



Indicator on pesticides in European waters Methodology paper

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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 45 priority substances (or groups of substances) under the Priority Substances Directive (2013/39/EU), 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.

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.

EEA first published an indicator of pesticides in waters across Europe in 2021, as well as a standardised methodology to assess pesticides contamination in aquatic ecosystems over space and time.

This methodology is based on data reported by Eionet countries to WISE SoE - Water Quality in Inland, Coastal and Marine waters (WISE-6).

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.).

Based on available data we developed a standardised methodology to obtain an overview of pesticides in the aquatic environment across Europe.

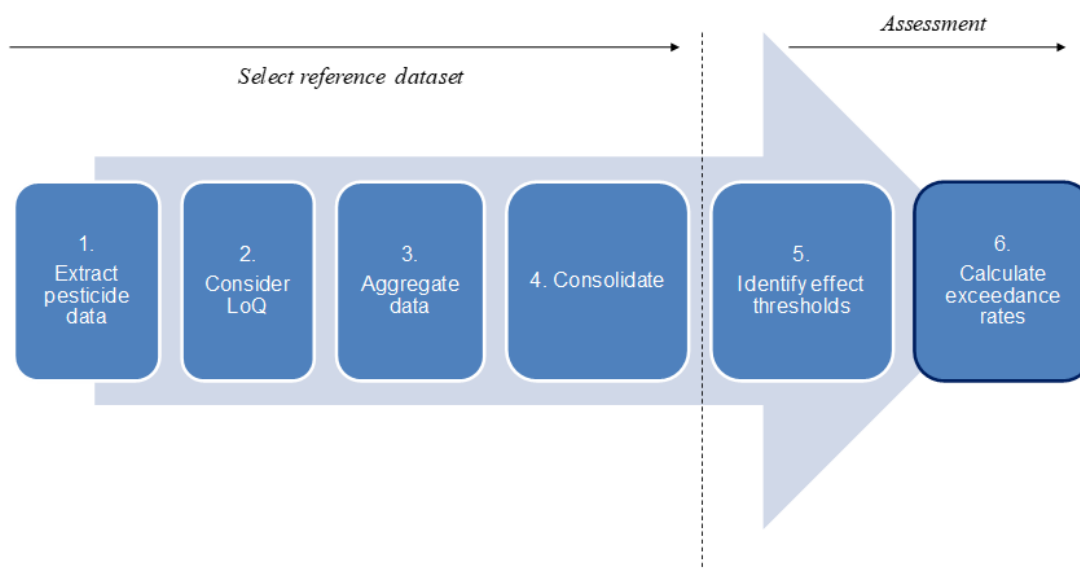
- The indicator may not be comparable with nationally developed assessments on pesticides because of differing methodologies towards exceedance calculation.

⁽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 4 are related to the selection of reference dataset. Step 5 addresses the selection of threshold values concerning effects. Step 6 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 ICM ⁽³⁾ is a database containing water quality data in rivers, lakes and groundwater which have been reported to EEA by up to 39 European countries under the WISE SoE reporting stream.

The database includes concentration data on nearly 500 hazardous substances altogether, including more than 200 pesticides. When the pesticide data have been temporally aggregated to annual means, this contributes to over 4 million records (i.e. annual mean of a concentration of a distinct substance at a distinct monitoring site).

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 2022 covering the data up to 2020.

⁽³⁾ Source: [Waterbase - Water Quality ICM — European Environment Agency \(europa.eu\)](https://www.eea.europa.eu/en/waterbase/water-quality-icm).

The monitoring sites that provide data to Waterbase – Water Quality ICM are located in European waterbodies and reported – along with their descriptive attributes – to 'WISE WFD reference spatial 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 ⁽⁸⁾ and its predecessor WISE-4 ⁽⁹⁾. Where records show an annual mean above or below the extreme limits ⁽¹⁰⁾ for a given substance; 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. Surface water data from the 'suspended particulate matter' matrix were excluded.
- iii. Data with unknown monitoring site location were excluded.
- iv. Data with unit issues 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

⁽⁴⁾ Available at [WISE WFD reference spatial data sets — European Environment Agency \(europa.eu\)](#).

⁽⁵⁾ Available at [WISE EIONET spatial data sets — European Environment Agency \(europa.eu\)](#).

⁽⁶⁾ See definition of the disaggregated data at: [Table - DisaggregatedData/WISE SoE - Water Quality ICM \(europa.eu\)](#).

⁽⁷⁾ See definition of the aggregated data at: [Table - AggregatedData/WISE SoE - Water Quality ICM \(europa.eu\)](#).

⁽⁸⁾ Information on QC rules for WISE-6, applicable from 2020 is available https://cdr.eionet.europa.eu/help/WISE_SoE/wise6

⁽⁹⁾ Information on QC rules applied to data reported before 2020 can be found here: [WISE SoE_QCRules_v2.2_2019](#)

⁽¹⁰⁾ The defined upper limits for each substance for aggregated as well as disaggregated data by EEA QC rules can be found here: [WISE6_ObservedProperty_QC_reference](#)

Directive requires for an uncertainty of measurement of 50 % or below ($k = 2$), estimated at this concentration.

Within Waterbase – Water Quality ICM, 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.

To increase the number of observed values and to increase the reliability of the overall assessment, we have refined the approach to dealing with LoQ in comparison to 2021. Within Waterbase – Water Quality ICM, nine different cases for the use of LoQ for disaggregated data were defined and considered in the assessment as illustrated in the examples.

	IF	THEN	Example procedure LOQ Value	Example result Observed Value	Example OUTPUT
1	reported value = reported LOQ value and flagged as below LOQ	reported LOQ value /2	0.5	0.5	0.25
2	reported value = reported LOQ value/2 and flagged as below LOQ	reported LOQ value /2	0.5	0.25	0.25
3	reported value < reported LOQ value (but not half of it) and flagged as below LOQ	reported LOQ value /2	0.5	0.1	0.25
4	reported value > reported LOQ value and flagged as below LOQ	reported LOQ value /2	0.5	3	0.25
5	reported value = reported LOQ and not flagged as below LOQ	reported value	0.5	0.5	0.5
6	reported value = reported LOQ value/2 and not flagged as below LOQ	reported LOQ value /2	0.5	0.25	exclude
7	reported value < reported LOQ value (but not half of it) and not flagged as below LOQ	exclude	0.5	0.1	exclude
8	reported value > reported LOQ value and not flagged as below LOQ	reported value	0.5	3	3
9	No reported LOQ value available	exclude	Not reported	0.1	exclude

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) ⁽⁸⁾. 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 2020, pesticide data in Waterbase – Water Quality ICM were reported by a total of 30 European countries (EU-27 and cooperating countries). Furthermore, records for 243

pesticides, 22 082 monitoring sites (10 219 for surface waters and 13 863 for groundwater) as well as 4 million annual records were extracted (Table 1), (Annexes 1, 2).

		2013	2014	2015	2016	2017	2018	2019	2020	Total
Number of countries	SW	19	20	25	25	25	27	24	25	29
	GW	18	18	18	18	17	18	19	20	22
Number of reported monitoring sites	SW	2 327	2 487	3 238	2 967	3 523	4 669	4 851	4 767	10 219
	GW	5 789	5 638	5 402	5 870	8 100	8 290	8 256	9 112	13 863
Number of reported records (annual mean)	SW	115 154	125 688	149 750	151 099	199 130	230 361	310 994	302 458	1 584 634
	GW	251 874	250 448	196 275	223 996	295 731	314 937	442 631	453 141	2 429 033
Number of reported pesticides	SW	156	157	193	198	189	195	219	221	228
	GW	143	146	145	155	161	158	223	226	228

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 ⁽¹¹⁾ of the pesticides listed under the priority substances of the Water Framework Directive (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 23 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 the WFD; version 4.0, 2021 ⁽¹²⁾. This gave thresholds for three pesticides.
- The maximum acceptable detection limit, according to the Watch List under Commission Implementing Decision (EU) 2015/495, Commission Implementing Decision (EU) 2018/840, Decision (EU) 2020/1161 ⁽¹³⁾. 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/EC. 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

⁽¹¹⁾ 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.

⁽¹²⁾ 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

⁽¹³⁾ New Version of Watch List was published in 2022 (Decision (EU) 2022/1307)

detection limit is an indicator of the likely order of magnitude. This provided thresholds for nine pesticides.

- EQS for 84 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). The basis of all EQS under the WFD are the provisions of the 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 ⁽¹⁴⁾. Furthermore, all pesticides were considered into the assessment, if at least one country nationally regulated a substance as RBSP. This was decided according to the precautionary principle. To increase and updated number of EQS of pesticides, also selected national Regulations and related information were checked (AT, 2020; CH, 2020; CY, 2015; DK, 2017; EE, 2019; FI, 2022; 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 persistent organic pollutants (UNEP, 2018) ⁽¹⁵⁾ including the Persistent Organic Pollutants (PoPs) Regulation 2019/102/EU.

Annex 4 list the effect thresholds 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 ⁽¹⁶⁾

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

⁽¹⁴⁾ 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.

⁽¹⁵⁾ List of persistent organic pollutants: <http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx>

⁽¹⁶⁾ 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."

Label	CAS
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’ for the given year.
- 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’ for the given year. A Maximum 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’ for the given year.

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 per year in surface waters and groundwater in Europe weighted by country area

$$(a) \quad \sum \frac{\text{Monitoring sites with exceedances per country}}{\text{Monitoring sites reported}}$$

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

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 in time period 2013 – 2020

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 ⁽¹⁷⁾: if the monitoring site is located on the main drain (river segment connecting functional elementary catchments – FEC), monitoring site catchment (total area located upstream of a monitoring site) is used:
 - <100 km²: "Rivers, small"
 - >=100 km² - <100 000 km²: "Rivers, medium"
 - >=100 000 km²: "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 km², the monitoring site is assigned to "Rivers, small".

Calculation:

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

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

⁽¹⁷⁾ Data source: [European catchments and Rivers network system \(Ecrins\) — European Environment Agency \(europa.eu\)](http://europa.eu)

4. References

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