EEA/NSV/13/002 – ETC/ICM

European Environment Agency
European Topic Centre on Inland, Coastal and Marine Waters

Indicator on pesticides in European waters Technical paper

Version: 4.0
Date: 21.10.2021
EEA activity: 1.1.8.1
ETC/ICM task, milestone: 5i

Prepared by / compiled by: Jeanette Völker, Volker Mohaupt, Gasper Subelj, Silvie Semeradova, Ingo Kirst
Organisation: UBA, TC Vode, CENIA

EEA project manager: Caroline Whalley

Contents

1. Introduction

There has long been a need to portray the environmental contamination of water by pesticides. With the Green Deal (EC, 2019) and its associated strategies and actions, such as Farm to Fork Strategy (EC, 2020c), Biodiversity Strategy (EC, 2020b), Chemicals Strategy for Sustainability (EC, 2020a) and Zero Pollution Action Plan (EC, 2021), there is renewed ambition to significantly reduce the use and risk of pesticides.

Legislation concerning pesticides in environmental waters is primarily set by the Water Framework Directive (WFD) (2000/60/EC). For surface waters, environmental quality standards (EQS) are set in the EQS Directive (2008/105/EC), as updated by the Priority Substances Directive (2013/39/EU). EQS are based on toxicity to organisms in or via the aquatic environment. There are 33 priority substances (or groups of substances) rising to 45 in the next WFD reporting in 2022, in which there are a limited number of pesticides. Member States can also identify "River Basin Specific Pollutants" (RBSPs) for which they set the EQS. For groundwaters, the Groundwater Directive (2006/118/EC) as updated by 2014/80/EU, sets a common threshold of 0.1 ug/l for any individual pesticide substance, which is not a health-based, but a general precautionary limit value. Member States should report on "total pesticides" in groundwater (with threshold value of 0.5 ug/l) and can select which substances to measure and report.

So far, we lack an overview of pesticides in waters across Europe, as well as a standardised methodology in form of an indicator to assess pesticide contamination in aquatic ecosystems over space and time.

To form the basis of an indicator, an ETC/ICM data assessment on pesticides in European rivers, lakes and groundwater was performed (Mohaupt et al., 2020). As the most comparable dataset across Europe available, the report focused on data reported by countries to the EEA, providing an initial overview of the available information on pesticide concentrations in surface water and groundwater in Europe.

This methodology sets out the steps to deriving an indicator for pesticides in rivers, lakes and groundwater in Europe, based on data reported by Eionet countries to WISE-SOE water quality.

Existing EU level indicators are already available which are based on pesticides sales data (e.g. HR1) ([1]). In contrast, this indicator focuses on pesticides in rivers, lakes and groundwater, based on measured concentrations and assessed against effect thresholds.

([1]) Source: https://ec.europa.eu/food/plant/pesticides/sustainable_use_pesticides/harmonised-risk-indicators/trends-hri-eu_en

2. Definitions and Disclaimer

EU legislation divides pesticides into plant protection products (PPP) and biocides. Plant protection products and biocides contain at least one active substance, that act against 'pests' on plants, parts of plants or plant products. Active substance can be chemical, plant extract, pheromone or micro-organism (including viruses).

- For the indicator, we used all reported active substances, including their relevant metabolites ([2]) and call all these "pesticides".

Active substances used in plant protection products and/or biocides are approved at EU level. EU countries authorise the placing on the market of plant protection products containing those active substances on their territory and ensure compliance with EU rules. Some substances measured and reported have already been restricted, owing to long residence times in groundwater or soil. As the focus of this indicator is on water quality, they are included because they can still affect aquatic ecosystems.

- For the indicator, all reported pesticides were used, regardless of their approval status.

Currently, non-relevant Metabolites (nrM) are not regulated by the Groundwater Directive (2006/118/EC). The Directive sets quality standards for pesticides in Annex I, for *"Active substances in pesticides, including their relevant metabolites, degradation and reaction products"* and explains that *"'Pesticides' means plant protection products and biocidal products as defined in Article 2 of Directive 91/414/EEC and in Article 2 of Directive 98/8/EC, respectively"*. The Directive's definition and the references do not include nrM. However, in the recently recast Drinking Water Directive (2020/2184/EU), Member States will need to take into account non-relevant pesticide metabolites, and to set a guidance value for them by 2023, though quality standards for nrM are not yet available.

- For the indicator, non-relevant metabolites (nrM) were excluded from the assessment for pesticides in groundwater.

Once a pesticide has reached the environment, it is not usually possible to ascertain the original source or use of it. Organisms experiencing the resultant mixture do not discriminate by source, though such information is helpful for the identification of appropriate prevention measures.

- The results of this indicator cannot be categorically attributed to particular sources or sectors (agriculture, biocidal use, aquaculture, forestry, etc.).

Until now, we have lacked an overview of pesticides in the aquatic environment across Europe, as well as a standardised methodology in form of an indicator to assess pesticide contamination in aquatic ecosystems over space and time.

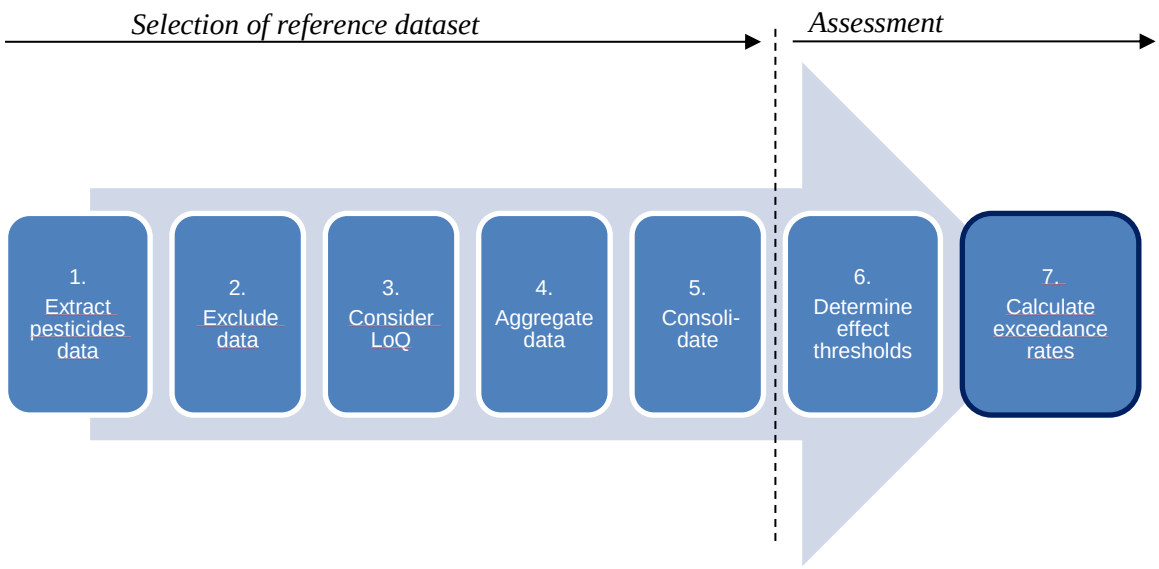
- The indicator may not be comparable with nationally developed assessments on pesticides because of differing methodologies towards exceedance calculation.

([2]) Metabolites (also degradation product, breakdown or reaction products) from an active substance of pesticides are seen as products of biological, physical, or chemical degradation processes or other chemical reactions, which then can be found as contaminants associated with the parent compounds.

3. Methodology

Figure 3.1 illustrates the stepwise approach for the data assessment for the indicator on pesticides in rivers, lakes and groundwater in Europe.

Figure 3.1 Overview of stepwise approach



Within this stepwise approach, steps 1 to 5 are related to the selection of reference dataset. Step 6 addresses the selection of threshold values concerning effects. Step 7 is the assessment.

3.1. Selection of reference dataset

The selection of reference dataset is based on Waterbase – Water Quality. The voluntary reporting obligation for WISE SoE - Water Quality (WISE-6) is an EIONET core data flow. Waterbase – Water Quality ([3]) is a database containing water quality data in rivers, lakes and groundwater reported to EEA by up to 39 European countries under the WISE SoE reporting stream.

Disaggregated water quality data are records representing one sample at a specific monitoring site, at a specific time, for a specific parameter. Aggregated data are reported to EEA as annual statistics for each monitoring site and substance. Prior to 2015, a larger share of records for pesticides were reported as aggregated data but since 2015, most such data have been reported as disaggregated data. The updated versions of the database are published annually, with the version published in May 2021 covering the data up to 2019.

The monitoring sites that provide data to Waterbase – Water Quality are located in European waterbodies and reported – along with their descriptive attributes – to 'WISE WFD reference spatial

([3]) Source: https://www.eea.europa.eu/data-and-maps/data/waterbase-water-quality-icm-1.

data sets' ([4]) and 'WISE EIONET spatial data sets' ([5]). For the reference dataset, monitoring sites in rivers, lakes, and groundwater were used.

3.1.1. Extraction of pesticide data

The extraction of disaggregated ([6]) and aggregated ([7]) data records on pesticides used all records reported for the period since 2013. In cases where both disaggregated records and the corresponding aggregated record were reported, the disaggregated records were used.

3.1.2. Exclusion of data

The following criteria were used for the exclusion of data:

i. Outliers are automatically screened as part of the quality control procedures for WISE-6 and its predecessor WISE-4 ([8]). Where records show an annual mean above or below the extreme limits ([9]) for a given substance in aggregated data; or for records that were beyond the standard deviation threshold within a year (Z-score of 5.5) or through a complete time series (Z-score of 3.0), those records are excluded.

ii. Observed values below the reported limit of quantification (LoQ). Such records indicate possible reporting errors and are of low reliability.

iii. Surface water data from the "dissolved" matrix were included in the reference dataset. Those in the 'suspended particulate matter' matrix were excluded.

3.1.3. Consideration of Limit of Quantification (LoQ)

The Limit of Quantification (LoQ) is a term used to describe the smallest concentration of a substance that can be reliably measured by an analytical procedure (Armbruster and Pry, 2008).

Based on the definitions given in Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water status 'limit of quantification' means a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample and may be obtained from the lowest calibration point on the calibration curve, excluding the blank.

According to the principles of Directive 2009/90/EC, the LoQ of the method needs to be equal to or lower than one third of the defined Environmental Quality Standard (EQS) and the precision the Directive requires for an uncertainty of measurement of 50 % or below (k = 2), estimated at this concentration.

([4]) Available at https://www.eea.europa.eu/data-and-maps/data/wise-wfd-spatial-3.

([5]) Available at https://www.eea.europa.eu/data-and-maps/data/wise-eionet-spatial-3.

([6]) See definition of the disaggregated data at: https://dd.eionet.europa.eu/tables/11122.

([7]) See definition of the aggregated data at: https://dd.eionet.europa.eu/tables/11500.

([8]) More information on QC rules can be found here: https://cdr.eionet.europa.eu/help/WISE_SoE/wise4/WISE_SoE_QCRules_v2.2.pdf

([9]) The defined upper limits for each substance for aggregated as well as disaggregated data by EEA QC rules can be found here: https://cdr.eionet.europa.eu/help/WISE_SoE/wise4

Within Waterbase – Water Quality, countries were encouraged to report LoQ for each substance since 2010 and have been required to do so for data reported since 2015. Actual LoQ is requested for disaggregated data. For the reporting of aggregated data, specific rules are defined especially for the calculation of annual mean substance concentration, where concentration values below LoQ must be replaced with half of the LoQ value ([7]). For annual aggregated records, the highest LoQ in a series of measurements within a year should be reported, although typically the same analytical method is used at the site throughout the year. LoQ for the same pesticides can vary between countries, owing to different analytical techniques.

3.1.4. Aggregation of disaggregated data

The disaggregated data (reported concentration for each substance and monitoring site) were aggregated to annual mean concentration (arithmetic annual mean). In addition, the yearly maximum concentration was extracted. In combination with the LOQ, the mean and maximum values of the annual aggregated record are used to define the threshold exceedance.

3.1.5. Consolidation – selection of pesticides and characterisation

An effect threshold was assigned to each substance (if available) (see section 3.2.1), and information on water category was assigned to each monitoring site (see section 3.2.2).

Within the period 2013 to 2019, pesticide data in Waterbase – Water Quality were reported by a total of 29 European countries (Member States of the EU and EEA member and cooperating countries). Furthermore, records for 232 pesticides, 22 873 monitoring sites (9 327 for surface waters and 13 592 for groundwater) as well as 3.5 million annual records were extracted (Table 1), (Annexes 1, 2).

Table 1 Overview of extracted pesticide data in time period 2013 to 2019

		2013	2014	2015	2016	2017	2018	2019	Total
Number of countries	SW	18	19	25	25	25	26	24	29
	GW	18	18	18	18	17	18	19	22
Number of reported monitoring sites	SW	2 317	2 476	3 653	2 782	2 877	4 500	4 906	9 327
	GW	5 510	5 348	6 719	5 958	8 102	8 290	9 442	13 544
Number of reported records (annual mean)	SW	115 023	125 703	162 300	154 192	171 150	219 369	312 249	1 259 986
	GW	251 594	248 867	248 769	226 384	296 933	315 606	500 806	2 088 959
Number of reported pesticides	SW	156	157	156	193	165	168	215	218
	GW	143	145	144	155	161	158	223	223

Note: SW = surface waters (rivers and lakes); GW = groundwater
Source: Database Waterbase – Water Quality. https://www.eea.europa.eu/data-and-maps/data/waterbase-water-quality-icm-1

The number of monitoring sites and monitored pesticides in European countries is listed in Annex 3.

3.2. Assessment

3.2.1. Determination of effect thresholds

For the calculation of exceedance rates, it is crucial to determine a threshold for each pesticide. To determine the threshold of each pesticide, the following sources were considered:

Surface waters

- Environmental quality standards – EQS ([10]) of the pesticides listed under the priority substances of the WFD; AA-EQS (annual average EQS), which are protective against chronic toxicity, and MAC-EQS (maximum allowable concentration EQS), which should protect against acute toxicity. This gives thresholds for 21 pesticides regulated with EQS-Directive 2008/108/EC following the amendment of this Directive in 2013. Furthermore, substance candidates for the list of priority substances under Water Framework Directive; version 4.0, 2021 ([11]). This gives thresholds for two pesticides.

- The maximum acceptable detection limit, according to the Watch List under Commission Implementing Decision (EU) 2015/495, Commission Implementing Decision (EU) 2018/840 and Decision (EU) 2020/1161. Detection limit of watch list substances is derived on the basis of preliminary EQS according to the provisions of the QA/QC-directive 2009/90/EG. The Watch List for surface waters lists substances including several pesticides that must be monitored to confirm whether they pose a risk at European level. It does not set EQS, but the detection limit is an indicator of the likely order of magnitude. This provides thresholds for nine pesticides.

- EQS for 83 pesticides listed by EU Member States and EEA Member Countries as River Basin Specific Pollutants (RBSPs), if available: AA-EQS (annual average EQS) and MAC-EQS (maximum allowable concentration EQS). Basis of all EQS under WFD are the provisions of WFD, Annex V, 1.2.6 and the CIS-guideline No 27 on EQS-derivation.
  The EQS value for RBSPs can vary between countries. For the assessment the lowest reported ecotoxicologically-based EQS for a substance was used ([12]).
  Furthermore, all pesticides were considered into the assessment, if at least one country nationally regulated a substance as River Basin Specific Pollutant (RBSP). This was decided according to the precautionary principle.
  To increase and update number of EQS of pesticides, also selected national Regulations were checked (AT, 2020; CH, 2020; DK, 2017; FR, 2018; IT, 2015; NL, 2015; SE, 2019; UK, 2020).

- One substance listed under the UN Stockholm Convention, which recommends the ban of specific substances, *inter alia* pesticides, to protect human health and the environment from

([10]) *An environmental quality standard is a limit for environmental disturbances, in particular, from ambient concentration of pollutants and wastes, that determines the maximum allowable degradation of environmental media*. Glossary of Environment Statistics, Studies in Methods, Series F, No. 67, United Nations, New York, 1997.

([11]) Source: https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/f3f3d157-3099-44a9-8e2e-5ba208ac042c?p=1&n=10&sort=modified_DESC

([12]) In Italy, for all individual pesticides (including metabolites) except an ecotoxicological-based EQS, a precautionary value of 0.1 μg/l applies. This value was not considered as effect threshold.

persistent organic pollutants (UNEP, 2018) ([13]) including the Persistent Organic Pollutants (PoPs) Regulation 2019/102/EU.

Annex 4 list the effect threshold of pesticides, that were used for the assessment.

Groundwater

- The Groundwater Quality Standard of 0.1µg/l was used in accordance with the Directive 2006/118/EC for each active substance in pesticides, including their relevant metabolites, degradation and reaction products. The quality standard of 0.5 µg/l for the total sum of pesticides was not considered.

- Furthermore, the following non-relevant Metabolites were excluded from the assessment ([14]):

Label	CAS
2,6-dichlorobenzamide	2008-58-4
Aminomethylphosphonic acid (AMPA)	1066-51-9
Aldoxycarb	1646-88-4
Desethylterbuthylazine	30125-63-4
Desisopropylatrazine	1007-28-9
Dimethenamid ESA	205939-58-8
Dimethenamid OA	380412-59-9
Flufenacet ESA	201668-32-8
Hydroxyatrazine	2163-68-0
Hydroxyterbuthylazine	66753-07-9
Idicarb sulfoxide	1646-87-3
N,N-dimethylsulfamide	3984-14-3

3.2.2. **Calculation of exceedance rates**

Surface waters

→ If at least one annual average pesticide value exceeds the annual average effect threshold and the reported LoQ, the monitoring site is classified as ‘Threshold exceedance’.

→ If at least one annual maximum pesticide value exceeds the maximum effect threshold and the reported LoQ, the monitoring site is classified as ‘Threshold exceedance’. A Maximum

([13]) List of persistent organic pollutants: http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx

([14]) These metabolites were reported as "non relevant” in a report for the EU CIS ‘Working Group Groundwater’: WFD CIS Voluntary Groundwater Watch List Process on non-relevant pesticide Metabolites (nrM). Groundwater Monitoring Data Collection and Initial Analysis (Draft V.3.3 / 06th June 2021), not yet published.
The same report concluded that the group had “identified sufficient evidence of a widespread presence of nrM in European groundwater and recommended to consider nrM for inclusion in Annex I of the Groundwater Directive.”

Acceptable Concentration (MAC) EQS is not available for all pesticides. In these cases, only the annual average calculation method occurs.

Groundwater

→ If at least one annual average pesticide value exceeds the quality standard of 0.1µg/L and the reported LoQ, the monitoring site is classified as 'Quality standard exceedance'.

Exceedance rates were calculated for each record and based on the one-out-all-out-principle as follows:

Figure 1 of the Indicator: Percentage of reported monitoring sites with pesticides exceeding thresholds in surface waters and groundwater in Europe weighted by country area

(a)

$$\sum \frac{Monitoring\ sites\ with\ exceedances\ per\ country}{Monitoring\ sites\ reported}$$

(b)

$$\sum \frac{Percentage\ of\ monitoring\ sites\ with\ exceedances\ per\ country\ [\%]\ x\ country\ area\ [km^2]}{Area\ of\ countries\ with\ reported\ monitoring\ sites\ per\ year\ [km^2]}$$

Figure 2 of the Indicator: Percentage of reported monitoring sites with pesticides exceeding thresholds in surface waters, different sized rivers, lakes and groundwater in European countries, 2013 – 2019

Each monitoring site was assigned to the catchment size up to the site: 'rivers, small' (catchment size <100 km²); 'rivers, medium' (100 to 100 000 km²); 'rivers, large' (> 100 000 km²); 'lakes' (all monitoring sites in lakes), and groundwater (all monitoring sites in groundwater). The assignment of monitoring sites to catchment size has been carried out according to the following priorities. If the site could not be assigned under step 1, step 2 was followed. If it couldn't be assigned under step 2, then step 3 was followed. Some sites could not be assigned under any of these steps.

1. Assignment of monitoring sites to water bodies under WFD and broad types for rivers and lakes (Lyche Solheim et al., 2019)

2. Based on Ecrins ([15]): if monitoring site is located on main drain (river segment connecting functional elementary catchments − FEC), monitoring site catchment (total area located upstream of a monitoring site) is used:
   <100 km^2: "Rivers, small"
   >=100 km^2 - <100 000 km2: "Rivers, medium"
   >=100 000 km^2: "Rivers, large"

3. Based on Ecrins: if monitoring site is not located on main drain (secondary drain within a FEC) and the FEC is smaller than 100 km^2, the monitoring site is assigned to "Rivers, small".

([15]) Data source: https://www.eea.europa.eu/data-and-maps/data/european-catchments-and-rivers-network

The following table shows an overview of the reported monitoring sites for each water category.

	Number of reported monitoring sites
Surface waters	9 327
Rivers, large	257
Rivers, medium	4 501
Rivers, small	2 642
Lakes	1 049
Groundwater	13 544

Note: Catchment size could not be assigned to all monitoring sites in rivers (so total number of reported monitoring sites in surface waters does not equal the sum of lakes plus large, medium and small rivers).

Calculation:

$$\sum \frac{Monitoring\ sites\ with\ exceedances\ per\ country}{Monitoring\ sites\ reported}$$

The rate of exceedances was classified into four categories: <=10%; >10<=20%; >20<=30% and >30%.

4. References

Armbruster, D. A. and Pry, T., 2008, 'Limit of blank, limit of detection and limit of quantitation', *The Clinical Biochemist. Reviews* 29 Suppl 1, pp. S49-52.

EC, 2019, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions — The European Green Deal, COM(2019) 640 final.

EC, 2020a, Communication from the Commission to the European Parliament, the Council, the Economic and Social Committee and the Committee of the Regions - Chemicals Strategy for Sustainability Towards a Toxic-Free Environment, COM(2020) 667 final

EC, 2020b, Communication from the Commission to the European Parliament, the Council, the Economic and Social Committee and the Committee of the Regions - EU Biodiversity Strategy for 2030. Bringing nature back into our lives., COM(2020)380 final

EC, 2020c, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions 'A Farm to Fork Strategy for a fair, healthy and environmentally-friendly food system', COM(2020) 381 final.

EC, 2021, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions – Pathway to a Healthy Planet for All – EU Action Plan: 'Towards Zero Pollution for Air, Water and Soil', COM(2021) 400 final.

Lyche Solheim, A., Globevnik, L., Austnes, K., Kristensen, P., Moe, S. J., Persson, J., Phillips, G., Poikane, S., van de Bund, W. and Birk, S., 2019, 'A new broad typology for rivers and lakes in Europe: Development and application for large-scale environmental assessments', Science of The Total Environment 697, pp. 134043 (https://linkinghub.elsevier.com/retrieve/pii/S0048969719340203) accessed August 19, 2020

Mohaupt, V., Völker, J., Altenburger, R., Birk, S., Kirst, I., Kühnel, D., Semeradova, S., Šubelj, G. and Whalley, C., 2020, *Pesticides in European rivers, lakes and groundwaters – Data assessment*, ETC/ICM Technical Report, 1/2020,

UNEP, 2018, 'Chemicals proposed for listing under the Convention', *Stockholm Convention* (http://chm.pops.int/TheConvention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx) accessed November 6, 2018.