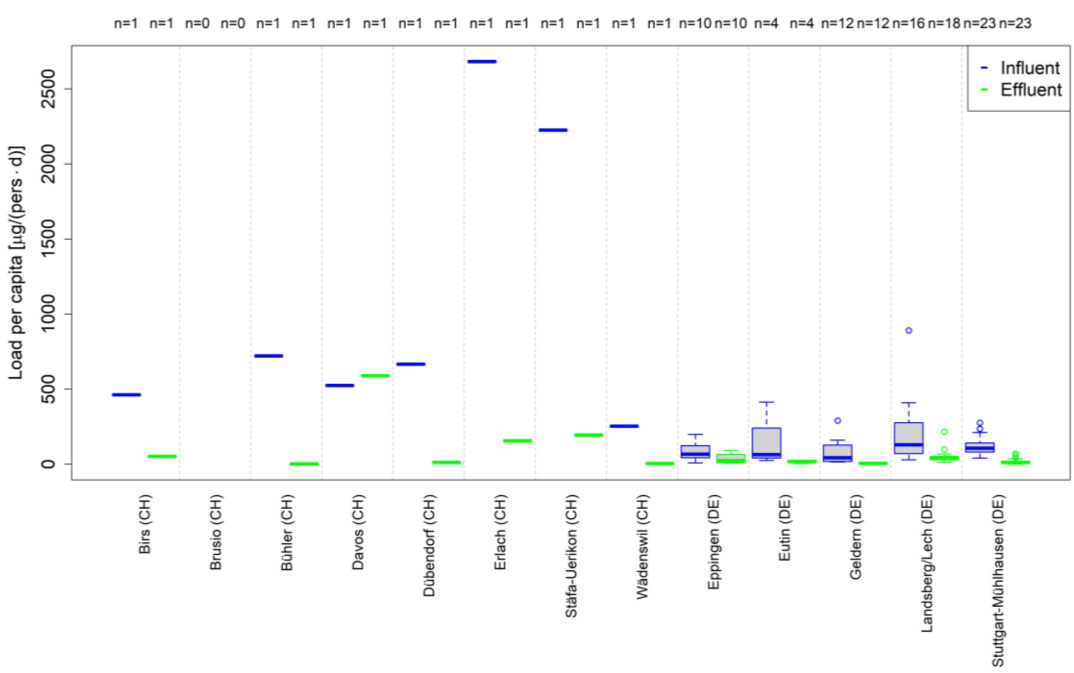

Figure 13: Calculated DEET loads per person per day for eight WWTPs in Switzerland (Otto et al., 2014) and five WWTPs in Germany (UBA 2020). The loads were divided by the resident equivalent data (including industrial emissions accounted for as person equivalents). The number of samples is indicated above with "n=". The detection rate for all sites is 100 %. The load for the Brusio WWTP could not be calculated because the wastewater flow is unknown.

4.2.2 WWTP Effluents

DEET-concentrations in the treated wastewater were obtained for additional 67 WWTPs in the canton of Zürich and the canton of St. Gallen. Figure 14 illustrates the average concentration and loads in the effluents of all 80 WWTPs evaluated (Otto et al., 2014; UBA 2020; AWEL 2018; AWE 2016).

The average effluent concentrations ranged between 0.2 µg/L and 2.68 µg/L with an average of 0.28 µg/L DEET (n=80). The effluent concentrations are about a factor 10 lower compared to the influent concentrations. The absolute daily loads ranged between 0.03 g and 31.3 g DEET, with an average of 2.5 g per day discharged in surface waters. The normalized loads per capita ranged between 3 µg/d and 1055 µg/d with an average of 100 µg/d per inhabitant equivalent.

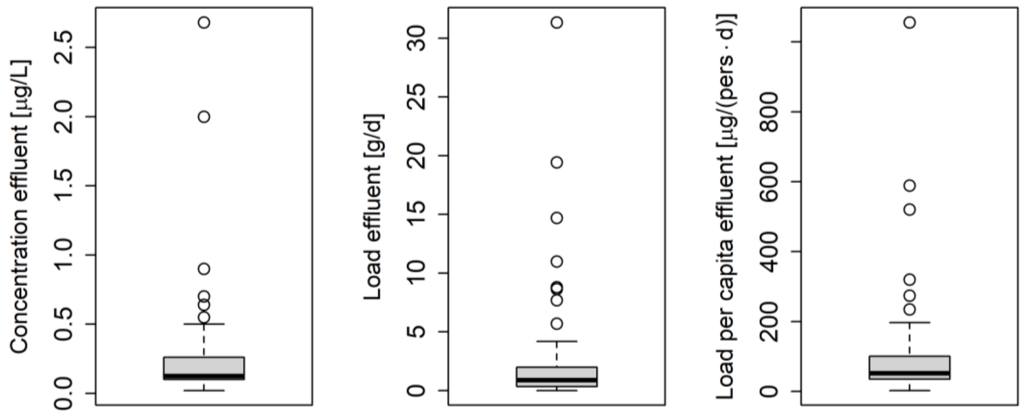

Figure 14: Measured concentrations as well as calculated absolute loads and normalized loads per capita in 75 Swiss and 5 German WWTPs. LOQs: 0.02-0.05 µg/L.

In Table 5, the average concentrations as well as absolute and normalized loads for all WWTPs measurements are summarized. These values are further discussed in Chapter 6 as they are compared with the emission estimations based on the ESD of the BPR.

Table 5: Average DEET concentrations and loads of 13 Swiss and German WWTP influents as well as the average DEET concentrations and loads of 80 WWTP effluents (75 Swiss WWTPs and 5 German WWTPs).

Parameter	Unit	Influent (n=13)	Effluent (n=80)
Average conc.	µg/L	2.56	0.28
Average absolute load	g/d	26.6	2.52
Average normalized loads	µg/pers/day	686	101

4.2.3 Temporal Pattern in WWTP

Consumption of DEET varies according to seasonal use with most usage during the summer. A recent study in the US found that DEET had a diurnal variation in a wastewater influent, with a maximum in the late afternoon (Marques dos Santos et al., 2019). Similarly, the high-resolution wastewater influent measurement data from a small Swiss WWTPs (10'000 equivalent residents) indicates that peak concentrations occurs around the afternoon with no apparent correlation to the influent flow (Figure 15). One hypothesis responsible for this emission dynamic could be the release of DEET from laundering of clothes.

This unique high temporal resolution data (20 min sampling) obtained with the MS2Field during winter time indicates much larger fluctuation of DEET concentrations in WWTP influents, compared to the data presented in Figure 12 obtained with conventional sampling techniques. That being said, the average DEET influent concentration of 530 µg/L is in line with average concentrations of the other WWTP influents.

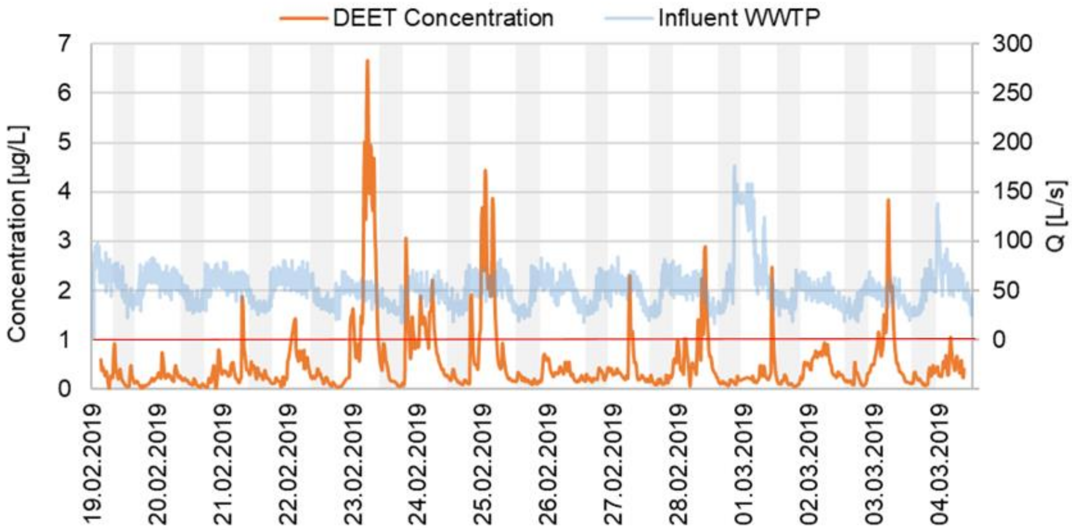

Figure 15: MS2field measurements of DEET with 20 min resolution in the influent of a Swiss wastewater treatment plant for two weeks (Eawag, unpublished data; for method see Stravs et al., 2021). Vertical lines are representing the date at 12 p.m. midday. Light gray columns indicate nighttime hours (12 p.m. to 8 a.m.). Values above 1 µg/L are above the calibration range and should be considered qualitative (red line). LOQ 15 ng/L.

4.2.4 Point Sources

Due to cantonal monitoring programs, a few point source emissions of DEET to wastewater have been identified in association with formulators.

For example, during the inspection of a formulator in the canton of St.Gallen, the cantonal authority for the environment noticed the production of DEET containing products. This led to the monitoring of DEET concentration in the WWTP serving this specific formulator. Consequently, an emission of about 2.5 kg DEET was detected in the days following manufacturing of DEET products. This emission occurred as a result of the cleaning of the formulator's equipment. Although environmental quality standards for DEET were not exceeded, mitigation measures were implemented in collaboration with the formulator. In particular it was decided to first rinse the equipment with ethanol and only subsequently with water. The obtained ethanol solution was stored and reused in the next production cycle. This simple, but clever solution reduced the DEET loss by about 90 %. This success story shows how a positive collaboration between environmental authorities and chemical companies can lead to positive effects both for the environment and the industry.

Another point source of DEET, likely of industrial nature, was discovered during the review of the monitoring data from canton Zürich. A peak concentration of 5.25 µg/L was observed in a weekly composite sample in June 2018 in the effluent of one specific WWTP. This emission event resulted in the discharge of ca. 270 g DEET into a small river within a week. This amount is equivalent to a load per capita of about 2.1 mg per day, 20 times higher than the calculated average value of 100 µg per person and day. Considering an average DEET product content of 30 % (Table A1, CH BPR) and an average WWTP degradation rate of 0.73 (Chapter 4.2.5), this emission would be equivalent to the spilling of ca. 3.5 liters of a common DEET containing product. Notably the highest concentration of DEET in a Swiss river observed in this study (8 µg/L, Chapter 4.1.1) was observed downstream of this WWTP in September 2015. Under the above mentioned assumptions and for an average water flow during the sampling period of ca. 0.16 m^3/s, this second emission event would have been equivalent to the spilling of ca. 2.8 kg DEET or 10 L of a common DEET containing product. Further investigations showed that a formulator was discharging to the WWTP in question, which could explain the described emission. The peak load emission of 2.8 kg would be in accordance with the 2.5 kg detected from the formulator in the canton of St.Gallen. By looking at the concentration of DEET in the river downstream of the WWTP in 2015 (Figure 16), a strongly fluctuating concentration profile can be observed, typical for industrial point source emissions (Anliker et al., 2020).

The question was raised whether the above-mentioned emissions of 2016 in the canton of St.Gallen and of 2015 and 2018 in the canton of Zürich could be traced to the peak concentrations detected in the river Rhine (Figure 6). After taking into consideration the date of emission and dilution factor in the river Rhine, no conclusive link to specific peak concentrations could be drawn. The concentration caused by these point source emissions in the river Rhine would be near the limit of quantification (ca. 3 ng/L). However, it is noted that this statement is based on weekly composite samples. The actual emission peaks might have occurred in a shorter period of time, which could lead to detectable increase of concentrations in the Rhine. The relevance of emission of DEET from formulators compared to emission from human use is discussed in Chapter 5.

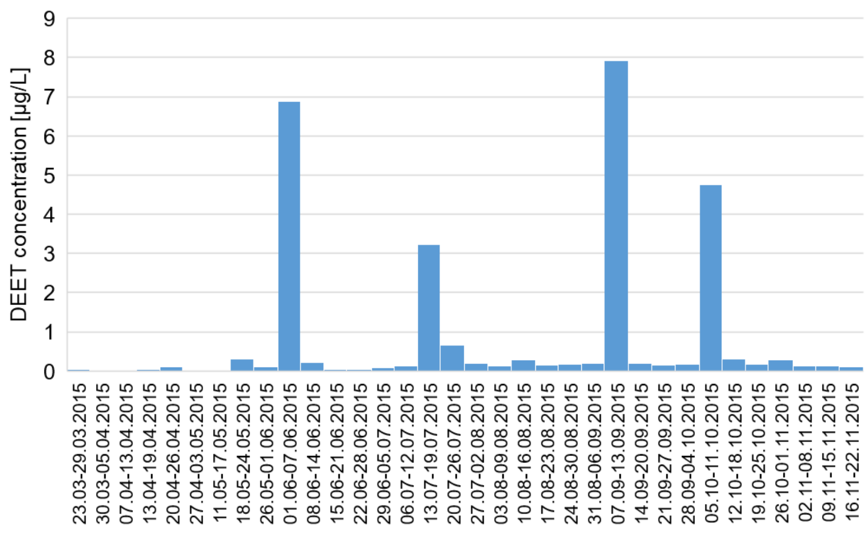

Figure 16: DEET concentration in a river of the canton of Zürich with a formulator in the catchment. The concentration peaks are likely linked to losses during formulation events. LOQ: 0.01 µg/L.

4.2.5 Elimination in WWTP

A review of scientific literature states that the biodegradability of DEET in WWTPs varies between 10 % and 90 % (Bernhard et al., 2006; Marques dos Santos et al., 2019). This is contradictory to results demonstrating "readily biodegradability" under controlled laboratory test conditions (see 2.5).

Helbling et al. (2010) studied biotransformation pathways and resulting transformation products in WWTPs and found that DEET degraded through multiple pathways initiated by different transformation steps. The biotransformation rate constant (k_{bio} 0.3 L/g_{ss}/d) estimated for DEET was not attributed to a single reaction type. This might explain some of DEET's varying WWTP elimination rates, since the different conditions and matrices might more or less favor biodegradation.

The data collected from WWTPs in Switzerland and Germany confirms that DEET has highly varying WWTP elimination rates (Figure 17, Figure 18). The average WWTP degradation was 73 % with no significant difference between Switzerland and Germany. The highest degradation rate observed was 99.6 %, the lowest 0 %. Several factors might influence the transformation processes during treatment e.g. process train, temperature, size of plant, dilution due to rain events, microbial community and more. Especially, the highly varying elimination rates during rainy weather, possibly caused by lower hydraulic retention times due to higher wastewater inflows, indicate that higher amounts of DEET might enter the receiving surface waters during rain events.

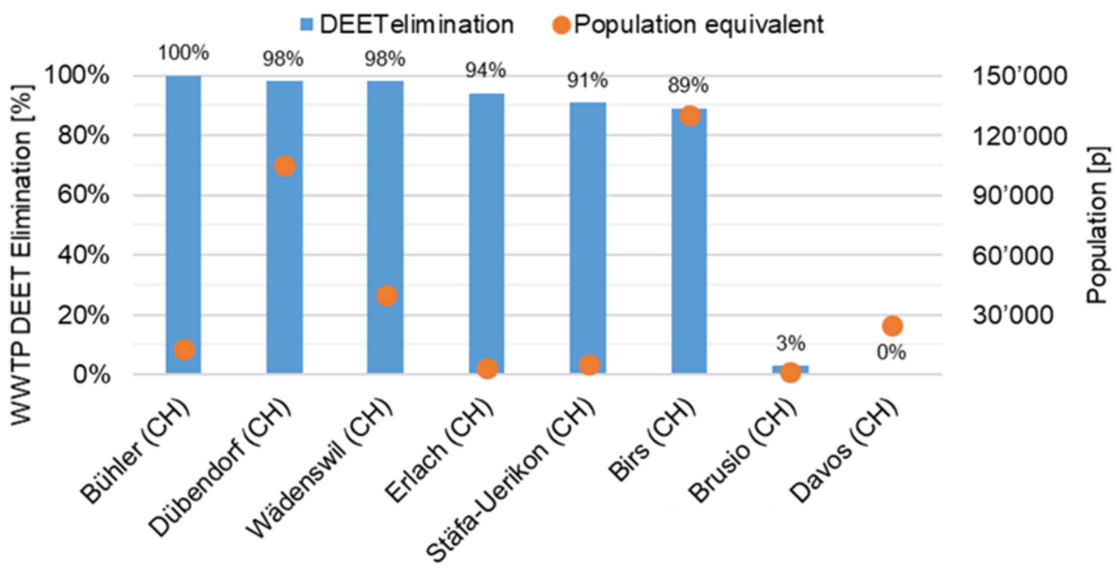

Figure 17: Elimination of DEET for eight WWTPs in Switzerland (Otto et al., 2014).

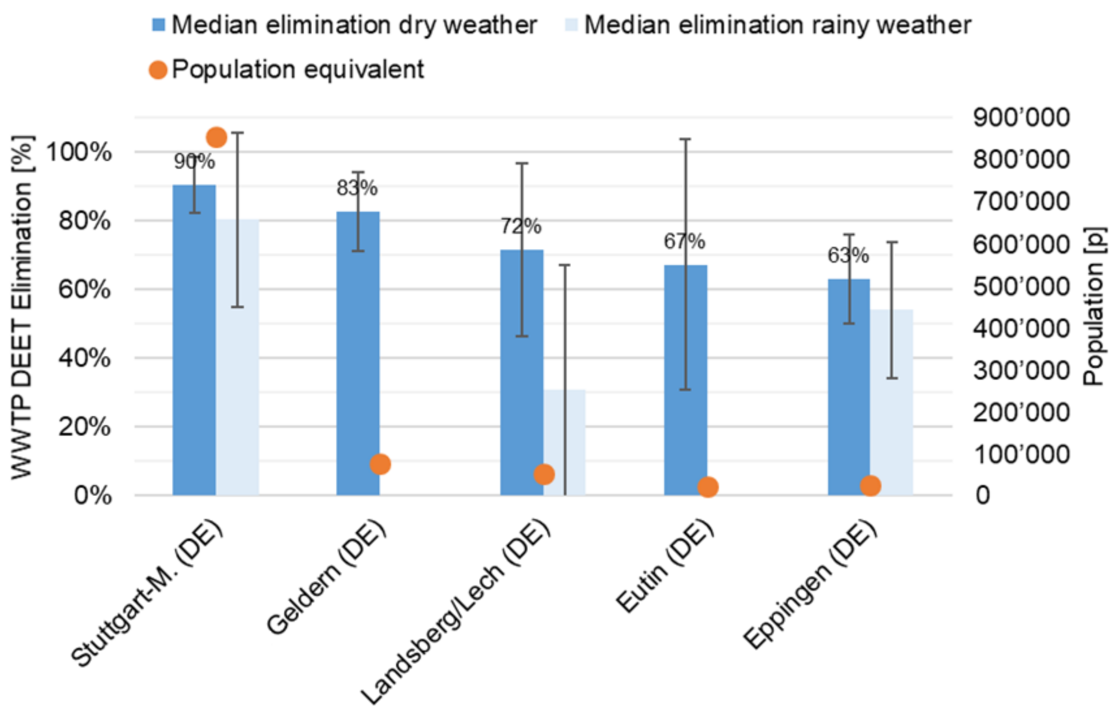

Figure 18: Elimination of DEET during rainy and dry weather in five WWTPs in Germany (median for 4 to 12 measurements 2017-2019; data from UBA 2020).

4.3 Occurrence of DEET in Swiss air and rainwater

Recently, a pilot study was conducted in Switzerland with the primary objective of developing appropriate methods for the analysis of pesticides in air and rainwater and to provide a first description of the occurrence of pesticides in these environmental media (Carbotech, 2021). Over 100 organic chemicals, including DEET, were analyzed in four-week composite samples at nine sampling sites in Switzerland over a period of approximately six months (March 23 to September 08, 2020). The Sampling sites were selected to include a range of different land uses (e.g., absence or presence of intensive agriculture, in biotopes, near a forest and close to an airport). DEET was detected in 55 of the 56 rainwater samples (98 %) and 38 of the 54 air samples (70%) and at all sampling sites. The average DEET concentration in the air samples in which DEET was detected was ca. 0.4 ng/m3, while the amount of DEET found in rainwater averaged 25 ng per sample (Carbotech, 2021), suggesting DEET concentrations in rainwater in the order of nanograms per liter based on the reported sample volumes. Although the same authors pointed out that possible contamination during sampling due to carryover from employed personnel or passers-by could not be entirely excluded, the results suggest that atmospheric transport and deposition of DEET may play a role in explaining the ubiquitous detection of this substance in aquatic systems. Additional studies would be required to clarify this point, which is not further discussed in this report.

5 DEET Mass balance

5.1 Bottom-up Approach using Monitoring Data

The river Rhine is a great model for Switzerland as it drains ca. 36'500 km^2 land, on which 70 % of the Swiss population lives (FOEN, 2017). In this sense, the Rhine is as a sort of collection basin for most of Switzerland's DEET emissions to the environment.

Based on DEET concentrations in Swiss rivers retrieved from the cantonal monitoring programs, a mass balance for the river Rhine was calculated (Table 6). This mass balance was obtained by aggregating the yearly average DEET loads of the main tributaries of the river Rhine as well as the load originating from the Bodensee until the monitoring station of the RÜS, where the Rhine enters Germany. Based on this, a total of 333 kg/year at the RÜS was estimated, which fits well with the average measured load of ca. 350 kg/year DEET measured from 2017 to 2019 at the RÜS station. Still missing from this estimate are the emissions from WWTPs located directly at or in the immediate vicinity of the Rhine between lake Constance and the RÜS. These WWTPs serve approximately 1.3 million person equivalents (map.geo.admin.ch, 2021). By using the average daily load per capita in WWTP effluents of 100 µg presented in Chapter 4.2.2, an additional emission of ca. 47 kg can be estimated from these WWTPs, resulting in a total estimated DEET load at the RÜS of ca. 380 kg, compared to the average yearly load of 350 kg measured at the RÜS from 2017 to 2019. This observation indicates that the actual degradation of DEET in Swiss surface waters is likely not as high as expected from literature.

Table 6: Estimated DEET loads/ mass balance for the river Rhine based on available monitoring data from canton Zürich, AWEL and NAWA, FOEN (Annex, Table A2 & A4). Also included is an estimation of the yearly DEET load emitted from WWTPs located at the Rhine between the Bodensee and the RÜS. [1]Sum of DEET load from Jonen and Küntenerbach. [2]Sum of DEET load from Beggingerbach, Landgraben und Zwärenbach. [3]Estimate based on the average daily effluent DEET per capita load in Swiss and German WWTP effluents presented in Chapter 4.2.2 and 1.3 million person equivalents.

Sampling point	River	DEET load [kg/a]
Bodensee	Bodensee	88
Brugg	Aare	111
Limmat at Dietikon EKZ	Limmat	34
Reppisch at Dietikon	Reppisch	2
	Reuss[1]	11
Döttingen, at Pegel ALG	Surb	2
Glatt before Rhine	Glatt	15
Freienstein	Töss	8
Andelfingen, Brücke	Thur	52
	Wutach[2]	2
Birskopf	Birs	8
Sum from monitoring data		**333**
Estimated additional load from WWTPs[3]		**47**
Total sum from mass balance		**380**
Measured at Rhine 2017-2019, RÜS		**350**

Dividing the measured load of 350 kg per year at the RÜS by the number of persons living in the Rhine catchment (ca. 6.7 million; Mazacek et al., 2016) results in a load of 140 µg DEET per person and day. This value is in the same range compared to the 100 µg DEET per person and day determined from Swiss WWTP effluents (Chapter 4.2.2), underlining that most DEET is discharged to the environment by WWTPs.

By extrapolating the load of 350 kg at the RÜS to the Swiss population and accounting for the fraction of DEET released to wastewater after use of 0.89 (Ctgb, 2014) and an average WWTP degradation of 0.73 (Chapter 4.2.5), a total consumption of about 2 tons DEET is estimated in Switzerland by consumers (Figure 19).

The amount of 2 tons is equivalent to the use of about 45'000 bottles of DEET per year in Switzerland (150 mL, 30 % DEET) or one bottle every 194 persons per year (<1 % of the Swiss population)[1].

5.2 Top-down Approach using Production Data

The total consumption of DEET in Switzerland can be independently estimated from (a) the amount of DEET produced by manufacturers; (b) the amount of DEET contained in the products sold by distributors; (c) the amount of DEET blended into commercial products by formulators. These estimates are discussed below. The most accurate estimate for the total consumption of DEET in Switzerland is likely the amount of DEET sold to consumers by distributors, as this stage of the supply chain is the closest to the actual consumption of the product. However, the amounts estimated from the manufacturers and formulators provide valuable information to characterize the supply chain and validate the estimate from the distribution of DEET containing products.

DEET from producers

A total consumption of 4 tons of DEET in Switzerland is estimated on the basis of information provided by Clariant for the EU as described in Chapter 3 (Figure 19).

DEET from distributors

Twelve distributors disclosed data accounting for ca. 13 tons of DEET sold in Switzerland per year, representing at least 75% of the Swiss market share. For the other 15 distributors no specific information was received. By extrapolating the value of 13 tons to the entire Swiss market, a total amount of ca. 17 tons DEET distributed in Switzerland can be estimated (Figure 19). No direct emissions of DEET in Switzerland from distributors are expected.

DEET from formulators

According to the information received from Swiss formulators, about 30 to 80 tons of DEET are blended into DEET containing products in Switzerland each year (Chapter 3.1.2). Of this amount, about 30 % is sold in Switzerland (9 to 24 tons) and 70 % is sold

[1] This calculation neglects any degradation occurring in the surface waters until DEET reaches the RÜS, but at the same time applies the same degradation rate of WWTPs to DEET released directly into water bodies (e.g. by swimming).

abroad (21 to 56 tons). A mass flow of the DEET formulated and used in Switzerland is shown in Figure 19.

According to literature, formulating pharmaceutical/chemical industries release less than <1 % (0.001-0.55 %) of production into surface waters (Anliker et al., 2020). In Switzerland, 30 to 80 tons of DEET are used by formulators yearly, so that the loss of DEET from formulators into surface waters can be estimated between 0.3 kg to 440 kg per year. The latter value is unrealistic, as there is no evidence from Swiss monitoring data and information from production sites to support such a large amount, which would surpass the yearly load measured in the Rhine at the RÜS. As of 2019, 90 % of the DEET formulated in Switzerland is processed in two facilities with effective mitigation measures. Therefore, we estimate the current emissions of DEET from Swiss formulators to surface waters to be in the low tens of kilogram range of DEET per year, about one order of magnitude smaller compared to emissions from human and animal use. Some indications suggest that larger emissions might have indeed occurred in the past (Chapters 4.1.1.1 and 4.2.4).

The question was raised as to how much of the DEET sold in Switzerland is effectively applied in Switzerland and how much abroad, for example during holidays. A tentative answer to this question was provided by the two largest Swiss formulators, which account for over 90 % of the DEET formulated in Switzerland. These formulators observed a decline in domestic orders of ca. 75 % during the 2020 coronavirus pandemic, a year in which travel abroad was severely restricted, but outdoor activities in Switzerland mostly permitted (especially during the summer, with some limitations on the number of people at gatherings). It could be argued that the decline in orders was caused by a lower Swiss domestic consumption. However, this appears to be only partially the case, since the amount of DEET measured at the RÜS decrease by only ca. 20 % in 2020 compared to the previous 3 years. Based on this observation it is believed that the majority of DEET sold in Switzerland is used abroad; according the information presented above a value between 50 % and 75 % is estimated.

Considering this information, a Swiss consumption of ca. 4 tons DEET is estimated according to information provided by manufacturers, of ca. 2 to 12 tons[2] for information provided by formulators and of ca. 4 to 8.5 tons[3] for information provided by distributors (Figure 19).

5.3 Top-down vs. Bottom-up

The consumption of 2 tons of DEET derived from monitoring data (bottom-up) lays in the lower range of the 2 to 12 tons estimated from production data (top-down). These results clearly indicate that the yearly amount of DEET detected in Swiss surface waters can be explained through consumption as an insect repellent alone. Questions remain about the discrepancy between DEET detections in winter despite an apparent seasonal use of DEET. No single reason was found to explain the discrepancy between the ubiquitous

[2] Low estimate: 9 t * 0.25 = 2.25 t ; high estimate: 24 t * 0.5 = 12 t
[3] Low estimate: 17 t * 0.25 = 4.25 t ; high estimate: 17 t * 0.5 = 8.5 t

detection of DEET in Swiss waters despite its seasonal use. However, some hypotheses are presented below.

- Washing of contaminated clothes: A possible source of emissions during winter time might be the release of DEET when washing clothes worn during application of the biocide. In particular, one exploratory study reported DEET could be emitted from clothes even after three washing cycles (Wieck et al., 2018). This could be relevant when people return from trips to warm regions of the world during the Swiss winter season and launder clothes that have been in contact with products containing DEET. In fact, as described in Chapter 5.2, the amount of DEET used by Swiss inhabitants abroad likely surpasses domestic consumption. Moreover, in the winter of 2020-21, when travel was restricted due to the coronavirus pandemic, the average load of DEET measured at the RÜS was about 40 % lower compared to the average load measured in the previous 4 winters (2016-20).

- Seasonal degradation patterns: A study conducted in 2015 reported the lack of a seasonal pattern for DEET in the effluent of a US WWTP, but the presence of a seasonal pattern in the WWTP influent of the same WWTP, thus suggesting seasonal differences in DEET WWTP degradation (Merel et al., 2015). A higher degradation of DEET during warm months could in this sense contribute to the apparent discrepancy between DEET seasonal use and detection patterns in WWTP effluents. The authors proposed sampling WWTP influents rather than WWTP effluents to better elucidate DEET emission dynamics. Having this said, no seasonal influence on the WWTP degradation rate of DEET could be observed in the dataset from Germany (UBA, 2020).

- Lakes acting as buffers: Lakes can accumulate large amounts of DEET, buffering summer emissions and resulting in continuous emission of DEET to tributaries in winter and autumn. In the case of the Rhine at the RÜS sampling site, it is estimated that about one third of the winter load of DEET can be explained by DEET originating from lake Bodensee alone. This finding naturally challenges the notion that the half-life of DEET in surface water is in the range of 5 to 15 days.

- Analytical interferences: Some authors attribute this seasonal discrepancy to possible analytical interferences (Merel & Snyder 2016). Although possible analytical interferences cannot be completely disregarded, an overestimation of DEET concentrations in Switzerland seems unlikely (Chapter 2.6).

- Other sources: DEET could be released from an unaccounted source, however as discussed in Chapter 2.2, such a source could not be identified.

- Transformation product: DEET found in wastewater could partly be resulting from the degradation of another organic compound, of which DEET might be a transformation product. Although no reference to this was found in scientific literature, further studies would be required to verify this aspect.

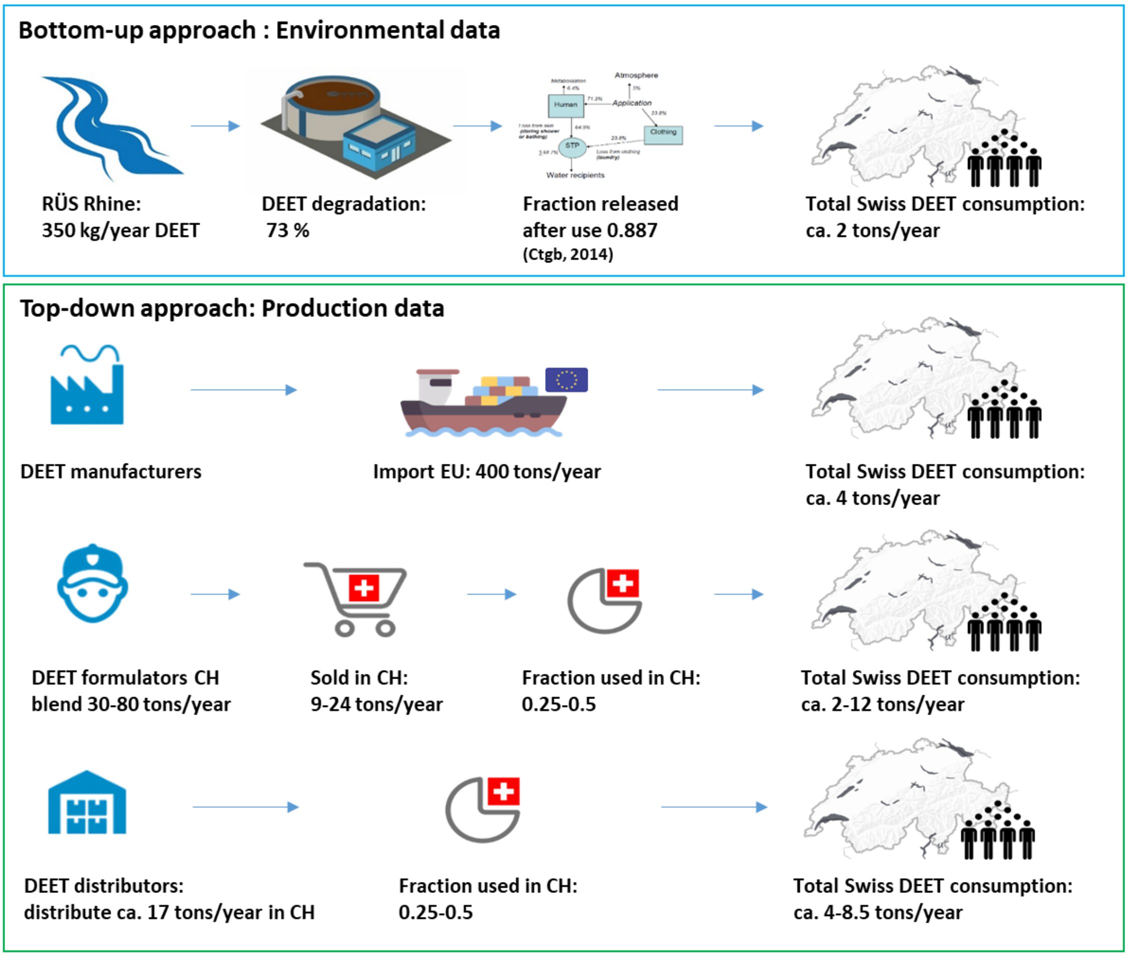

Figure 19: DEET mass balance in Switzerland based on the monitoring data measured at the RÜS in the river Rhine (bottom up approach) and on production data (top-down approach).

6 Emission Scenario Documents (ESD)

Emission scenario documents (ESD) are used in chemical risk assessments of the European Union and Switzerland to estimate the initial release of substances from biocidal products to the environment. DEET containing products generally fall under PT 19 "Repellents and attractants". The most relevant ESD are presented below using the established input parameters (ECHA, CAR 2010). In this study, only ESD leading to emissions in surface waters are included, since this is the main emission pathway of DEET to the environment. Emissions to soil are considered negligible (Chapter 2.4). These calculations are then compared to actual concentrations and loads of DEET measured in Swiss surface waters and WWTPs. Finally, refinements of the ESD are proposed for Switzerland based on the findings of this report.

6.1 Emission Estimations

6.1.1 Emission to WWTP from Human Use

According to the ESD for PT19, the release of repellents used on human skin and garments to wastewater can be estimated using a tonnage-based approach (ECHA ESD PT19, 2015; Table 3-1) or a consumption-based approach (ECHA ESD PT19, 2015; Table 3-6). The approach that provides the highest emission rate is usually selected during the authorization process. Accordingly, only the consumption-based approach is presented in this study, as this approach provides the worst-case scenario. Table 7 describes the local emission rate to wastewater of DEET from a repellent product applied on human skin in a standardized catchment of 10'000 inhabitants using the consumption-based approach. For this calculation, the established input parameters from DEET's chemical assessment report were used (ECHA, CAR 2010). A local emission rate to wastewater of 6.3 kg/d DEET is determined based on this approach for a product containing 30 % DEET.

Table 7: Emission scenario for calculating the release of repellents used on human skin and garments based on average consumption (ECHA ESD PT19, 2015; Table 3-6).

Parameter	Symbol	Value	Unit	Reference / Explanation
Number of inhabitants feeding one sewage treatment plant	Nlocal	10000	cap	ECHA ESD PT 19; default value
Active substance in the product (weight)	$Cform_{weight}$	300	g/kg	Swiss RPC, Annex Table A1
Consumption per application	$Qform_{appl}$	0.6	mg/cm^2	ECHA ESD PT 19; Table 3.6
Number of applications per day (Human skin, ≥ 12h)	Nappl	2	d^{-1}	ECHA ESD PT 19; Table 3.2
Treated area of human skin or garments	$AREA_{skin/garments}$	10660	cm^2	ECHA ESD PT 19; Table 3.3 Head+Arms+Hands+Legs+Feet
Fraction released to wastewater	F_{water}	0.887	[-]	Ctgb, 2014 ; $F_{water} = 1 - (F_{air} + F_{skin})$
Fraction of inhabitants using a repellent product	F_{inh}	0.37	[-]	ECHA, CAR 2010
Market share of repellent	F_{penetr}	0.5	[-]	ECHA ESD PT 19; default value
Specific density of the product	RHOform	1000	kg/m^3	ECHA ESD PT 19; default value
Output				
Local emission rate to wastewater	$Elocal_{water}$	**6.3**	kg/d	$Elocal_{water} = N_{local} * N_{appl} * Q_{formappl} * AREA_{skin/garment} * Cform_{weight} * F_{inh} * F_{water} * F_{penetr} * 10^{-9}$

6.1.2 Direct Emission to Surface Water from Human Use due to Swimming

Following the same principle as before, the direct emission into surface waters from human use of DEET containing products due to swimming activities is presented in Table 8 using the established parameters from DEET's ESD (ECHA, CAR 2010). According to this scenario, the local emission rate of DEET to a surface water body is based on 1500 daily swimmers. Furthermore, the resulting concentration over 91 days in a surface water body containing 435'000 m^3 of water is determined. The degradation of DEET in the surface water is calculated with a first order biodegradation rate constant of 0.047 d^{-1} (TGD, 2003) assuming readily biodegradability of DEET and a DT_{50} of 15 days. Based on these assumptions a local emission rate to surface water of 0.058 kg/d and a concentration of 3 µg/L after 91 days is estimated with degradation and 12 µg/L without for a product containing 30 % DEET.

Table 8: Emission scenario for calculating the release of repellents used on human skin due to swimming activities in surface waters and calculation of resulting surface water concentrations (ECHA ESD PT19, 2015; Table 3-7 & 3-8).

Parameter	**Symbol**	**Value**	**Unit**	**Reference / Explanations**
Daily number of swimmers	$N_{swimmer}$	1500	[-]	ECHA ESD PT 19; default value
Fraction of swimmers using the repellent product	F_{swim}	0.02	[-]	ECHA ESD PT 19; default value
Number of applications per day	N_{appl}	1	d^{-1}	ECHA ESD PT 19; default value
Fraction released to surface water body	$F_{waterbody}$	1	[-]	ECHA ESD PT 19; default value
Active substance in the product	$Cform_{weight}$	300	g/kg	Swiss RPC, Annex Table A1
Consumption per application	$Qform_{appl}$	0.6	mg/cm^2	ECHA ESD PT 19; Table 3.6
Treated area of human skin or garments	$AREA_{skin/garments}$	10660	cm^2	ECHA ESD PT 19; Table 3.3 Head+Arms+Hands+Legs+Feet
Specific density of the product	RHOform	1000	kg/m^3	ECHA ESD PT 19; default value
Volume of water body	$V_{waterbody}$	435000	m^3	ECHA ESD PT 19; default value
First order rate constant for biodegradation in surface water	$kdeg_{water}$	0.047	d^{-1}	TGD 2003, Table 7
Number of emission days (emission period of 1 day)	$T_{emission,1d}$	1	d	ECHA ESD PT 19; default value
Number of emission days (emission period of 91 days)	$T_{emission,91d}$	91	d	ECHA ESD PT 19; default value
Number of emission events	$N_{emission,91d}$	91	[-]	ECHA ESD PT 19; default value
Output				
Local emission rate to surface water	$Elocal_{water}$	**0.058**	kg/d	$Elocal_{water} = N_{swimmer} * N_{appl} * Qform_{appl} * AREA_{skin} * Cform_{weight} * F_{swim} * F_{waterbody} * 10^{-9}$
Local concentration in water body after one day	$Clocal_{water,1d}$	**0.0001**	mg/L	$Clocal_{water,1d} = Elocal_{water} * 10^3 * T_{emission,1d} / V_{waterbody}$
Local concentration in water body over 91 days	$Clocal_{water,91d}$	**0.0120**	mg/L	$Clocal_{water,91d} = Elocal_{water} * 10^3 * T_{emission,91d} / V_{waterbody}$
Refined local concentration in water body over 91 days (including degradation)	$Clocal_{water,91d\text{-}ref}$	**0.0028**	mg/L	$Clocal_{water,91d\text{-}ref} = Clocal_{water,1d} * \{ [1-(e^{-kdegwater * Temission,1d})^{Nemission,91d}] / [1-e^{-kdegwater * Temission,1d}] \}$

6.1.3 Emission from Use on Animal Skin

The emission due to application of DEET containing products on animals as described in the assessment report (ECHA, CAR 2010) is addressed in this section. Specifically, Table 9 estimates the release of DEET used on equine skin due to spray drift and the resulting concentration in a surface water body with a flow of 25920 m^3/d (300 L/s). The reference product used in this case contains 5 % DEET and is sprayed on 50 horses. A total emission rate of ca. 2 g per day and an estimated local concentration of 70 ng/L in the surface water results from this scenario.

Table 9: Emission scenario for calculating the release of repellents used on horse skin due to spray drift – emission to paved ground and calculation of resulting surface water concentrations (ECHA ESD PT19, 2015; Table 3-12 & 3-13).

Parameter	Symbol	Value	Unit	Reference/ Explanation
Number of horses	N_{horses}	50	[-]	ECHA ESD PT 19; default value
Fraction released to water by spray drift	F_{water}	0.1	[-]	ECHA ESD PT 19; default value
Active substance in the product	$Cform_{weight}$	50	g/kg	Swiss RPC, Annex Table A2 animal use
Consumption per application	$Qform_{appl}$	0.6	mg/cm^2	ECHA ESD PT 19; Table 3.6
Number of applications per day	N_{appl}	1	d^{-1}	ECHA ESD PT 19; default value
Treated area of skin	$AREA_{skin}$	58300	cm^2	ECHA ESD PT 19; Table 3.9
Fraction of riders treating the complete horse	F_{rider}	0.2	[-]	ECHA ESD PT 19; default value
Volume of receiving water body	$FLOW_{surfacewater}$	25920	m^3/d	ECHA ESD PT 19; default value
Output				
Local emission rate to wastewater	$Elocal_{water}$	**0.0017**	kg/d	$Elocalwater = N_{horses} * N_{appl} * Q_{formappl} * AREA_{skin} * Cform_{weight} * F_{rider} * F_{water} * 10^{-9}$
Local concentration in surface water	$Clocal_{water}$	**6.7E-05**	mg/L	$Clocal_{water} = Elocal_{water} / FLOW_{surfacewater} * 10^3$

6.2 Comparison of ESD Estimations with Swiss Monitoring Data

6.2.1 Emission Rates

In this section, the emission rates calculated according to the ESD are compared to the Swiss monitoring data presented in Chapter 4. For this purpose, the results from the ESD scenarios are first aggregated and normalized. All ESD estimates are converted to an emission rate per capita, i.e. daily load per capita.

Figure 20 shows the daily loads per capita to surface waters from the ESD scenarios:

a. Emission to WWTP from human use – 6.1.1
b. Direct emission from human use due to swimming – 6.1.2
c. Emission from use on horse skin due to spray drift – 6.1.3

For the emission to WWTP from human use, an average WWTP degradation of 73 % (Chapter 4.2.5) was applied to determine the daily load released to surface water. Moreover, the emission from use on horse skin is normalized by considering the number of horses per inhabitant in Switzerland (Statista, 2019).

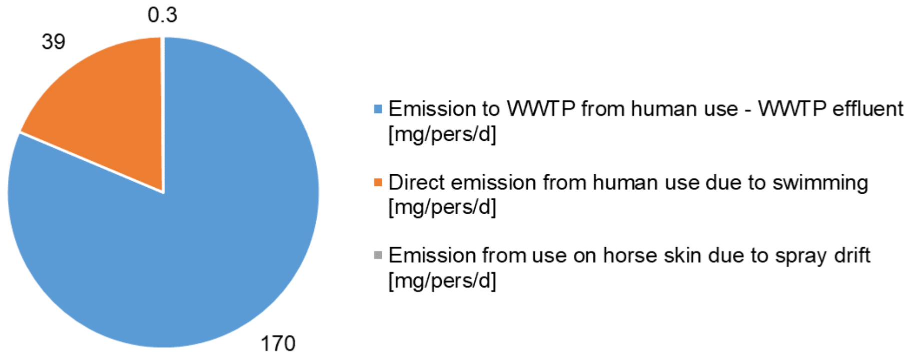

Figure 20: Normalized DEET emission rates per capita emitted to surface water based on the ESD for product type 19.

According to the calculated ESD scenarios, most DEET is released to the environment through WWTP effluents (ca. 80 %; Figure 20). This observation is in agreement with Swiss monitoring data. Direct emissions from human use due to swimming only accounts for ca. 20 % of the total emissions and the release of DEET used on horse skin appears to be negligible (<0.5 %). A total emission rate of 210 mg per person and day results from all the calculated ESD combined.

The comparison of the ESD estimates with Swiss monitoring data clearly demonstrates that the ESD provide a worst-case scenario. The total estimated emission rate to surface water of 210 mg per capita and day from all ESD combined is about 1500 times higher than the average 140 µg per capita and day observed in the river Rhine at the RÜS measuring station (Chapter 5.1). Further, the estimated ESD emission rate of 170 mg per capita and day in WWTP effluents is about 1700 times higher than the average 100 µg per capita and day observed in Swiss and German WWTP effluents and ca. 80 times higher compared to the largest emission rate per capita observed in a single

WWTP effluent sample (Chapter 4.2.2). Extrapolated to the whole Swiss population, the ESD emission rate would indicate an emission of more than 650 tons DEET per year, more than the total estimated import of DEET in Europe (ca. 400 tons, Chapter 3). The large difference between ESD scenarios estimates and monitoring data is illustrated in Figure 21.

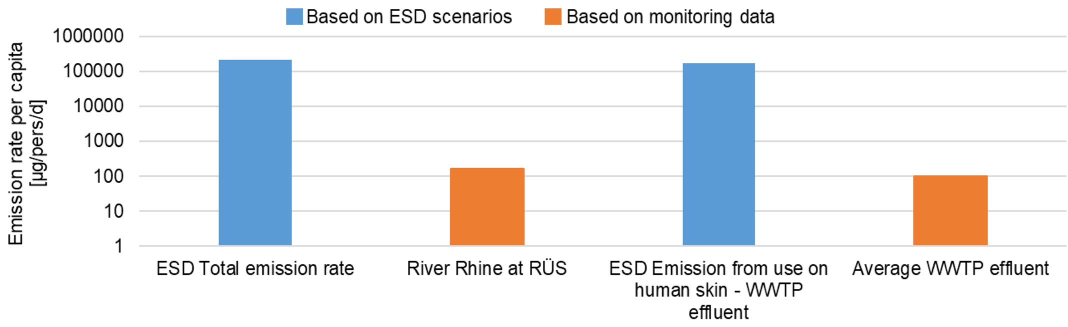

Figure 21: Comparison of ESD emission rates with Swiss monitoring data. Please note the logarithmic scale of the y-axis.

6.2.2 Concentrations

In the ESD concentrations in local surface water arising from direct emission into surface water from human use due to swimming in a water body and from the application on animals are also estimated. In the following, these estimates are compared with measured concentrations in Swiss surface waters.

The ESD scenario for direct emission into surface water from human use due to swimming in a water body of 435000 m^3 leads to a concentration of 12 µg/L after 91 days of consecutive swimming by 1500 people, assuming no degradation. Accounting for degradation results in a concentration of about 3 µg/L. The estimate concentration after one single day of swimming is 0.1 µg/L (see Chapter 6.1.2).

The use of DEET on 50 horses leads to a concentration of ca. 0.07 µg/L in a river with a flow of about 26'000 m^3/d according to the ESD scenario for the release of DEET due to spray drift (see Chapter 6.1.3).

This report does not include monitoring data for lakes or rivers of similar size for whose only source of DEET is proven to be human swimming or emissions from equine applications. Nevertheless, Table 10 compares the concentrations based on ESD calculations presented in this paragraph with the real concentrations in samples of Swiss lakes and rivers with multiple sources of DEET presented in Chapter 4.1.1 and 4.1.2. The ESD concentration estimates are presented as a percentile rank of the monitoring environmental concentrations.

It can be seen that all ESD estimate concentrations are higher than the concentrations measured in Swiss lakes. Even the lowest ESD estimate of 0.07 µg/L resulting from the emission scenario from application on horse skin was still 3.5 times higher than the largest DEET concentration in the lake water samples. The ESD scenario for direct emission from human use due to swimming after 91 days without degradation also had a concentration above all river water samples, while only six river water samples showed larger concentrations if degradation is included (99.6 percentile rank). Finally, 89 % of river water samples concentrations were below the ESD estimate for emissions from human use due to swimming after 1 day and 81 % were below the ESD estimate for emissions from use on horse skin. In summary the ESD provide a rather conservative approach for the estimation of concentrations in Swiss surface waters.

Table 10: Comparison of measured DEET concentrations in Swiss rivers and lakes with estimate concentrations from the ESD for product type 19. The ESD concentrations are expressed as a percentile rank of the measured environmental concentrations.

	ESD concentration [µg/L]	Percentile rank compared to measured concentrations in	
Direct emission from human use due to swimming[1]		**Swiss rivers[3] [%]**	**Swiss lakes[4] [%]**
Local concentration in water body after 1 day	0.1	89	100
Local concentration in water body after 91 days	12	100	100
Local concentration in water body after 91 days (including degradation)	2.8	99.6	100
Emission from use on horse skin due to spray drift[2]			
Local concentration in surface water	0.07	81	100

[1]ECHA ESD PT19, 2015; Table 3-7 & 3-8. [2]ECHA ESD PT19, 2015; Table 3-12 & 3-13. [3]FOEN, AWEL, AWE, Annex Table A2, A3, A4 (2887 samples, 91 sampling sites) [4]Götz et al., 2015 & Singer et al., 2009 (18 samples, 5 lakes).

6.3 Potential Refinements

Based on the results of the environmental monitoring, product research and market data refinements for DEET's ESD can be proposed for Switzerland. The refinements of these parameters are not intended to render the ESD estimate less conservative, but rather to adapt these estimates for a better characterization of DEET emission in Switzerland. The application of precautionary principle for product assessment is still recommended and current ESD provide an appropriate characterization of DEET emissions in this sense. Table 11 summarizes possible refinements to the input parameters.

Fraction of inhabitants using a repellent product

Based on the mass balance for DEET (Chapter 5), the yearly Swiss consumption of DEET is likely in the range of 2 to 12 tons. Based on a worst-case estimate of 12 tons and ignoring any consumption for animals, this would correspond to an annual use in Switzerland of one bottle by ca. 3 % of the population (270'000 bottles, 150 ml, 30 % DEET). For this reason, the fraction of inhabitants using a repellent products has been refined from 0.37 to 0.03 for the ESD scenario for emissions to WWTP from human use. Reducing the fraction of inhabitants using a repellent product from 37 % to 3 % reduces the emission rate of the ESD for emissions to WWTP from human use by 92 %.

According to DEET's ESD for emissions to WWTP from human use (ECHA ESD PT19, 2015, Table 3-6), an application of 0.6 mg/cm^2 twice a day on an area of 10'660 cm^2 (head, arms, hands, legs and feet) is considered for human use. This corresponds to a daily consumption of approximately 3.8 g DEET per person or about one-twelfth of a 150 ml bottle containing 30 % DEET. Even with only 3 % of the population using DEET, these parameters imply a Swiss daily consumption of ca. 1 ton DEET. In other words, the estimated Swiss annual consumption of 12 tons DEET (worst-case) would be exceeded in just under 2 weeks. For this reason, it is suggested to refine the consumption per application, the number of applications per day and the total area of human skin or garment treated.

Treated area

The treated area is reduced from 10'660 cm^2 (head, arms, hands, legs and feet) to arms, legs and hands only (8420 cm^2), this since the head is usually not treated, nor are the feet or at least the entirety of the legs. Refining the treated area from 10'660 cm^2 to 8420 cm^2 reduces the emission rates of the ESD for emissions to WWTP from human use as well as the emission rate and concentration in the water body of the ESD for direct emissions due to swimming by 21 %.

Consumption per application and number of applications per day

For this project, one of the best-selling DEET containing product available in Switzerland was tested. The product is generally packed in a 150 ml spray bottle. It was empirically determined that the volume contained in one bottle is sufficient for about 1000 individual activations of the spray bottle. According to the established ESD parameters for product type 19, a consumption per application of 0.6 mg/cm^2 twice a day on a surface of 10'660 cm^2 is assumed, which is equivalent to ca. 12.8 g product or about one-twelfth of a 150 ml bottle per day. Accordingly, this amount also corresponds to approximately 85 daily spray activations per person of the tested product. The actual use of 85 daily sprays by an average consumer is regarded as unlikely, with a lower consumption being more probable. The consumption per application is therefore tentatively reduced to 0.30 mg/cm^2 once a day only, instead of 0.60 mg/cm^2 twice a day, so that one bottle (150 ml, 30 % DEET) would last on average 60 days (i.e. about 17 spray activations per day)[4]. For a more accurate estimate, the consumer behavior during the application of DEET products should be studied. The discussed change in the consumption amount per application and number of applications per day would reduce the emission rate of the ESD for emissions to WWTP from human use by 75% and the emission rate and concentration in the water body of the ESD for direct emissions due to swimming by 50 %[5].

Including all above indicated refinements, the estimated Swiss domestic consumption of 12 tons (worst-case) is reached in about 2 months of continuous use by 3 % of the population using the ESD scenario for emission to WWTP from human use.

[4] The 17 spray activations per day were calculated using a refined application area of 8420 cm^2.
[5] In the case of the ESD for direct emissions from human use due to swimming the default number of applications per day is already set to 1.

Table 11: Proposed refinements of the parameters for DEET's ESD for product type 19. [1]ECHA ESD PT19, 2015.

ESD Variable/Parameter	Symbol	Original value[1]	Refined value
Fraction of inhabitants using a repellent product	F_{inh}	0.37	0.03
Consumption per application	$Qform_{appl}$	0.6 mg/cm²	0.3 mg/cm²
Number of applications per day	N_{appl}	2 d^{-1}	1 d^{-1}
Treated area of human skin or garments	$AREA_{skin/garments}$	10660 cm²	8420 cm²

Presented below in Table 12 are the results of the ESD calculations for DEET emissions to WWTP from human use (6.1.1) and direct emission from human use due to swimming (6.1.2) with revised parameters. These are compared with the ESD using the established parameters (ECHA ESD PT19, 2015; ECHA, CAR 2010).

The emissions to WWTP from human use using the refined parameters for Switzerland are about 60-times smaller compared to the scenario using the established parameters, while direct emissions from human use due to swimming are about 2.5 times smaller. However, it should be noticed that even accounting for the proposed refinements the normalized emissions rates to surface water are still one to two orders of magnitude larger than emission rates per capita observed in WWTP effluents (100 ug/pers/d; Chapter 4.2.2). The ESD for use on horse skin due to spray drift is not considered as no parameter refinement is proposed.

Table 12: DEET Emission rates based on ESD calculations using established input parameters (ECHA ESD PT19, 2015; ECHA, CAR 2010) compared to the same calculations with refined parameters for Switzerland. [1]Assuming 73 % WWTP degradation (Chapter 4.2.5).

ESD Parameter	Emissions to WWTP from human use		Direct emission from human use due to swimming	
	Original	Refined	Original	Refined
Local emission rate to WWTP/ Surface water	6.3 kg/d	0.10 kg/d	0.058 kg/d	0.023 kg/d
Local emission rate per capita to surface water[1]	170 mg/pers/d	3 mg/pers/d	39 mg/pers/d	15 mg/pers/d

7 Conclusions

Analysis of Swiss monitoring data, particularly from the Rhine River, indicates an annual Swiss consumption of 2 tons of DEET, which is consistent with the estimate of 2 to 12 tons of DEET estimated from production data provided by DEET manufacturers, distributers and formulators. These values provide a first indicative mass balance for DEET in Switzerland and demonstrate that, from a mass balance perspective, the widespread detection of DEET in Swiss waters can be corroborated by consumption of DEET as an insect repellent alone. Other potential sources of DEET as well as analytical mimics were researched in literature and discussed in consultation with DEET manufacturers, material scientist, federal and cantonal authorities and laboratories, but could not be identified for Switzerland. Some indication of the possible presence of DEET or an analytical mimic in plastics is suspected, but further detailed investigations would be required to test the validity as well as relevance of this thesis.

Questions remain about the temporal distribution of DEET in the environment, which is frequently detected in the winter months despite its supposed seasonal use, and for which no conclusive explanation could be identified. Several hypotheses have been formulated in this regard, suggesting that this could be due to a combination of factors. One aspect likely contributing to this observation is the washing of garments sprayed with DEET by Swiss tourists returning from vacations in warm countries during the Swiss winter. In fact, there are indications that most DEET purchased in Switzerland is applied abroad. Another factor contributing to the detection of DEET in environmental samples during wintertime is likely the buffer capacity of lakes, which can lead to continuous emission of DEET to tributaries during the year.

The relevance of industrial emission of DEET was also investigate in this report. Although several evidence of point source emissions of up to 2.8 kg DEET probably originating from formulation activity were identified in the past, effective mitigation measures at the source have been implemented in recent years. This has likely contributed to the observed decline in peak emission of DEET in the Rhine over the last decade, although no direct link between these peaks and point source emissions from formulators could be explicitly demonstrated. The total contribution of point source emissions from DEET is estimated to be about 10 % compared to emissions from human and animal use, even though the quantity of DEET processed in Switzerland is certainly larger than the Swiss consumption of DEET due to export of DEET containing products.

Finally, established environmental risk assessment models used in the EU and CH (ECHA ESD PT19) were compared with the occurrence of DEET in the Swiss aquatic environment. The ESD-based environmental risk assessment significantly overestimates the release and occurrence of DEET in surface water and therefore provides a worst-case scenario that is consistent with the precautionary principle. In summary, this report provided a characterization of DEET occurrence in Swiss waters as well as DEET Swiss consumption to extrapolate a first indicative mass balance of DEET for Switzerland and compare this to established models for environmental risk assessment (ESD). This approach could be exemplary for other biocidal products whose emissions and occurrence in Switzerland are unclear and which are characterized by higher ecotoxicity than DEET.

8 Acknowledgements

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Appendix

Table A 1: DEET containing biocidal products registered in CH (Swiss RPC extract June 2021) *Data anonymised.

Name*	Application	Company*	Canton	% DEET
Product 1	Animal	Company 1	AG	5
Product 2	Animal	Company 1	AG	5-10
Product 3	Animal	Company 2	AG	8
Product 4	Animal	Company 2	AG	5.5
Product 5	Animal	Company 3	BE	0.5
Product 6	Animal	Company 4	BE	5
Product 7	Animal	Company 5	BE	5
Product 8	Animal	Company 6	BL	5.5
Product 9	Animal	Company 7	BS	30
Product 10	Human	Company 7	BS	30
Product 11	Human	Company 7	BS	9.5
Product 12	Human	Company 8	FR	30
Product 13	Human	Company 8	FR	15
Product 14	Animal	Company 9	LU	8
Product 15	Animal	Company 10	LU	5
Product 16	Animal	Company 10	LU	5
Product 17	Animal	Company 10	LU	5
Product 18	Animal	Company 11	LU	5
Product 19	NA	Company 12	SZ	NA
Product 20	Human	Company 13	TG	30
Product 21	Human	Company 14	TG	30
Product 22	Surfaces	Company 15	VD	1.2
Product 23	Animal	Company 16	VD	5
Product 24	Human	Company 17	VD	25
Product 25	Human	Company 18	ZG	30
Product 26	Animal	Company 19	ZG	2.5-5
Product 27	Human	Company 20	ZH	30-35
Product 28	Human	Company 20	ZH	50-55
Product 29	Human	Company 21	ZH	25
Product 30	Human	Company 21	ZH	20
Product 31	Human	Company 21	ZH	20

Product 32	Human	Company 21	ZH	25
Product 33	Animal	Company 22	ZH	5.5
Product 34	Human	Company 23	BE	30
Product 35	Human	Company 24	BE	50
Product 36	Human	Company 25	BE	50
Product 37	Human	Company 26	FR	50
Product 38	Human	Company 27	NL	40
Product 39	Human	Company 27	NL	50
Product 40	Human	Company 28	BE	NA
Product 41	Human	Company 28	BE	40

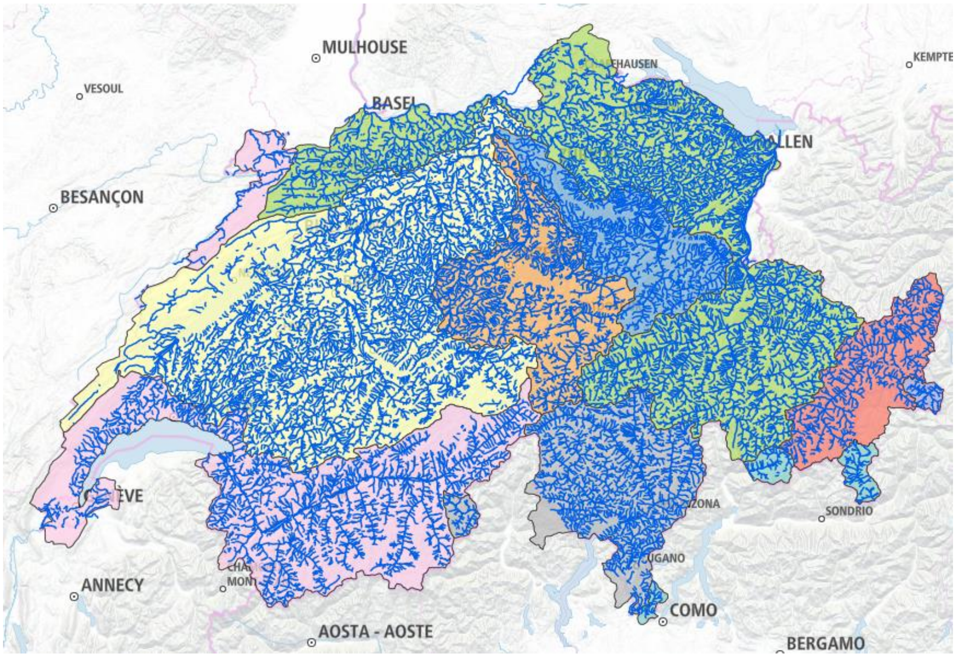

Figure A1: Rhine main catchment area (green), Aare (yellow), Reuss (orange) und Limmat (blue).

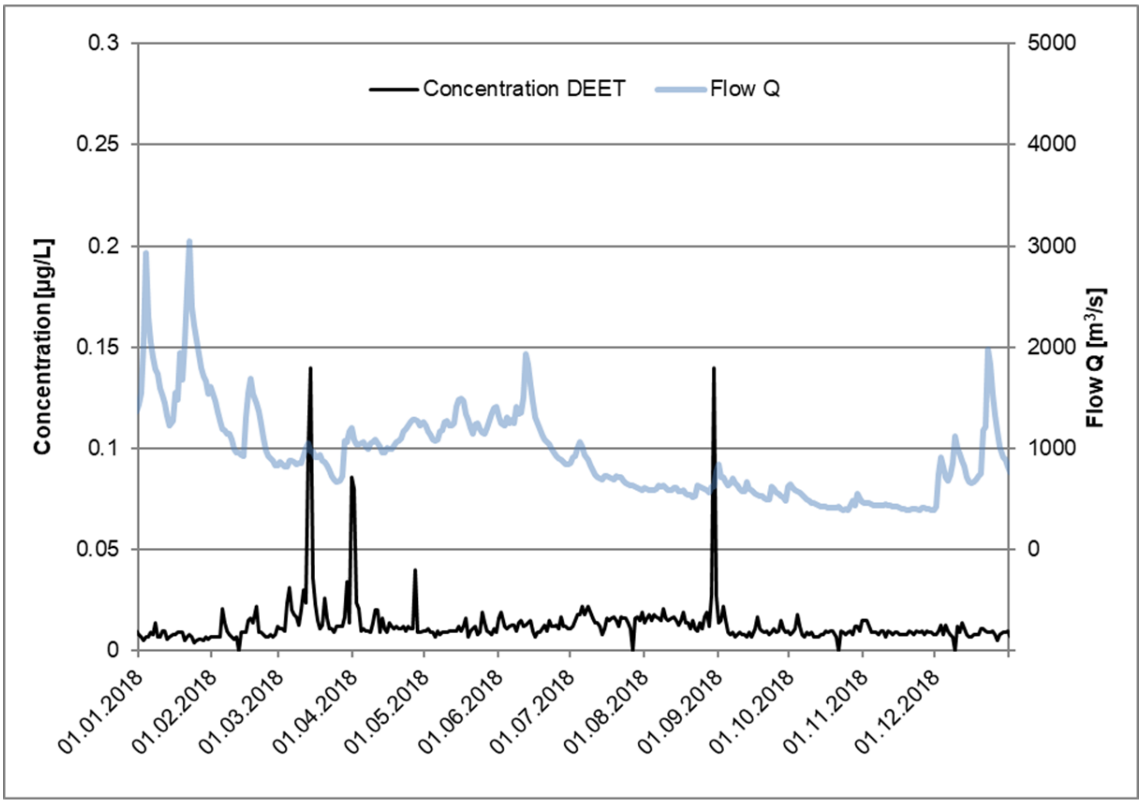

Figure A2: Daily variability of DEET concentrations for 2018 in the river Rhine at sampling point RÜS and water flow.

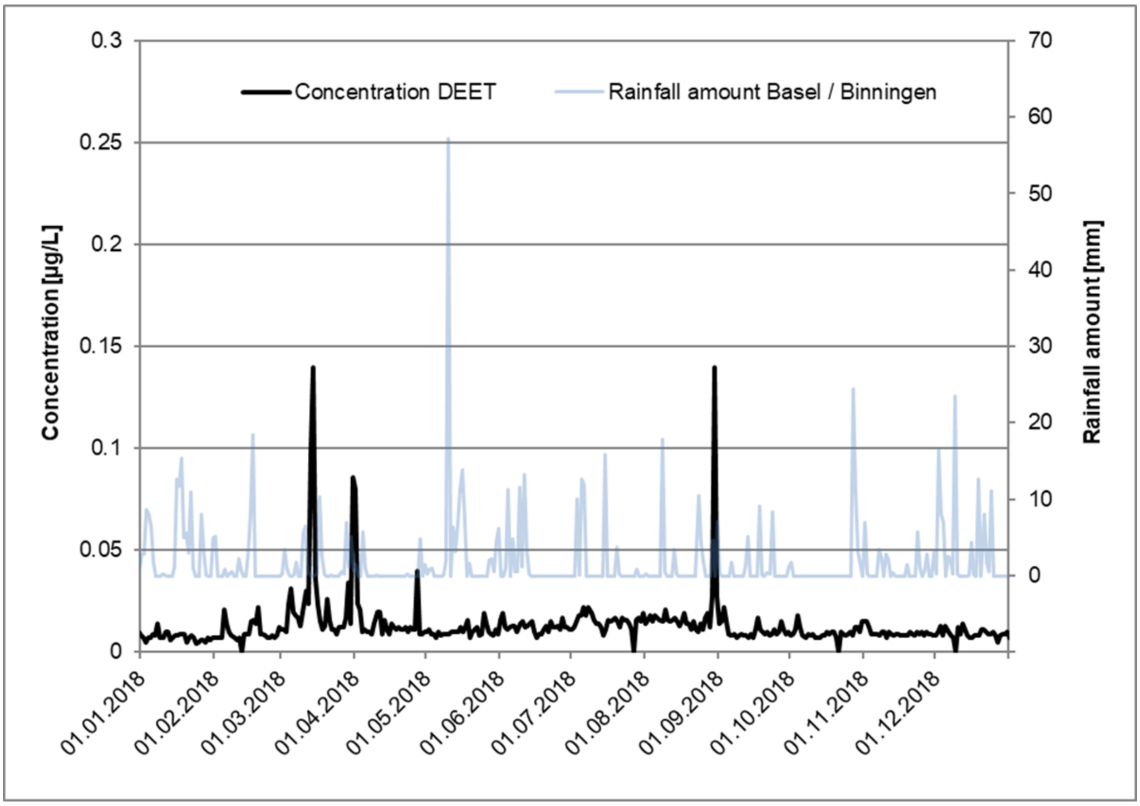

Figure A3: Daily variability of DEET concentrations for 2018 in the river Rhine at sampling point RÜS and rainfall amount.

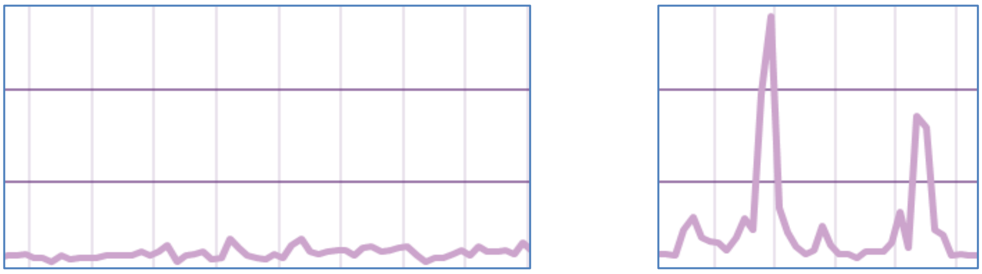

Figure A4: Examples of basis emissions (left) vs. peak emission >0.3 µg/L (right) profiles.

Figure A5: Spatial distribution of the groundwater sampling sites in the canton in Zürich where DEET was detected (AWEL, map: Stadt Zürich).

Table A2: Approximated/extrapolated DEET Loads estimated based on measurements from AWEL, Zürich.

Station/River name	Period	Ø DEET-conc. [µg/L]	Ø Flow Q [m^3/s]	DEET-Load [kg/a]	Reference flow values
Furtbach vor Trockenloo-Kanal	2019	0.016	0.17	0.09	map.geo.admin
Furtbach nach ARA Buchs	2019	0.075	0.48	1.14	map.geo.admin
Aabach vor Gossauer-bach	2018	0.005	0.41	0.06	map.geo.admin
Furtbach nach ARA Re-gensdorf	2019	0.073	0.27	0.62	map.geo.admin
Hofibach vor Hedigen	2019	0.006	0.12	0.02	map.geo.admin
Riedikerbach bei Riedi-kon	2018	0.088	0.23	0.63	map.geo.admin
Breitwiesenkanal vor Furtbach	2019	0.014	-		
Mülibach vor Furtbach	2019	0.004	-		
Bännengraben vor Furt-bach	2019	0.002	-		
Oberwiesenbach vor Furtbach	2019	0.001	-		
Harberenbach vor Furt-bach	2019	0.019	-		
Katzenbach vor Leutschenbach	2018	0.011	-		
Chimlibach vor Glatt	2018	0.018	0.26	0.15	map.geo.admin
Leutschenbach bei SF	2018	0.020	0.42	0.26	map.geo.admin
Töss bei Rämismühle (Zell)	2015-19	0.029	3.42	3.07	map.geo.admin
Töss bei Freienstein	2010 + 2015-19	0.028	9.19	8.01	map.geo.admin
Kempt vor Töss	2015-19	0.025	1.28	0.99	map.geo.admin
Eulach vor Töss	2015-19	0.053	1.88	3.11	map.geo.admin
Glatt Abfluss Greifensee	2015-19	0.040	3.95	4.92	map.geo.admin
Glatt bei Oberglatt	2015-17	0.051	7.17	11.49	map.geo.admin
Glatt vor Rhine	2012 + 2015-19	0.058	8.40	15.35	map.geo.admin
Limmat Hönggersteg (Zürich)	2015-19	0.008	86.42	20.44	AWEL Messdaten
Limmat bei Dietikon EKZ	2015-17	0.012	92.34	33.97	AWEL Messdaten
Sihl beim Sihlhölzli (Zü-rich)	2015-19	0.079	13.20	32.89	map.geo.admin
Reppisch bei Dietikon	2015-19	0.069	0.84	1.83	AWEL Messdaten
Furtbach bei Würenlos	2011 + 2014-19	0.063	0.91	1.80	map.geo.admin
Aa bei Niederuster	2015-19	0.063	1.73	3.42	map.geo.admin
Aabach bei Mönchaltorf	2010-11 + 2013 + 2015-19	0.062	1.17	2.27	map.geo.admin
Jonen nach ARA Zwilli-kon	2015-19	0.452	0.79	11.27	map.geo.admin
Jona nach Rüti	2015-19	0.020	2.44	1.50	map.geo.admin
Thur bei Andelfingen (NADUF)	2018-19	0.020	36.57	23.07	NAWA Daten
Glatt bei Rhinesfelden (NADUF)	2018-19	0.042	8.40	11.16	map.geo.admin

Table A3: DEET concentrations in rivers in the canton of St.Gallen (AWE, St.Gallen).

Station name	River	Period	Ø DEET-conc. [µg/L]
Buechental	Glatt (Buechental)	2016 & June 2019-Jan 2021	0.040
Bruggerhorn	Rheintaler Binnen-kanal	2016 & Jan. 2019-Jan.2021	0.030
Golfplatz	Thur	2016 & Sept 2018-Jan 2021	0.068
Berstel	Thur	2016	0.007
Biäsche (Abfluss Walensee)	Linthkanal	2016	0.005
Bruggen-Au	Sitter	2016	0.011
Felsegg	Thur	2016	0.317
Flooz	Thur	2016	0.176
Gäsi (Mollis / Glarus Nord)	Linth	2016	0.005
Glatthalde, nach ARA Ober-glatt	Glatt	June 2016 – Nov 2016	0.042
Grinau Linthkanal	Linthkanal	2016	0.005
Gross Allmeind	rechtss. Hintergraben	2016	0.018
Härti Pt. 412 Aabach	Aabach	2016	0.004
Isenhammer, ob Glatt	Dorfbach Gossau	2016	0.009
Glatt	Isenhammer ob Dorf-bach	2016	0.016
Kubel ob Sitter	Urnäsch	2016	0.008
Leebrugg	Sitter	2016	0.021
Letzi Necker	Necker	2016	0.007
Marina Alter	Rhein	2016	0.026
Mattenhof	Steinach	2016	0.015
Mülau	Thur	2016	0.376
Necker	Necker	2016	0.008
Neumüli	Mülbach	2016	0.017
Pegel Appenzell	Sitter	2016	0.007
Schluch	WBK	2016	0.011
Schwarzenbach	Thur	2016	0.426
Ziegelhütte	Seez	2016	0.005

Table A4: Approximated/extrapolated DEET Loads estimated based on measurements from the National Surface Water Quality Monitoring Programme (NAWA, FOEN). *Best case: for the load calculations values below LOQ were set to 0, in the worst case scenario the values were set equal to the LOQ.

	NAWA Station Nr.	Station name	River	Period	Notes	Ø DEET-conc. (µg/L) best case*	Ø DEET-conc. (µg/L) worst case*	Ø Flow Q (m^3/s)	Ref Q	Estimated DEET-Load [kg/a]
	2078	Weil, Palmrain-brücke	Rhine	2018-19	Mittelwerte über ca. 336 h	0.012	0.012	973	hydrodaten.admin	359.16
	1837	Porte du Scex	Rhone	2018-19	Mittelwerte über ca. 140-180h	0.006	0.006	201	hydrodaten.admin	37.52
	1833	Brugg	Aare	2018-19	Mittelwerte über ca. 240-400h	0.013	0.013	279	hydrodaten.admin	110.83
	6264	Trasadingen	Landgraben	2018-19	Mittelwerte über ca. 336 h	0.058	0.060	0.89	map.geo.admin (Karte mitt-lere Abflüsse)	1.66
#	6265	Beggingen vor ARA	Begginger-bach	2018-19	Mittelwerte über ca. 336 h	0.012	0.017			0.00
	6260	Mettlen, Waldrand	Ballmoosbach	2018	Mittelwerte über ca. 336 h	0.012	0.016	0.09	map.geo.admin (Karte mitt-lere Abflüsse)	0.05
	6259	Chüechumatt	Chrümlisbach	2018	Mittelwerte über ca. 336 h	0.011	0.016	0.08	map.geo.admin (Karte mitt-lere Abflüsse)	0.04
	1064	Otelfingen	Furtbach (ZH)	2018-19	Mittelwerte über ca. 50-430h	0.041	0.066	0.59	NAWA	1.22
	1824	Rheinsfelden	Glatt (ZH)	2018-19	Mittelwerte über ca. 70-360h	0.022	0.055	6.03	hydrodaten.admin	10.40
#	6272	Hochdorf, Sem-pacherstrasse	Ron	2018-19	Mittelwerte über ca. 260-360h	0.001	0.001	0.55	map.geo.admin (Karte mitt-lere Abflüsse)	0.17
	6270	Aval Canal d'U-vrier, Batassé	Canal D'U-vrier	2018	Mittelwerte über ca. 336 h	0.001	0.020	0.50	NAWA	0.31
	3206	Agno, Muzzano	Vedeggio	2018-19	Mittelwerte über ca. 170-336h	0.010	0.050	3.01	NAWA	5.06
	2103	Lac	Boiron-de-Morges	2018	Mittelwerte über ca. 300-360h	0.084	0.084	0.34	NAWA	0.91
	6261	La Vounaise	Bainoz	2018	Mittelwerte über ca. 336 h	0.012	0.018	0.08	map.geo.admin (Karte mitt-lere Abflüsse)	0.05
	1096	Andelfingen, Brücke	Thur	2018-19	Mittelwerte über ca. 70-430h	0.011	0.045	37	NAWA	51.67
#	6267	Amriswil, vor ARA	Salmsacher Aach	Jun 2018- Dez 2019	Mittelwerte über ca. 60-336h	0.015	0.017	0.36	map.geo.admin (Karte mitt-lere Abflüsse)	0.19
#	6266	Moosburg	Eschelisbach	Jul 2018 - Dez 2019	Mittelwerte über ca. 60-336h	0.012	0.013			0.00
	6257	Künten	Küntenerbach	Sept 2018 - Dez 2019	Mittelwerte über ca. 84-336h	0.046	0.046	0.08	map.geo.admin (Karte mitt-lere Abflüsse)	0.11
	4331	Ob RBK, Bernecker Riet	Zapfenbach	Sept 2018 - Dez 2019	Mittelwerte über ca. 170-336h	0.036	0.037	0.40	NAWA	0.47

#	6263	Balgacher Riet	Mittlerer See-graben	Sept 2018 - Dez 2019	Mittelwerte über ca. 336 h	0.030	0.031	0.11	map.geo.admin (Karte mitt-lere Abflüsse)	0.11
	6262	Fregiécourt, laiterie	Erveratte	2019	Mittelwerte über ca. 336 h	0	0.05	0.18	map.geo.admin (Karte mitt-lere Abflüsse)	0.28
	1072	Mönchaltorf	Aabach (ZH)	2019	Mittelwerte über ca. 70-336h	0.031	0.059	0.78	NAWA	1.44
	6402	Schleitheim	Zwärenbach	2019	Mittelwerte über ca. 336 h	0.004	0.004	0.16	map.geo.admin (Karte mitt-lere Abflüsse)	0.02
	4330	Au, ob RBK Zing-gen	Äächeli	2019	Mittelwerte über ca. 84 h	0.011	0.014	0.06	map.geo.admin (Karte mitt-lere Abflüsse)	0.03
#	6269	Pampigny, Le Se-lier	Le Com-bagnou	Mai 2019 - Dez 2019	Mittelwerte über ca. 70-336h	0.073	0.073	0.09	map.geo.admin (Karte mitt-lere Abflüsse)	0.21
	6268	Amont Mau-guettaz	Ruisseau de Gi	Mai 2019 - Dez 2019	Mittelwerte über ca. 70-336h	0.075	0.075	1.60	map.geo.admin (Karte mitt-lere Abflüsse)	3.78
	2885	Birskopf	Birs	Mai 2019 - Dez 2019	Mittelwerte über ca. 260-340h	0.015	0.015	15.74	NAWA	7.65
	1291	Kyburg	Limpach	April 2012- Juli 2012	Mittelwerte über ca. 336 h	0.025	0.025	1.61	map.geo.admin (Karte mitt-lere Abflüsse)	1.28
	1064	Otelfingen	Furtbach (ZH)	April 2012- Juli 2012	Mittelwerte über ca. 336 h	0.101	0.100	0.11	map.geo.admin (Karte mitt-lere Abflüsse)	0.35
	1402	Salmsach	Salmsacher Aach	April 2012- Juli 2012	Mittelwerte über ca. 336 h	0.018	0.022	0.73	map.geo.admin (Karte mitt-lere Abflüsse)	0.50
	2119	La Mauguettaz	Mentue	April 2012- Juli 2012	Mittelwerte über ca. 336 h	0.109	0.109	1.60	map.geo.admin (Karte mitt-lere Abflüsse)	5.49
	1373	Döttingen, bei Pe-gel ALG	Surb	April 2012- Juli 2012	Mittelwerte über ca. 336 h	0.051	0.051	1.04	map.geo.admin (Karte mitt-lere Abflüsse)	1.66

= no close station for flow measurement; used next station with similar flow

Table A5: Overview of all monitoring data used for this project. *Data was provided with the promise of confidentiality and therefore anonymized.

River / WWTP name / Municipality	Sampling station	Water body type	Resolution	Period	Sample Type	Data source	Nr. samples	LOQ [ug/L]
Rhein	Weil am Rhein	Surface water	24h	2010-2019	Composite sample	RÜS	3651	0.003
Rhein	Weil, Palmrainbrücke	Surface water	336 h	2018-19	Composite sample	BAFU (NAWA)	52	0.001
Rhone	Porte du Scex	Surface water	140-180h	2018-19	Composite sample	BAFU (NAWA)	101	0.001
Aare	Brugg	Surface water	240-400h	2018-19	Composite sample	BAFU (NAWA)	52	0.001
Landgraben	Trasadingen	Surface water	336 h	2018-19	Composite sample	BAFU (NAWA)	53	0.016
Beggingerbach	Beggingen vor ARA	Surface water	336 h	2018-19	Composite sample	BAFU (NAWA)	80	0.016
Ballmoosbach	Mettlen, Waldrand	Surface water	336 h	2018	Composite sample	BAFU (NAWA)	26	0.01
Chrümlisbach	Chüechumatt	Surface water	336 h	2018	Composite sample	BAFU (NAWA)	26	0.01
Furtbach (ZH)	Otelfingen	Surface water	50-430h	2018-19	Composite sample	BAFU (NAWA)	9	0.007
Glatt (ZH)	Rheinsfelden	Surface water	70-360h	2018-19	Composite sample	BAFU (NAWA)	78	0.05
Ron	Hochdorf, Sempa-cherstrasse	Surface water	260-360h	2018-19	Composite sample	BAFU (NAWA)	51	0.001
Canal D'Uvrier	Aval Canal d'Uvrier, Ba-tassé	Surface water	336 h	2018	Composite sample	BAFU (NAWA)	23	0.004-0.06
Vedeggio	Agno, Muzzano	Surface water	170-336h	2018-19	Composite sample	BAFU (NAWA)	51	0.05
Boiron-de-Morges	Lac	Surface water	300-360h	2018	Composite sample	BAFU (NAWA)	35	0.009-0.1
Bainoz	La Vounaise	Surface water	336 h	2018	Composite sample	BAFU (NAWA)	27	0.009-0.1
Thur	Andelfingen, Brücke	Surface water	70-430h	2018-19	Composite sample	BAFU (NAWA)	41	0.05
Salmsacher Aach	Amriswil, vor ARA	Surface water	60-336h	Jun 2018- Dez 2019	Composite sample	BAFU (NAWA)	67	0.016
Eschelisbach	Moosburg	Surface water	60-336h	Jul 2018 - Dez 2019	Composite sample	BAFU (NAWA)	65	0.016
Küntenerbach	Künten	Surface water	84-336h	Sept 2018 - Dez 2019	Composite sample	BAFU (NAWA)	33	0.001
Zapfenbach	Ob RBK, Bernecker Riet	Surface water	170-336h	Sept 2018 - Dez 2019	Composite sample	BAFU (NAWA)	58	0.006
Mittlerer Seegraben	Balgacher Riet	Surface water	336 h	Sept 2018 - Dez 2019	Composite sample	BAFU (NAWA)	31	0.006
Erveratte	Fregiécourt, laiterie	Surface water	336 h	2019	Composite sample	BAFU (NAWA)	27	0.05
Aabach (ZH)	Mönchaltorf	Surface water	70-336h	2019	Composite sample	BAFU (NAWA)	50	0.05
Zwärenbach	Schleitheim	Surface water	336 h	2019	Composite sample	BAFU (NAWA)	23	0.016
Äächeli	Au, ob RBK Zinggen	Surface water	84 h	2019	Composite sample	BAFU (NAWA)	50	0.006
Le Combagnou	Pampigny, Le Selier	Surface water	70-336h	Mai 2019 - Dez 2019	Composite sample	BAFU (NAWA)	40	0.02-0.12
Ruisseau de Gi	Amont Mauguettaz	Surface water	70-336h	Mai 2019 - Dez 2019	Composite sample	BAFU (NAWA)	42	0.02-0.12
Birs	Birskopf	Surface water	260-340h	Mai 2019 - Dez 2019	Composite sample	BAFU (NAWA)	16	0.001
Limpach	Kyburg	Surface water	336 h	April 2012- Juli 2012	Composite sample	BAFU (NAWA)	9	0.007
Furtbach (ZH)	Otelfingen	Surface water	336 h	April 2012- Juli 2012	Composite sample	BAFU (NAWA)	79	0.05
Salmsacher Aach	Salmsach	Surface water	336 h	April 2012- Juli 2012	Composite sample	BAFU (NAWA)	1	0.016
Mentue	La Mauguettaz	Surface water	336 h	April 2012- Juli 2012	Composite sample	BAFU (NAWA)	9	0.007
Surb	Döttingen, bei Pegel ALG	Surface water	336 h	April 2012- Juli 2012	Composite sample	BAFU (NAWA)	9	0.007
WWTP Birs	Birs	WWTP Influent & Effluent	72h	17.6 - 19.6.2013 & 20.6 - 22.6.2013	Composite sample	EAWAG	1	0.02 & 0.03
WWTP Brusio	Brusio	WWTP Influent & Effluent	72h	22.5 - 25.5.2013	Composite sample	EAWAG	1	0.02 & 0.03
WWTP Bühler	Bühler	WWTP Influent & Effluent	72h	11.8 - 14.8.2013	Composite sample	EAWAG	1	0.02 & 0.03
WWTP Davos	Davos	WWTP Influent & Effluent	72h	14.7 - 17.7.2013	Composite sample	EAWAG	1	0.02 & 0.03
WWTP Dübendorf	Dübendorf	WWTP Influent & Effluent	72h	14.7 - 17.7.2013	Composite sample	EAWAG	1	0.02 & 0.03

WWTP Erlach	Erlach	WWTP Influent & Effluent	72h	07.7 - 10.7.2013	Composite sample	EAWAG	1	0.02 & 0.03
WWTP Stäfa-Uerikon	Stäfa-Uerikon	WWTP Influent & Effluent	72h	30.6 - 03.7.2013	Composite sample	EAWAG	1	0.02 & 0.03
WWTP Wädenswil	Wädenswil	WWTP Influent & Effluent	72h	30.6 - 03.7.2013	Composite sample	EAWAG	1	0.02 & 0.03
Aa	Aa bei Niederuster	Surface water	168-336h	2015-2019	Composite sample	AWEL	42	0.05
Aabach	Aabach bei Mönchaltorf	Surface water	48h-336h	2010-2019	Composite sample	AWEL	192	0.01 & 0.05
Aabach	Aabach vor Gossauerbach	Surface water	336h	04.2018-09.2018	Composite sample	AWEL	12	0.05
Bännengraben	Bännengraben vor Furt-bach	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Breitwiesenkanal	Breitwiesenkanal vor Furt-bach	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Chimlibach	Chimlibach vor Glatt	Surface water	336h	04.2018-09.2018	Composite sample	AWEL	12	0.05
Eulach	Eulach vor Töss	Surface water	168-336 h	2015-2019	Composite sample	AWEL	20	0.05
Furtbach	Furtbach bei Würenlos	Surface water	48-336h	2011-2019	Composite sample	AWEL	159	0.01 & 0.05
Furtbach	Furtbach nach ARA Buchs	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Furtbach	Furtbach nach ARA Re-gensdorf	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Furtbach	Furtbach vor Trockenloo-Kanal	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Glatt	Glatt Abfluss Greifensee	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Glatt	Glatt bei Oberglatt	Surface water	168h	2015-2017	Composite sample	AWEL	12	0.05
Glatt	Glatt bei Rheinsfelden (NADUF)	Surface water	24-336h	2018-2020	Composite sample	AWEL	66	0.05
Glatt	Glatt vor Rhein	Surface water	168-336h	2012-2019	Composite sample	AWEL	92	0.01 & 0.05
Harberenbach	Harberenbach vor Furtbach	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Hofibach	Hofibach vor Hedigen	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Jona	Jona nach Rüti	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Jonen	Jonen nach ARA Zwillikon	Surface water	168-336h	2015-2019	Composite sample	AWEL	77	0.01 & 0.05
Katzenbach	Katzenbach vor Leutschen-bach	Surface water	336h	04.2018-09.2018	Composite sample	AWEL	12	0.05
Kempt	Kempt vor Töss	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Leutschenbach	Leutschenbach bei SF	Surface water	336h	04.2018-09.2018	Composite sample	AWEL	12	0.05
Limmat	Limmat bei Dietikon EKZ	Surface water	168h	2015-2017	Composite sample	AWEL	12	0.05
Limmat	Limmat Hönggersteg (Zü-rich)	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Mülibach	Mülibach vor Furtbach	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Oberwiesenbach	Oberwiesenbach vor Furt-bach	Surface water	336h	03.2019-10.2019	Composite sample	AWEL	14	0.05
Reppisch	Reppisch bei Dietikon	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Riedikerbach	Riedikerbach bei Riedikon	Surface water	336h	04.2018-09.2018	Composite sample	AWEL	12	0.05
Sihl	Sihl beim Sihlhölzli (Zürich)	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Thur	Thur bei Andelfingen (NADUF)	Surface water	336h	2018-2020	Composite sample	AWEL	41	0.05
Töss	Töss bei Freienstein	Surface water	168-336h	2010-2019	Composite sample	AWEL	55	0.01 & 0.05
Töss	Töss bei Rämismühle (Zell)	Surface water	168-336h	2015-2019	Composite sample	AWEL	20	0.05
Thur	Berstel	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002

Linthkanal	Biäsche (Abfluss Walen-see)	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Sitter	Bruggen-Au	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
RBK	Bruggerhorn	Surface water	Grab sample & 336h	2016 & 01.2019-01.2021	Grab sample & Compo-site sample	AWE	64	0.002 & 0.006
Glatt	Buchental	Surface water	Grab sample & 336h	2016 & 06.2019-01.2021	Grab sample & Compo-site sample	AWE	45	0.002 & 0.006
Thur	Felsegg	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Thur	Flooz	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Linth	Gäsi (Mollis / Glarus Nord)	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Glatt	Glatthalde, nach ARA Oberglatt	Surface water	Grab sample	2016	Grab sample	AWE	3	0.002
Thur	Golfplatz	Surface water	Grab sample & 336h	2016 & 09.2018-01.2021	Grab sample & Compo-site sample	AWE	73	0.002 & 0.006
Linthkanal	Grinau	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
rechtss. Hintergraben	Gross Allmeind	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Aabach	Härti Pt. 412 Aabach	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Dorfbach Gossau	Isenhammer, ob Glatt	Surface water	Grab sample	2016	Grab sample	AWE	15	0.002
Glatt	Isenhammer ob Dorfbach	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Urnäsch	Kubel ob Sitter	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Sitter	Leebrugg	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Necker	Letzi	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Alter Rhein	Marina	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Steinach	Mattenhof	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Thur	Mülau	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Necker	Necker Pt.632	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Mülbach	Neumüli	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Sitter	Pegel Appenzell	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
WBK	Schluch	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Thur	Schwarzenbach	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
Seez	Ziegelhütte	Surface water	Grab sample	2016	Grab sample	AWE	12	0.002
WWTP A*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP B*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP C*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP D*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP E*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP F*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP G*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05

WWTP H*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP I*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP J*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP K*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP L*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP M*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP N*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP O*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP P*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP Q*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP R*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP S*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP T*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP U*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP V*	-	WWTP Effluent	168 h	04.06.-11.06.2018 & 01.10-07.10.2018	Composite sample	AWEL	2	0.05
WWTP Altstätten	Altstätten	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Appenzell (AI)	Appenzell (AI)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Au-Rosenberg-sau	Au-Rosenbergsau	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Bad Ragaz	Bad Ragaz	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Bendern (FL)	Bendern (FL)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Benken	Benken	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Bilten (GL)	Bilten (GL)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Buchs	Buchs	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Bühler-Gais (AR)	Bühler-Gais (AR)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Bütschwil	Bütschwil	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Ebnat-Kappel	Ebnat-Kappel	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Eschenbach	Eschenbach	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Flawil-Oberglatt	Flawil-Oberglatt	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Flums-Seez	Flums-Seez	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05

WWTP Gams	Gams	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Ganterschwil	Ganterschwil	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Hemberg	Hemberg	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Herisau (AR)	Herisau (AR)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Jonschwil-Schwarzenbach	Jonschwil-Schwarzenbach	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Kirchberg-Bazenheid	Kirchberg-Bazenheid	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Neckertal-Tüfi	Neckertal-Tüfi	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Nesslau-Churfirsten	Nesslau-Churfirsten	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Nesslau-Rechenweid	Nesslau-Rechenweid	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Niederbüren	Niederbüren	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Obermarch (SZ)	Obermarch (SZ)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Oberriet	Oberriet	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Quarten-Mittensee	Quarten-Mittensee	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Rapperswil-Jona	Rapperswil-Jona	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Rüthi	Rüthi	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Sargans-Saar	Sargans-Saar	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Schmerikon-Obersee	Schmerikon-Obersee	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Sennwald	Sennwald	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP St.Gallen-Au	St.Gallen-Au	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP St.Gallen-Hofen	St.Gallen-Hofen	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Steinach-Morgental	Steinach-Morgental	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Teufen (AR)	Teufen (AR)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Thal-Altenrhein	Thal-Altenrhein	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Uzwil	Uzwil	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Waldstatt (AR)	Waldstatt (AR)	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Walenstadt	Walenstadt	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Wartau	Wartau	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Wattwil	Wattwil	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Wil	Wil	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Wildhaus-Sägenboden	Wildhaus-Sägenboden	WWTP Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP Zuzwil	Zuzwil	WWTP Influent & Effluent	168h	04.04-11.04-2016	Composite sample	AWE	1	0.05
WWTP KA Stuttgart	KA Stuttgart	WWTP Influent & Effluent	NA	2017-2018	NA	UBA	47	0.01 & 0.05
WWTP KA Geldern	KA Geldern	WWTP Influent & Effluent	NA	2017-2018	NA	UBA	24	0.01 & 0.05
WWTP KA Landsberg	KA Landsberg	WWTP Influent & Effluent	NA	2017-2019	NA	UBA	34	0.01 & 0.05
WWTP KA Eutin	KA Eutin	WWTP Influent & Effluent	NA	2017-2018	NA	UBA	8	0.01 & 0.05
WWTP KA Eppingen	KA Eppingen	WWTP Influent & Effluent	NA	2017-2019	NA	UBA	20	0.01 & 0.05

Adliswil	Soodmatte	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01
Affoltern a.A.	Moos 1	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Andelfingen	Seelenstall	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bachenbülach	Churzäglen	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bachs	Alt-Bachs	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bäretswil	Bussental 2	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bassersdorf	Baltenswil	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Bassersdorf	Schützenhaus	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bauma	Schwendi	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Birmensdorf	Schüren	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bubikon	Sennwald	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bülach	Herrenwies	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Dinhard	Vordergrüt	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Dorf	Roswis (Volken)	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Dürnten	Feldhof	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Eglisau	Stadtforen	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Elgg	Aadorferfeld (Hagenbuch)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Elsau	Schottikon	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Embrach	Kellersacker	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Fehraltdorf	Barmatt	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Flaach	Rheinhölzli	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Flurlingen	Kühles Thal	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	16	0.01 & 0.02
Gossau	Seewadel	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Gossau	Männetsried	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Hausen a. A.	Stäpfer	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Herrliberg	Tambel	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Hinwil	Moos	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Hinwil	Moos / Bachtel (Nr. 64)	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Hirzel	Spitzen	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Horgen	Tugstein	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Höri	Sali	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Kloten	Gerlisberg (Chüelimaas)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Kloten	Thal	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Küsnacht	Schmalzgrueb	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	18	0.01 & 0.02
Laufen-Uhwiesen	Chressen	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Lindau	Lindau	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	25	0.01 & 0.02
Maschwanden	Bibellos	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Mettmenstetten	Wissenbach (Knonau)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Neerach	Im Grund (Stein-maurstrasse)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Neftenbach	Hofstetten	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Niederhasli	Fahrn	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	20	0.01 & 0.02
Niederweningen	Huebwies	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	8	0.01 & 0.02
Oberembrach	Steinacker	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Oberglatt	Hofstetten	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Obfelden	Mettenholz	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	13	0.01 & 0.02

Opfikon	Eichlibrunnen	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Pfäffikon	Mettlen	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Pfäffikon	Büel	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Regensdorf	Altburg	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	20	0.01 & 0.02
Regensdorf	Adlikon	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rheinau	Seewerben	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rickenbach	Oberholz	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	11	0.01 & 0.02
Rifferswil	Sutermatten	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rorbas	Geissberg (Hard)	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Rümlang	Schmidbreiten	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Russikon	Riet	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rüti	Reckholderboden	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	8	0.01 & 0.02
Schlieren	Betschenrohr 2	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Schlieren	Risi	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Schöfflisdorf	Surbwies	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Seuzach	Wiesental (Hettlingen)	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	24	0.01 & 0.02
Stadel	Twerweg	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Trüllikon	Kohlplatz	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Trüllikon	Sperdikler	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Turbenthal	Gmeiwerch	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Unterengstringen	Schanzen	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Uster	Nänikon	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Uster	Mühleholz	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Volketswil	Giessen	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Volketswil	Hegnau	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Wallisellen	Einfang	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Waltalingen	Storchenacker 1	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	13	0.01 & 0.02
Wangen-Brüttisellen	Stiegenhof	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Wangen-Brüttisellen	Schlue	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Wangen-Brüttisellen	Büel	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	19	0.01 & 0.02
Weiach	Griessgraben	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Weisslingen	Chalcheren	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Wetzikon	Feld	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Wiesendangen	Rietacker	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Winterthur	Hard	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	15	0.01 & 0.02
Zürich	Erdbebenwarte 3R	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	9	0.01 & 0.02
Zürich	Burgwies-Wehrenbach G	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Bertschikon	Zünikon	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Birmensdorf	Landikon (uitikon)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	8	0.01 & 0.02
Bonstetten	Ribacher (Mischwasser nach Pumpe)	Groundwater	Grab sample	2011-2012	Grab sample	AWEL	3	0.01
Bubikon	Fuchsbühl	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Dägerlen	Berg/Bruggenmoos	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Dägerlen	Rutschwil	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	14	0.01 & 0.02
Dübendorf	Zelgli	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	7	0.01 & 0.02
Dürnten	Brunnenbühl	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	8	0.01 & 0.02

Elgg	See	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	14	0.01 & 0.02
Hedingen	Zelgli	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Hirzel	Müsli	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Hittnau	Hasel	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Illnau-Effretikon	Grützen (Chämleten) 3	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Illnau-Effretikon	Rikon	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Illnau-Effretikon	Horben-Mesikon (Misch-wasser in Sammelbr.st.)	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Illnau-Effretikon	Bachtel I	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	14	0.01 & 0.02
Laufen-Uhwiesen	Haselwies mitte	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Lufigen	Rain (Mischwasser im Res. Samichlaus)	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	14	0.01 & 0.02
Marthalen	Brunnenrain / Ellikon a. R.	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Mettmenstetten	Rietli	Groundwater	Grab sample	2010-2013	Grab sample	AWEL	6	0.01
Nürensdorf	Schürwies No. 14	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	15	0.01 & 0.02
Nürensdorf	Habak No. 15	Groundwater	Grab sample	2010-2019	Grab sample	AWEL	14	0.01 & 0.02
Nürensdorf	Hueb	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Oetwil	Bäpur 1922	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Opfikon	Pfändwiesen (Mischwasser nach UV?)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Opfikon	Pünten (Mischwasser nach UV?)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rifferswil	Lindenweid	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rorbas	Heerensteg	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Rümlang	Looren	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Russikon	Ried (Mischwasser im LB Berggass/Ebniweg bei ca. 700'813/250'107)	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Thalheim	Güttighausen	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Uster	Freudwil	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Uster	Sulzbach	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Volketswil	Wydacher	Groundwater	Grab sample	2011-2019	Grab sample	AWEL	16	0.01 & 0.02
Wangen-Brüttisellen	Bachtobel	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Wangen-Brüttisellen	Brüttisellen	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01
Weisslingen	Maienbühl	Groundwater	Grab sample	2010-2012	Grab sample	AWEL	3	0.01