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Long-term Data from the Swedish National Environmental Monitoring Program of Pesticides in Surface Waters

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Abstract

Environmental monitoring is essential for assessing the impact of human activities on the environment. Monitoring data are used to ascertain that environmental standards are met, to inform policy making, to determine trends, and to provide parameterization data for prediction models. The design of monitoring programs depends on what is being monitored, for what purpose, and available resources. Here we describe the strategy and design of the Swedish environmental monitoring program for chemical pesticides in surface waters and provide data generated within this program since 2002 (www.slu.se/en/pesticide_monitoring). We include examples of how the data can be used for toxicity assessments, trend analyses, and comparison between sampling strategies. Our goal is to increase awareness of this dataset and provide detailed information about the data so that it may be incorporated into meta-analytical research, comparison studies, model validation, and other scientific efforts.

Core Ideas

- Time-integrated data for >15 years from four small agricultural catchments are discussed.
- Broad-scale screening in a few intensely farmed areas captures worst-case risks.
- Partial scaling is possible by inclusion of data from two rivers.
- Long-term monitoring is necessary to follow up on agricultural risk-mitigation work.

Chemical pesticides are used in conventional agriculture to maintain high yields and improve crop quality. Rigorous testing and continuous product development are undertaken to ensure that pesticides harm only targeted pests and then disappear quickly from the environment without further effects. The European Union (EU) has a harmonized procedure for pesticide approval to ensure that environmental effects from pesticides are avoided (Regulation EC 1107/2009) (EU, 2009b). However, reports from environmental monitoring programs and targeted sampling efforts reveal that pesticide residues reach surface waters and groundwater, frequently in concentrations that may harm aquatic organisms and exceed drinking water standards (Smith et al., 2012; Stone et al., 2014; Allinson et al., 2015; Morrissey et al., 2015; Silva et al., 2015; Stehle and Schulz, 2015; Stenrød, 2015; Székács et al., 2015; Teklu et al., 2015; Yadav et al., 2015; Bradley et al., 2017; Szöcs et al., 2017). With the implementation of the European Water Framework Directive (2000/60/EC) (EU, 2000) and the Directive for Sustainable Use of Pesticides (2009/128/EC) (EU, 2009a), the legal demands for preventing such occurrences have increased, and there is greater incentive for implementing mitigating measures. National environmental monitoring programs have a vital role to play in achieving the goals set by the directives, as well as to ensure that the general public is informed about the current environmental status and has confidence in the effectiveness of regulated prevention and mitigation efforts. Long-term, continuous sampling programs provide the trend data needed for predicting goal trajectories and assessing effects of mitigating efforts. Further, the data collected can help locate sources and identify management practices, crops, or pesticides that are problematic in terms of off-target pesticide effects and occurrences. This is crucial information for increasing the efficiency of targeted research and development efforts. The continuous monitoring of a multitude of substances together with ecological indicators will also be important for understanding the combined effects of pesticides and other chemical stressors, which are increasingly being emphasized as the prioritized focus for water quality assessments (Chèvre et al., 2006; Schuler and Rand, 2008; McKnight et al., 2012; Rasmussen et al., 2013;

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Abbreviations: LOD, limit of detection; LOQ, limit of quantification; OMK, organic environmental chemistry; PTI, Pesticide Toxicity Index; WQO, water quality objective.

Malaj et al., 2014; Altenburger et al., 2015; Stenrød, 2015; Brack et al., 2017). Finally, environmental monitoring data are the basis for developing and testing models used for predicting pesticide behavior in the environment.

Broad-scale pesticide screening is associated with high analytical costs imposed by multimethod requirements to reliably detect and quantify organic compounds with a wide range of properties at low concentrations. This generally requires making compromises on spatial and/or temporal resolution, often in addition to narrowing the targeted substances to priority-listed chemicals or other subsets of substances depending on the aim, particularly within long-term monitoring programs. As a result, water quality assessment programs around the world vary widely in their design, depending on the longevity and extent of funding, the targeted aspects of water quality, and if the priority of the assessment is to capture the spatial distribution or temporal resolution or to provide comprehensive analyses of all occurring substances. Studies covering a wide spatial range have generally relied on grab sampling at relatively low frequency (Stone et al., 2014; Szöcs et al., 2017); others have sampled at higher frequency with smaller spatial coverage and over a limited time period (Papadakis et al., 2015). Studies combining different sampling methods have shown that grab sampling generally detects fewer substances than do time-integrated or event-triggered auto-samplers (McKnight et al., 2012; Rasmussen et al., 2013; Bundschuh et al., 2014; McKnight et al., 2015; Poulier et al., 2015). Passive samplers can detect pesticides at lower concentrations than other methods (e.g., Mazzella et al., 2007; Smith et al., 2012; Emelogu et al., 2013; Poulier et al., 2015), but monitoring is limited to substances conducive to the sampler and is associated with intrinsic uncertainties regarding the quantification of concentrations (Ahrens et al., 2015). Regardless of the sampling approach, most monitoring programs have narrowed the screened substances to a subset of relatively easy-to-analyze, commonly used, and/or priority-listed substances. While this approach lowers the cost per sample, it inevitably results in an underestimation of pesticide occurrences and associated toxicological and environmental risks (Moschet et al., 2014). However, a recent study indicated that it is possible to adequately assess risks with a reduced number of analyzed substances, as long as the appropriate substances are targeted and the sampling is conducted at a high temporal resolution and through composite samples (Spycher et al., 2018).

The Swedish monitoring program for chemical pesticides (Swedish University of Agricultural Sciences, 2019) was designed to capture the worst-case risks related to agricultural pesticide usage. Therefore, the monitoring is performed in four small catchments with predominantly arable land that are representative of, and located in, Sweden's major agricultural regions. The program is unique in its long-term (>15 yr), continuous (weekly or every other week), time-integrated, comprehensive analyses of all EU-listed priority substances and almost all active ingredients (and a number of metabolites) registered for use in Sweden, including glyphosate, which is often omitted from monitoring programs due to analytical complications. Additionally, the detection and quantification limits for the analytical methods used are low and allow for detection of substances, such as pyrethroids and neonicotinoids, that are highly toxic and otherwise often have a detection limit above the environmental quality standard or water quality objectives (WQOs). Thus, the dataset generated to date provides a uniquely comprehensive, long-term representation of how Swedish agricultural pesticide use affects surface water quality. In this publication, we aim to disseminate knowledge about this extensive and unique dataset so that others may contribute to expanding the use and informational gain from the data to their full potential.

Methods

Monitoring Locations

The Swedish monitoring program for chemical pesticides in surface waters in its current geographical extent began in 2002, through expanding a project initiated in 1990 (Kreuger, 1998). The program is performed in four small catchments (E21, M42, N34, and O18), referred to as *model catchments*, and two rivers, Skivarpsån and Vegeå, within separate, dominant agricultural regions in southern Sweden (Table 1, Fig. 1). The catchments are also included in the environmental monitoring program for nutrient losses from agriculture, which has been described elsewhere (Kyllmar et al., 2014). The focus of the two programs is to monitor agricultural contributions to pesticide occurrence and nutrient loads in surface waters. Note that the choice of model catchments and rivers was not based on randomized selection. Instead, informed decisions were made to target catchments and rivers that would be representative of the main agricultural regions in terms of soil types, agricultural practices, and major crops grown.

The catchments are small (8–16 km^2), with 85 to 92% of the area under farmland, which minimizes contributions from non-agricultural practices, such as pesticide and fertilizer use in parks,

Table 1. Catchment overview.

Catchment	Total area	Farmland	Mean temperature†	Mean precipitation†	Dominant soil type‡	Main crops
	km^2	%	°C	mm		
O18	7.66	92	7.2	628	Clay loam, silty clay loam	Cereals, oil seed
E21	16.32	89	7.2	567	Loam, clay loam	Cereals, oil seed, potato
N34	13.93	85	8.0	741	Sandy loam, loam	Cereals, forage, potato
M42	8.24	92	8.5	710	Sandy loam, loam	Cereals, sugar beet, oil seed
Skivarpsån	102.00	86	8.4	705		Cereals, forage, oil seed, sugar beet
Vegeå	488.00	66	8.7	700		Cereals, forage, oil seed, sugar beet

† Values represent averages for the period 2002–2016, using data from the closest operational weather station to each sampling location for each year (exact locations for nearest weather stations have varied over the period).

‡ Data from the Swedish Environmental Protection Agency arable land inventory (Eriksson et al., 2010), adapted to international particle-size standards according to Tranter et al. (2011) and Moeys (2014).

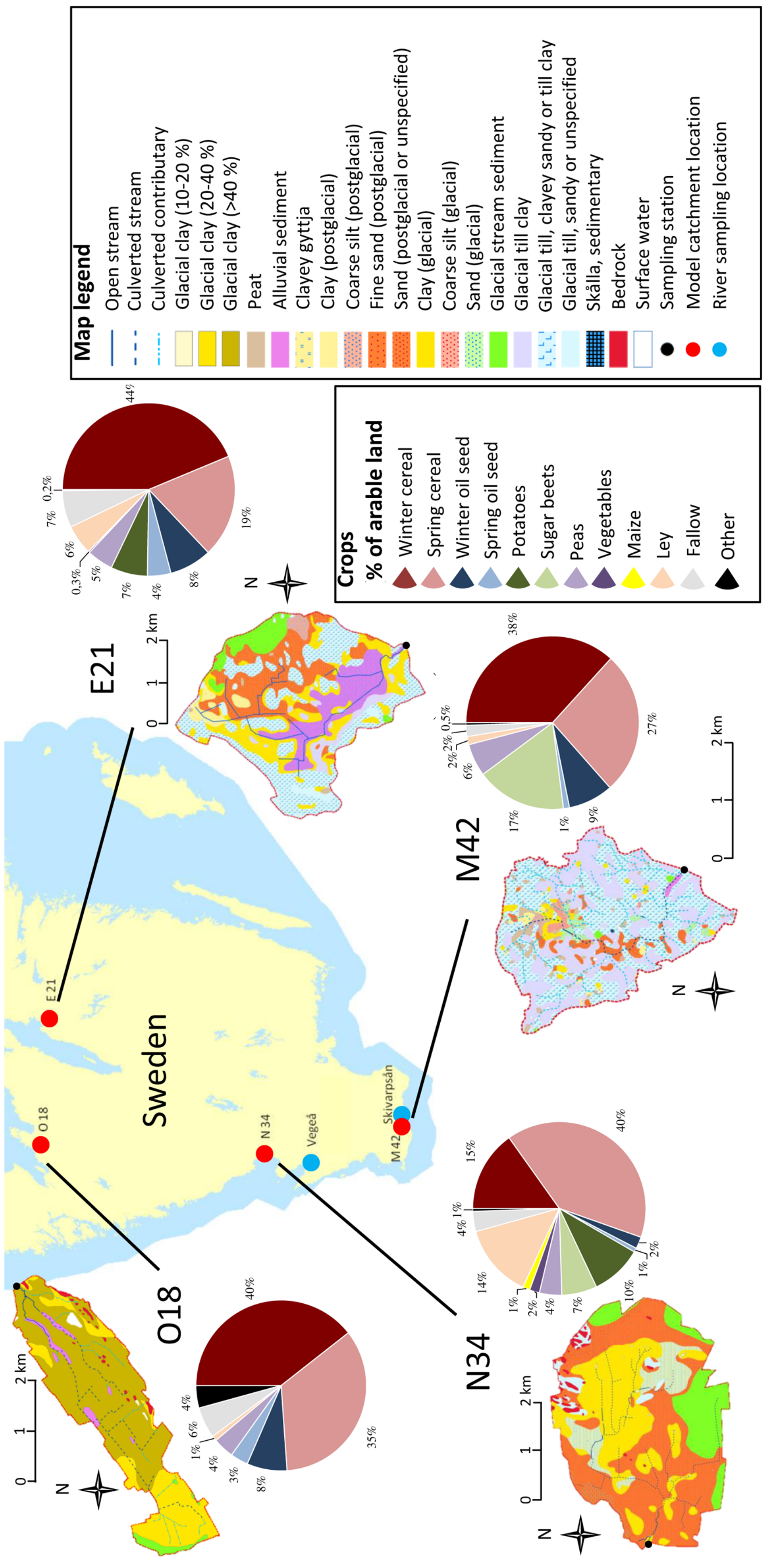

Fig. 1. Locations, soil maps, and dominant crops (average crop distribution during 2002–2012) within each of the four model catchments included in the Swedish monitoring program for pesticides in surface water: E21, M42, N34, and O18.

gardens, greenhouses, and turf. Another reason for choosing intensely farmed catchments was to provide worst-case assessments of the impact on surface water quality from agriculture. The pesticide usage within each catchment (Table 2) is higher than average for the corresponding region (data available through Statistics Sweden [SCB, 2018]).

The two rivers included in the monitoring program, Skivarpsån and Vegeå, were selected to represent medium-sized catchments (102 and 488 km^2 with 86 and 66% of the area under farmland) in Skåne, the most intensely farmed region in Sweden. The purpose of sampling the rivers is to provide large-scale comparison of data from the intensely monitored streams. Sampling in the rivers is less frequent and follows a different protocol, and less-detailed information is available regarding soil types, farming practices, pesticide usage, and so on. The median total concentration of pesticides is quite similar between the model catchments and the rivers, which supports the use of the model catchments to represent intensely farmed regions in Sweden (Fig. 2).

Data Collection for Agricultural Practices

Within the model catchments, all farmers are contacted yearly and asked to provide logs of their farming practices (crops, sowing and harvest dates, time and amount of pesticide applications) for each individual field within the catchment. Much effort has been made to inform the farmers of the importance of participation, accuracy, and completeness in providing the logs. They are asked specifically to proceed with their management practices as they would if they were not within the monitoring catchments. Nevertheless, as always when relying on voluntary participation, it cannot be guaranteed that the reported data are complete or fully accurate. The data from the questionnaires are shared with the monitoring program for nutrient losses. For privacy reasons, we can only report these data in aggregated form (tabulated data for the entire period 2002 to 2016 is available for download at www.slu.se/en/pesticide_monitoring [Swedish University of Agricultural Sciences, 2019]). A summary of the agricultural practices within each model catchment since the start of the monitoring program is provided herein (Fig. 1, Tables 1, 2, and 3) as background information for the pesticide occurrence data in the publicly available dataset. For the river catchments, no data regarding farming practices are collected through the monitoring program, but regional data are available through the Swedish Agricultural Board (SCB, 2018).

Table 2. Average pesticide use in the catchments for the period 2002–2016.

Catchment	Average dose				Portion of farmland treated			
	Herbicides	Fungicides	Insecticides	Total†	Herbicides	Fungicides	Insecticides	Total†
	kg ha^{-1}				%			
O18	0.50	0.17	0.07	0.58	85	43	17	87
E21	0.44	0.53	0.05	0.80	78	48	30	84
N34‡	0.93	1.18	0.04	1.57	62	39	24	65
M42	1.50	0.30	0.04	1.72	93	71	69	96

† Totals include growth regulators and substances used against slugs.

‡ Low percentages for treated farmland in N34 could be due to lower farmer participation in the questionnaires about management practices during the latter part of the period.

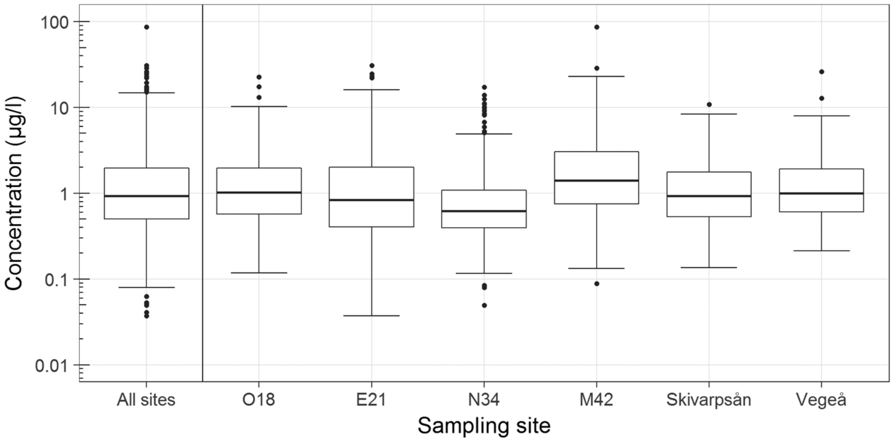

Fig. 2. Total concentration (µg L^{-1}) of pesticides per sample for all samples taken during the growing season (May–October). Note the logarithmic scale.

Water Sampling Procedures

Pesticide monitoring covers the agricultural cropping season, with weekly composite samples from the beginning of May until the end of October in catchments O18 and E21 and until the end of November in N34 and M42. This sampling period is referred to as the growing season. In catchments N34 and M42, the monitoring continues throughout the winter, but with longer sampling intervals (14 d) in the period December to April (winter season). The stream outlet from each catchment is equipped with an automatic ISCO sampler (initially 3700FR, now 6712FR since 2008 in M42, 2011 in O18, and 2013 in E21 and N34) including a +4°C refrigerator with one glass bottle and one plastic (high-density polyethylene) bottle for storing samples for different types of analyses (described below). Samples are collected every 90 min through Teflon tubing extending into the stream according to the following procedure: (i) air cleaning (air is pumped out to remove any material around the tube), (ii) water rinse (water is pumped into a detector and then back out to the stream), and (iii) sampling (20 mL water is divided between the two bottles). The bottles are changed weekly and shipped on ice to the laboratory for analysis. Thus, each analyzed sample is a composite of the water samples taken during 1 wk. The winter samples from N34 and M42 follow the same protocol, but with 180-min sampling intervals and bottles changed every 2 wk.

Table 3. Number of pesticides used and number of pesticides included in the analyses. The right column lists pesticides that have not been included in the analyses and which constitute >1% of applied quantities over the period 2002–2016 within each catchment.

Catchment	Total used	Total analyzed	Pesticides not analyzed with >1% of total application
O18	62	58	n/a†
E21	105	80	diquat, ethephone, chlormequat chloride, mancozeb
N34	89	73	diquat, mancozeb
M42	66	60	n/a

† n/a = not applicable.

In catchment M42, a second ISCO 6712 sampler unit was installed to take flow-proportional samples during the growing season to capture peak-flow specific patterns in pesticide concentrations. This unit has eight bottles and collects samples when a set volume of water has passed. The set water volume is manually adjusted to increase sampling at high flow events (i.e., shortly after precipitation). Between 2009 and 2011, one sample was taken per bottle. From 2012 onward, the sampling program changed to three subsamples per bottle to better cover the peaks. The bottles are changed weekly and kept frozen (−18°C) until the end of the growing season, when a fixed number of samples are selected for analysis based on the relative change in flow during a week (to compare with the composite weekly sample). For economic reasons, all flow-proportional samples cannot be analyzed; hence, it is possible that some concentration peaks at high flow are missed.

The rivers are sampled by manual grab samples twice per month in May to June and once per month in July to November. Sampling is conducted by attaching bottles to a rod that is extended into the river; thereafter, bottles are submerged and filled. One plastic (high-density polyethylene) and one glass bottle (each 1 L) are filled on each sampling occasion. The bottles are shipped on ice to the laboratory (normally arriving within 24 h from the time of sampling).

A blank sample is obtained every other year from each catchment and every year from the rivers to discover contamination risks during the handling of bottles and ensure that no contamination of the sampling equipment has occurred. The blank bottles are handled like the sampling bottles, but filled with deionized water. Filled blank bottles are placed among the other sample bottles in the ISCO refrigerator for a week, and river blanks are filled with deionized water at the sampling site. Blank samples have never indicated contamination from the sampling procedure.

A summary of the types and total number of samples taken in the period 2002 to 2016 is given in Table 4. A few gaps exist in the time series of weekly composite samples, either due to sampling being prevented by low flow or to mechanical failures of the ISCO samplers, with the latter usually being replaced by grab samples.

Pesticide Occurrence and Concentration Data—Analytical Procedures

All analyses during the entire period follow ISO/IEC 17025-accredited methods (ISO, 2017) conducted at the laboratory for organic environmental chemistry (OMK) at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences in Uppsala, Sweden. The laboratory routinely participates in international intercalibrations and conducts rigorous internal quality control to ensure that a high data quality standard is maintained.

The ambition of the program is to analyze all pesticides permitted for use within Sweden plus all pesticides listed as priority substances by the EU (Annex II of Directive 2008/105/EC [EU, 2008]), including those that have never been permitted for use in Sweden. New substances that are introduced into the market are normally added to the list of analytes the following year, as long as they are being used in the model catchments and there is an existing analytical procedure to detect them. Banned substances remain on the list of analytes until the concentrations are consistently below the analytical detection limit. Thus, the pesticides included in the analyses are reevaluated before each monitoring season in response to pesticide sales and usage regulations, but in general, the list is expanded yearly. In total, 148 different substances were analyzed in water samples during the period 2002 to 2016. The substances included in the analysis for each individual sample is noted in the dataset.

Despite extensive efforts to include all permitted and priority-listed substances, some substances used within the monitored catchments are too ephemeral to trace, some are too costly to analyze, or an analytical method for detection in natural waters has not yet been developed. The substances most commonly used but not analyzed within each model catchment are listed in Table 3. The OMK laboratory constantly refines and expands the ability to detect relevant substances using multi-residue methods, to meet the demands of introduced substances and the environmental quality standards. Since 2009, a combined liquid chromatography and tandem mass spectrometry method (OMK 57/OMK 58) (Jansson and Kreuger, 2010) has been used for the majority of substances. However, nonpolar substances require a separate method (OMK 51), as do glyphosate and its metabolite aminomethylphosphonic acid (AMPA) (OMK 59). A full list with short descriptions of the various methods used during the period 2002 to 2016 is provided in Table 5.

It should be noted that the introduction of OMK 57/OMK 58 increased the number of detectable substances and lowered the detection limit for substances formerly included in the analyses. As a consequence, increased pesticide occurrences logged in the dataset from 2009 onward, compared with before 2009, may not correspond to an actual increase in pesticide occurrence in the streams; instead, it could be an effect of an enhanced ability to detect pesticides that may have been present previously but not detected with the methods used before 2009. Hence, caution should be used when interpreting long-term trends related to the number of detected pesticides before and after 2009. However, it is still possible to conduct trend analyses over the entire period, for example, by excluding concentrations from 2009 to 2016 that are below the previous detection limits and/or limiting the trend analyses to a subset of substances that have consistently been included in all analyses and with robust detections above the detection limits over time.

When the concentration of a substance falls between the limit of detection (LOD) and the limit of quantification (LOQ),

Table 4. Total number and types of samples collected in catchment streams during the monitoring period 2002–2016.

Year	O18	E21	N34		M42			Skivarpsån	Vegeå
			Growing season	Winter	Growing season	Winter	Flow-proportional		
2002	21	20	19		24			8	8
2003	22	22	22		15			8	8
2004	19	21	20		28			9	9
2005	22	22	22		16			9	9
2006	21	19	21		29			9	9
2007	20	20	26	10	31	20		10	10
2008	20	20	21		27	11		9	9
2009	20	20	24		28	10	24	9	9
2010	20	20	30	11	26	10	42	9	9
2011	20	20	30	10	30	11	28	9	9
2012	20	20	31	12	28	11	28	9	9
2013	18	24	29	11	26	11	24	9	9
2014	21	21	30	11	25	11	14	9	9
2015	26	26	30	11	30	11	24	9	9
2016	20	21	30	11	27	10	24	11	11
Total	310	316	385	87	390	116	208	136	136

the exact concentration is less precise, as indicated by the annotation "trace value" in the dataset. Trace values recorded in the period 2002 to 2008 represent averages of the LOD and LOQ for each substance and analysis; trace values from 2009 onward are the actual measured concentrations. Although trace concentrations are less precise and, hence, should probably be omitted from long-term trend analyses, they are important to record to examine the contribution of high-flow events during the winter period to pesticide loads to surface water. Trace values are also crucial for recording the occurrence of highly toxic substances that have environmental standards below LOQ, such as some pyrethroids. Trace values recorded for the model catchments are included in total transport estimates.

Key Characteristics of the Dataset

The dataset from the Swedish environmental monitoring program for chemical pesticides is publicly available for download (www.slu.se/en/pesticide_monitoring [Swedish University of Agricultural Sciences, 2019]). The dataset contains the following information (recorded for each individual sample): sampling location, date collected, all substances included in the analyses, concentrations (including trace concentrations), LOD, and LOQ for each individual substance. Daily average water flow in the sampled stream or river is also available for download. For flow-proportional samples, in addition to the date, the exact time of sampling is recorded, together with the water flow at the sampling time.

There are a multitude of potential uses for this dataset. Here, we provide three examples: ecological risk assessments, examination of trends of individual substances, and evaluation of different sampling strategies.

Example 1: Toxicity Index

One of the main objectives of environmental monitoring programs is to provide data for environmental risk assessments. For chemical substances, there are a multitude of approaches for evaluating the ecological risk, most of which rely on comparing measured concentrations to established toxicological threshold values for indicator organisms, expressed as, for example, toxicity units (Sprague, 1970), risk quotients (EFSA, 2014), chemical risk indices (Malaj et al., 2014), water quality criteria (Chèvre et al., 2006), and water quality objectives (WQOs) (Gustavsson et al., 2017). In addition, a number of more sophisticated approaches have been proposed, such as species sensitivity distributions (Posthuma et al., 2002), multisubstance Potentially Affected Fraction (de Zwart and Posthuma, 2005), and effect-directed analysis of what drives the toxicological effects of chemical mixtures (Altenburger et al., 2015).

The dataset presented here constitutes by virtue of its extensiveness a valuable asset for evaluating ecological risks and different approaches for such evaluations. High temporal resolution, combined with almost complete inclusion of all substances being used within the monitored catchments, the low detection limits for highly toxic substances, and the extensive supporting data available for the catchments, provides the opportunity to combine this dataset with the ecotoxicological data and method of choice to calculate and/or model environmental risks associated with chemical pesticides. Within the monitoring program, we routinely calculate the Pesticide Toxicity Index (PTI) (Eq. [1]), which is equivalent to the sum of risk quotients calculated from the regulatory acceptable concentration (Szöcs et al., 2017):

$$\mathrm{PTI} = \sum_{i=1}^{n} \frac{C_i}{\mathrm{WQO}_i} \qquad [1]$$

where C_i is the measured concentration for the substance i and WQO_i is the water quality objective for the same substance, as established by the Swedish Agency for Marine and Water Management (HaV, 2018) or the Swedish Chemical Inspection Agency (KemI, 2015). Many of the substances analyzed within the program do not have nationally established WQOs, in

Table 5. Brief description of the analytical methodology used for detection and quantification of substances in surface water samples within the Swedish monitoring program for chemical pesticides. Number of substances in each method have changed with time, presented is the maximum number of substances per method for 2002–2016.

Method ID	Max. number of substances	Type of substances	Pretreatment	Extraction/filtration	Detection†
OMK 49	14	Sulfonylurea-herbicides (before 2009)	Acidification	Solid phase	LC-MS
OMK 50	12	Acidic (before 2009)	Acidification	1. Solid phase 2. Derivatization	GC-MS
OMK 51	76	Non-polar/semi-polar	None	Dichloromethane	GC-MS
OMK 53	2	Glyphosate/AMPA‡ (before 2012)	pH neutralization	1. Hydrophobic solid phase 2. Ion exchange 3. Derivatization	GC-MS
OMK 57	115	Semi-polar/polar	1. Split into 2 aliquots 2. pH adjusted to 5	Filtration (0.2 μm)	LC-MS/MS
OMK 58	19	Acidic semi-polar/polar (from 2009)	Acidification with 1% formic acid	Filtration (0.2 μm)	LC-MS/MS
OMK 59	2	Glyphosate/AMPA (from 2011)	1. Derivatization at pH 9 in the presence of EDTA§ 2. Acidification to pH 3 with formic acid	Filtration (0.2 μm)	LC-MS/MS

† LC-MS = liquid chromatography coupled with mass spectrometry; GC–MS = gas chromatography with mass selective detection (mass spectrometry); LC-MS/MS = liquid chromatography coupled with tandem mass spectrometry.

‡ AMPA = aminomethylphosphonic acid.

§ EDTA, ethylenediaminetetraacetic acid.

which case the WQO is replaced by a value calculated within the monitoring program (in the same manner as the national WQOs) (Andersson et al., 2009; Andersson and Kreuger, 2011). The most recent list of WQOs used in the monitoring program, with references for each substance, can be found with the data (www.slu.se/en/pesticide_monitoring [Swedish University of Agricultural Sciences, 2019]).

Due to the high toxicity at low concentrations of some substances, such as pyrethroids, the WQO is sometimes lower than the LOD. This is problematic, primarily because it means that these substances may be present at undetectable yet toxic levels in surface waters. Furthermore, a slight increase in concentration of such a substance (bringing it above LOD) can produce a tremendous jump in WQO-based summation toxicity indices. This can result in erroneous conclusions regarding toxicity trends and, as a consequence, substances with an LOD < WQO should be omitted from toxicity trend analyses, unless the probability of "false" nondetects of these substances can be calculated and accounted for in the trend analyses. To demonstrate this issue, we show the annual PTI calculated for each model catchment and the two rivers (summed for all samples from each sampling location each year), first with all detected substances (Fig. 3a–b) and then excluding substances with WQO below LOD (Fig. 3c–d). This example clearly shows how the detection of only one or a few single substances at concentrations close to LOD, but well above WQO, can generate a distinct peak in summed toxicity (note peaks present in Fig. 3a but not in Fig. 3c for N34 in 2003 and 2014, for M42 in 2005, and in Fig. 3b but not Fig. 3d for Skivarpsån in 2008). It further highlights the importance of improving the LODs for substances with a high toxicity at very low concentrations, as has been noted by others (Szöcs et al., 2017).

The PTI is just one example of how this dataset can be used for environmental assessments. We hope that publication of the dataset will encourage others to use it to test and develop alternative indices and methods of environmental assessment, such as those listed above, and to evaluate prioritized substances to include in monitoring programs. The data could also be used to guide the selection and concentrations of pesticides included in ecotoxicological tests of chemical mixtures, by providing long-term minimum, maximum, and average values of different substances in surface water within intensely farmed areas.

Example 2: Single Substance Trends

Another benefit of the Swedish monitoring program, and its long-term data with high temporal resolution, is that time series of individual substances can be evaluated. This can be of interest, for example, for substances that are newly introduced, recently banned, or subject to a dramatic change in demand, so that the environmental effect of such changes can be followed. Long-term data are also valuable for identifying substances of potential concern due to unexpectedly high concentrations or common occurrences compared with pre-approval testing and WQO values. To illustrate such changes for individual compounds, we present the long-term data for four substances (Fig. 4): (i) diflufenican, a commonly used herbicide in cereal crops, which is among the most frequently detected substances and the most frequently observed at concentrations above the WQO in the model catchments; (ii) glyphosate, another herbicide with a high detection frequency but that has never been detected in concentrations exceeding its WQO; (iii) imidacloprid, a neonicotinoid insecticide, for which a decrease of the LOD following the change in analytical method in 2009 led to a dramatic increase in the detection frequency; and (iv) terbuthylazine, an herbicide that has been prohibited from use in Sweden since 2003, with no sales registered since 1999. The slow decrease in detection frequencies and concentrations of terbuthylazine is an example of how substances can continue to affect the environment long after they have been banned (note occurrences above WQO on several occasions more than 10 yr after the

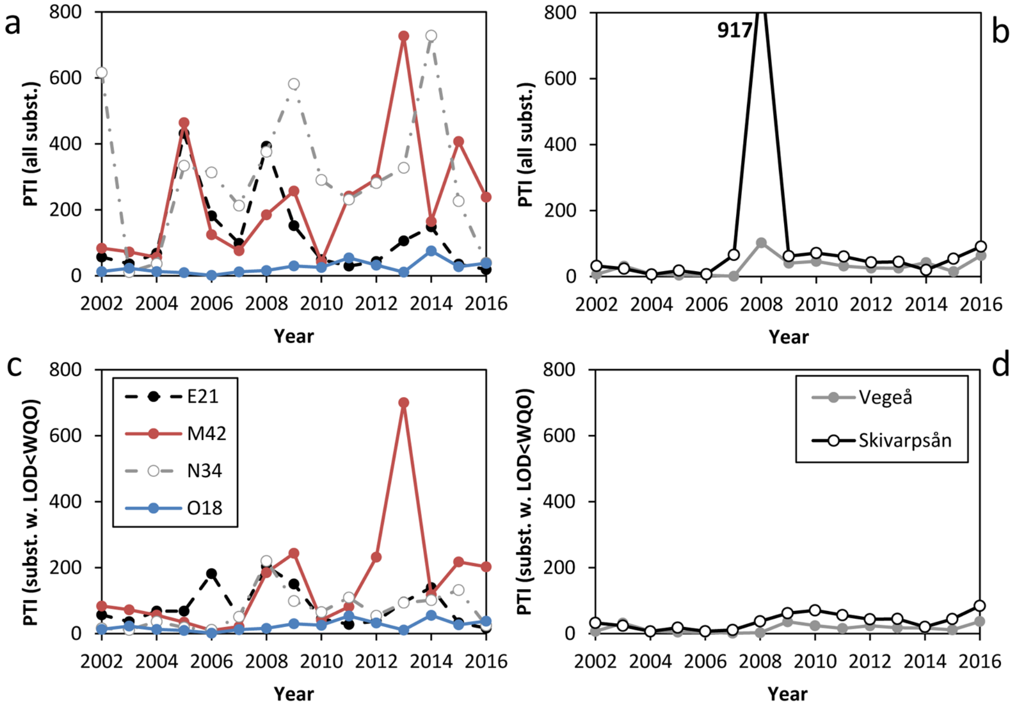

Fig. 3. Pesticide Toxicity Index (PTI) for the (a, c) model catchments and (b, d) rivers calculated for each growing season according to Eq. [1], with all detected substances (a, b) and without substances with a limit of detection (LOD) > water quality objective (WQO) (c, d). The PTI (917) for Skivarpsån in 2008 is noted numerically in (b) because it exceeded the *y* axis scale.

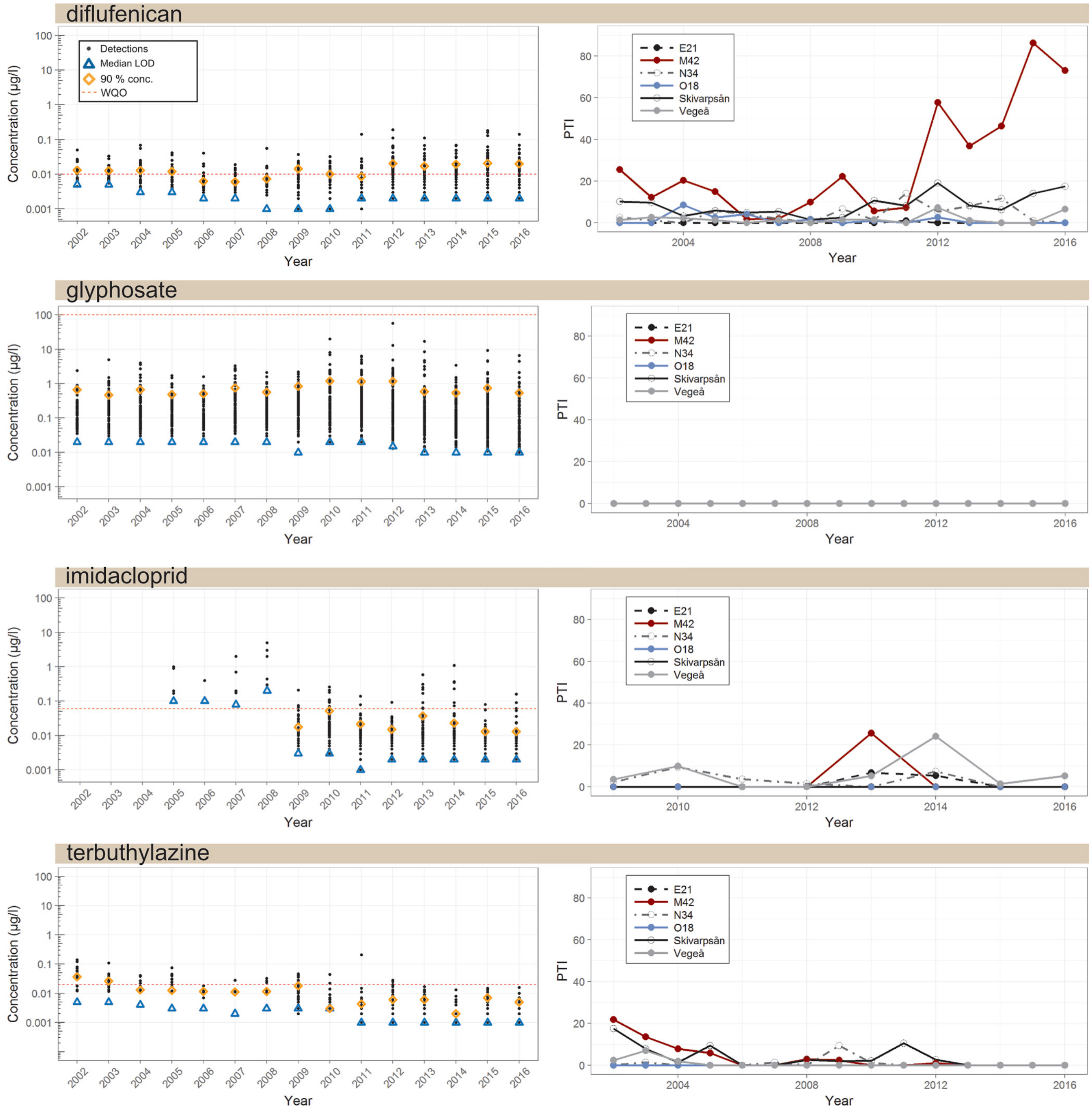

Fig. 4. Left-hand panels: All detected concentrations (µg L⁻¹) (black dots) of diflufenican, glyphosate, imidacloprid, and terbuthylazine plotted for each growing season (May–October, 2002–2016) together with the 90th percentile concentration for the same period (orange diamonds) and the median limit of detection (LOD) for each substance that year (blue triangles). The water quality objective (WQO) for each substance is indicated by a red dotted line within the respective panel. Right-hand panels: Corresponding Pesticide Toxicity Index (PTI) values for the same four substances within each sampling area for each growing season (2002–2016), calculated as the sum of *C*/WQO for samples with a concentration (*C*) exceeding the WQO.

last registered sale). Figure 4 also illustrates how different substances vary in importance between different areas, depending on the crops that are grown and the climate. Overall, the differences in detection frequencies and concentrations between the model catchments are consistent with the application data for these substances. However, there is likely more information to be gained from in-depth statistical investigations of these variations and trend analyses.

Example 3: Peak Concentrations and Time-Averaged Evaluations

One of the concerns with time-integrated sampling is that peak concentrations resulting in acute toxicity effects can be missed. For this reason, flow-proportional samples have been analyzed in parallel with the time-integrated samples in model catchment M42 since 2009. In general, the highest concentrations and highest number of detected substances occur in flow-proportional samples compared with corresponding weekly

Table 6. Total number of detected substances in flow-proportional samples compared to the time-integrated samples taken during the same week, per growing season in model catchment M42.

Total number of substances detected in ≥1 sample	2009	2010	2011	2012	2013	2014	2015	2016
Flow-proportional samples	36	37	68	63	67	51	63	63
Time-integrated samples	36	34	52	61	49	43	53	49
Detected in								
Both sample types	32	31	51	55	48	40	49	49
Flow-proportional samples only	4	6	17	8	19	11	14	14
Time-integrated samples only	4	3	1	6	1	3	4	0

composite samples (Table 6). This indicates that temporarily toxic concentrations of single substances or high summed concentrations may be missed by the time-integrated sampling approach. However, plotting the ratios of concentration in flow-proportional and corresponding time-integrated samples shows that, in general, the concentrations are relatively consistent between the sampling methods and that concentration discrepancies between the two sampling strategies occur in both directions (Fig. 5). Further, the quotient between the concentrations is very rarely outside of the range 0.1 to 10 (i.e., most diverging concentrations are still within an order of magnitude of each other), suggesting that the risk of missing toxic concentrations with the weekly time-integrated approach is relatively low, at least in this catchment.

Summary

Continuous monitoring for almost two decades of a large number of substances in four catchments characteristic of intensive Swedish agricultural regions makes the dataset of the Swedish national environmental monitoring program of pesticides in surface waters an exceptional resource for examining long-term trends in pesticide occurrences and environmental impact from agriculture. The dataset is unique in its high temporal resolution combined with the comprehensive screening of substances, including several that are normally omitted from monitoring programs (Moschet et al., 2014; Stone et al., 2014) due to analytical difficulties, e.g., glyphosate (which requires a separate method), neonicotinoids, and pyrethroids (which are toxic at concentrations below or around LOD for many analytical methods). Although the most intense monitoring activities are conducted in small catchments, the inclusion of the two rivers in the program links the observations from first-order streams to higher-order recipient rivers (Fig. 2), providing an important scaling feature of the dataset. The parallel flow-proportional sampling performed in one of the catchments provides the opportunity to examine the influence of sampling strategies, as well as the impact of high-flow events on the concentrations and number of detections and WQO exceedances. Additionally, continued time-integrated sampling through the winter season in two of the catchments provides insights into the off-season transport of pesticides and how this varies, depending on substance.

Because the monitoring program is performed in parallel with the program for environmental monitoring of nutrient losses from agriculture (Kyllmar et al., 2014), it offers unique

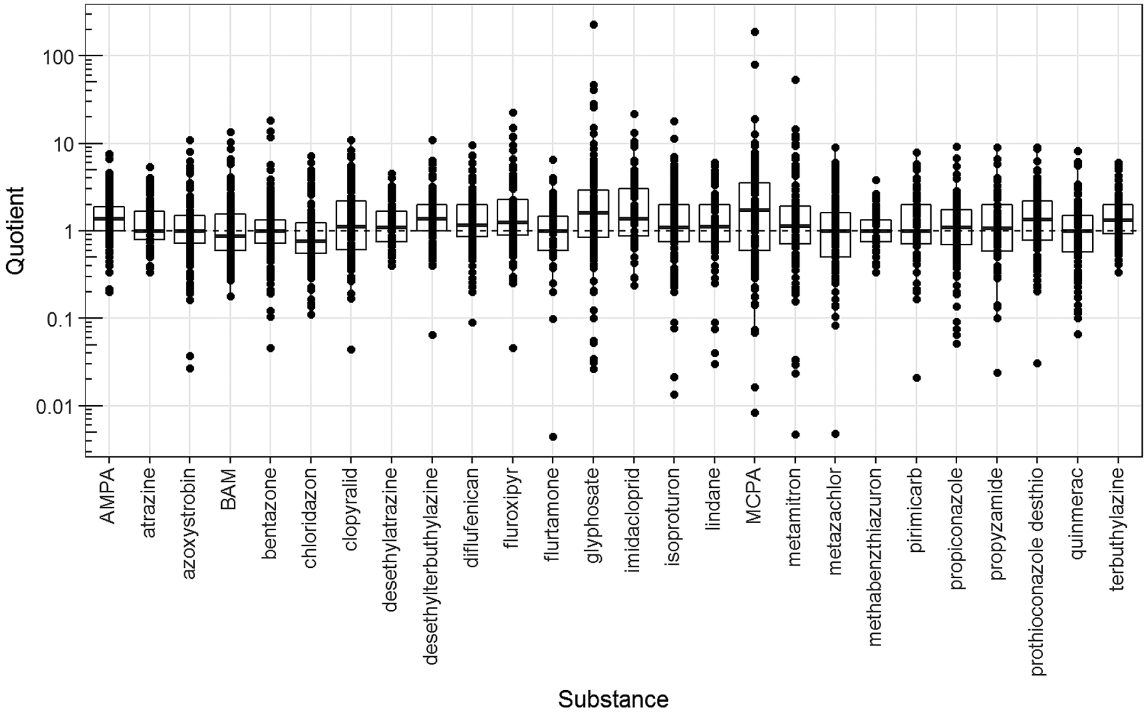

Fig. 5. Box-plot showing the quotient between concentrations in flow-proportional samples and time-integrated samples taken during the same week (2009–2016) in model catchment M42 for all substances with >80 detections in both types of samples. Only quotients where the flow-integrated samples were taken at a time of increased flow relative to the weekly average are included. AMPA, aminomethylphosphonic acid; BAM, 2,6-dichlorobenzamide; MCPA, (4-chloro-2-methylphenoxy)acetic acid.

opportunities for broad risk assessments of agricultural practices. Together, the two datasets provide a solid background for targeted studies, such as similarities and dissimilarities in pesticide substance and nutrient behaviors, overall ecological impacts of agriculture, or dominant transport processes related to soil type. Access to high-resolution, long-term data can, for example, help direct the timing or location of additional sample collection activities or the tailoring of questionnaires to obtain additional information from farmers. The extensive dataset is also a rich source of information for meta-analyses and efforts to validate models, and selected subsets of the dataset (depending on the question) can be included in international trend analyses or surveys of pesticide occurrences in surface waters.

It should be reemphasized that the aim of the program is to capture all pesticide occurrences in surface water within the model catchments, which together with the targeting of intensive agricultural catchments automatically puts the data in the "worst-case" scenario for current conventional agricultural management practices in these regions. Further, the program is designed to reflect reality in agricultural catchments, without manipulation or control over the management practices or natural processes. Thus, irregular events (e.g., unreported cleaning of equipment or preferential flow due to temporarily disturbed soil) that could lead to point-source leaching are not taken into account and may contribute to uncertainties in trend analyses and interpretations of causal mechanisms, as is often the case for environmental monitoring datasets. However, the no-interference design ensures that the data is representative of real-life agricultural impacts and not affected by experimental biases or manipulations.

Data Availability

The pesticide dataset from the Swedish environmental monitoring program for chemical pesticides and tabulated agricultural data, based on farmer responses to questionnaires, are available for download at www.slu.se/en/pesticide_monitoring (Swedish University of Agricultural Sciences, 2019). A list of WQOs, with references for each substance, that are used in the monitoring program can be found with the data.

Conflict of Interest

The authors declare no conflict of interest.

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