

Indicator on pesticides in European waters Technical 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.

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

 $^{(^1) \} Source: \ \underline{https://ec.europa.eu/food/plant/pesticides/sustainable_use_pesticides/harmonised-risk-indicators/trends-hri-eu_en$

plants or plant products. Active substance can be chemical, plant extract, pheromone or microorganism (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.

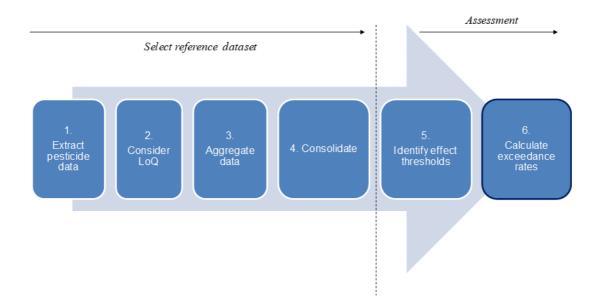
> The indicator may not be comparable with nationally developed assessments on pesticides because of differing methodologies towards exceedance calculation.

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

⁽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.



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 38 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 2013 data reporting, a larger share of records for pesticides were reported as aggregated data but since 2013, most such data have been reported as disaggregated data. The updated versions of the database are published annually.

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

⁽³⁾ Source: Waterbase - Water Quality ICM — European Environment Agency (europa.eu).

⁽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).

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 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.

⁽⁶⁾ See definition of the disaggregated data at: <u>Table - DisaggregatedData/WISE SoE - Water Quality ICM (europa.eu)</u>.

⁽⁷⁾ See definition of the aggregated data at: <u>Table - AggregatedData/WISE SoE - Water Quality ICM (europa.eu)</u>.

 $^(^8) Information on QC \ rules for WISE-6, applicable from 2020 \ is available \ \underline{https://cdr.eionet.europa.eu/help/WISE \ SoE/wise6}$

⁽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: $\underline{\text{WISE6_ObservedProperty_QC_reference}}$

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, ten different cases for the use of LoQ for disaggregated data were defined and considered in the assessment as illustrated in the table 1.

Table 1: Ten LoQ cases and procedure for disaggregated data.

	IF	THEN	Example procedureLOQ Value	Example resultObserved 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	exclude	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, but value flagged as below LoQ	exclude	Not reported	0.1	exclude
<u>10</u>	not reported LoQ value available and value not flagged as below LoQ	reported value	0.5	0.5	0.5

^{*}For Italy, 5 also leads to the exclusion of the data, as there were problems with the data retrieval.

In addition to the previous aggregation of disaggregated data and the handling of reported LoQ values, we tested the Kaplan-Meier, robust regression based on order statistics, and maximum likelihood estimation methods for their applicability to the WISE dataset. However, none of these statistical methods are appropriate for the present assessment due to low data availability at the scale of the monitoring sites (sample size of n= 6-12 per year, substance and monitoring site).

3.1.4. Aggregation of disaggregated data

The disaggregated data were aggregated into "annual average - measured environmental concentrations" (AA-MEC) by calculating the arithmetic mean of all records per monitoring site for each individual pesticide and year (8). In addition, the maximum measured environmental concentration (MAX-MEC) was extracted per monitoring site for each individual pesticide and year. In combination with the LoQ, the AA-MEC and MAX-MEC 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 2021, 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, 25 366 monitoring sites (11 014 for surface waters and 14 352 for groundwater) as well as 4 million annual records were extracted, (Annexes 1, 2).

Table 2: Statistics on reported data for surface waters and groundwaters for the time period 2013 - 2021.

		2013	2014	2015	2016	2017	2018	2019	2020	2021	Total
Number of countries	SW	19	20	25	25	25	27	25	25	25	29
	GW	18	18	18	18	17	18	19	20	15	22
Number of reported	SW	2,336	2,497	3,238	2,964	3,519	4,849	4,977	4,765	5,562	11,014
monitoring sites	GW	5,795	5,644	5,406	5,879	8,102	8,290	8,256	9,112	9,152	14,352
Number of reported records (annual mean)	sw	114,337	125,697	149,740	151,057	199,105	234,572	313,410	302,345	346,813	1,937,076
	GW	252,793	251,265	197,034	224,590	296,193	315,394	442,804	453,141	490,284	2,923,498
Number of reported pesticides	SW	156	157	193	198	189	195	219	221	227	236
	GW	143	146	145	155	161	158	223	226	236	243

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 an effect threshold for each pesticide. To determine the effect threshold of each pesticide, the following sources were considered:

Surface waters

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• 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

⁽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.

- 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, Commission Implementing Decision (EU) 2022/1307. 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 detection limit is an indicator of the likely order of magnitude. This provided thresholds for eleven pesticides.
- EQS for 81 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)

 $[\]begin{tabular}{ll} (12) Source: $https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/f3f3d157-3099-44a9-8e2e-5ba208ac042c?p=1&n=10&sort=modified_DESC \end{tabular}$

⁽¹⁴⁾ In Italy, for all individual pesticides (including metabolites) except an ecotoxicological-based EQS, a precautionary value of $0.1~\mu g/l$ 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 / 06^{th} 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
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
ldicarb sulfoxide	1646-87-3
N,N-dimethylsulfamide	3984-14-3

3.2.2. Calculation of exceedance rates

In a first step of the indicator calculation, individual monitoring sites are classified as "exceeded" for each year if for at least one pesticide (based on the "one-out-all-out principle") the measured environmental concentration (i.e., AA-MEC or MAX-MEC) exceeds the corresponding effect threshold (e.g., AA-MEC > AA-EQS). Specifically, this results in the following for surface waters and groundwater:

Surface waters

- → If at least one AA-MEC exceeds the annual average effect threshold (e.g., AA-EQS) and the reported LoQ, the monitoring site is classified as 'Threshold exceedance' for the given year.
- → If at least one MAX-MEC exceeds the maximum effect threshold (MAC-EQS) and the reported LoQ, the monitoring site is classified as 'Threshold exceedance' for the given year. A maximum effect threshold is not available for all pesticides. In these cases, only the annual average calculation method occurs.

Groundwater

Heast one AA-MEC 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.

Figure 1 of the Indicator: In a next step, the pesticide indicator for Figure 1 is calculated based on equation 1. In detail, the percentage of monitoring sites classified as "exceeded" is calculated for each country (i) and multiplied by the relative area of the respective country (i). The result per country (i) is then summed over all reporting countries. This calculation is done for each year individually and separately for surface water and groundwater in Europe. The results are shown in figure 1.

Equation 1:

$$WAT009_{1} \ for \ Figure \ 1 = \sum_{i=1}^{n} (\frac{S_{exceeded_{i}}}{S_{reported_{i}}} * 100 * \frac{area_{i}}{\sum_{i=1}^{n} area_{i}})$$

With:

 $S_{exceeded}$ – number of monitoring sites classified as "exceeded" $S_{reported}$ – number of monitoring sites reported i – country n – total number of countries reporting area – surface area in surface surface area in surface surface area ar

Figure 2 of the Indicator: In a next step, the pesticide indicator for Figure 2 is calculated based on equation 2. In detail, the percentage of monitoring sites classified as "exceeded" is calculated for each country (i). This calculation is performed across all years in the time period from 2013 to 2021 (monitoring sites reported in several years are counted only once, if in one of the years exceeded). The calculation is performed separately for five different types of water bodies, namely for small, medium and large rivers as well as for lakes and groundwater. The results were classified into four categories (<=10%; >10<=20%; >20<=30%; >30%) and are shown in figure 2.

Each monitoring site was assigned to one of the five water body types based on the catchment size up to the site: 'rivers, small' (catchment size $<100 \text{ km}^2$); '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:

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<100 km<sup>2</sup>: "Rivers, small"
>=100 km<sup>2</sup> - <100 000 km<sup>2</sup>: "Rivers, medium"
>=100 000 km<sup>2</sup>: "Rivers, large"
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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".

Equation 2:

With:

$$WAT009_2$$
 for Figure 2 = $\frac{S_{exceeded_i}}{S_{reported_i}} * 100$

⁽¹⁷⁾ Data source: <u>European catchments and Rivers network system (Ecrins)</u> — <u>European Environment Agency (europa.eu)</u>

 $S_{exceeded}$ – number of monitoring sites classified as "exceeded"

 $S_{reported}$ – number of monitoring sites reported

i-country

4. References

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