Reducing micropollutants in the Rhine catchment area - Monitoring and evaluation system

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Monitoring and evaluation system

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1. Introduction

The 16th Rhine Ministerial Conference took place on 13 February 2020 in Amsterdam. In the conference communiqué, the ministers stated that "substance entry via point sources and diffuse entry paths, including numerous micropollutants such as pharmaceuticals and plant protection products, continue to pose a problem for water quality and countermeasures, particularly with regard to diffuse entry paths, must be taken". Depending on the entry paths, however, point sources also need to be taken into consideration.

The Rhine 2040 programme presented during the Rhine Ministerial Conference stipulates that the "influx of micropollutants into waters from municipal waste water collection and treatment systems (hereafter "wastewater treatment plants"), industry and commerce (hereafter "industry") and agriculture is to be reduced by at least 30% in comparison to the period 2016-2018 – consistent with a longer-term ambition to further decrease pollution throughout the Rhine catchment area. In order to be able to numerically check the reduction in influx at regular intervals and, if necessary, to increase the reduction target, the ICPR is tasked with developing a joint evaluation system for the reduction across the three areas (hereafter "emission areas")."

The boundary conditions of the evaluation system were the reference period 2016-2018, the list of Rhine substances, which is to be taken as a basis for selecting representative parameters, and the requirement that substances be selected from the three emission areas wastewater treatment plants, industry and agriculture. The focus here was on the pollution of surface waters.

The ad hoc expert group EG MICROMIN was founded for the 2020-2022 period with the mandate to develop the aforementioned joint evaluation system for influx reduction.

As, for many substances, it is extremely difficult to quantify emissions via the various entry paths, progress achieved over time in influx reduction is measured using influx data. The easiest way to verify the reduction is through influx load measurements – particularly as the corresponding baseline data is available for the reference period 2016-2018. Future developments in the concentrations and loads of selected substances at the respective monitoring stations thus have to be considered in relation to implementation of the packages or programmes of measures which the countries have established or will establish to reduce influxes of micropollutants in waters – starting at the source right through to more extensive purification processes. Further information on this can be found, for example, in ICPR technical report no. 253.

2. EG MICROMIN mandate

The EG MICROMIN mandate was established for a fixed period and comprised the establishment of a waters monitoring system and the development of a joint evaluation system for the reduction of micropollutant influxes in waters across the three emission areas wastewater treatment plants, industry and agriculture.

To carry out this mandate, the expert group focussed on the following questions:

- What objects of protection are being considered? Aquatic ecosystems and drinking water production? (see 3 and 7.2)
- What is the initial list: List of Rhine substances? Specification of substances for the three emission areas. (see 3.2)
- When should the list be reviewed and should substances be removed from ("delisted") or added to the list? (see 3.2 and 8)
- At what monitoring stations will reductions be measured? (see 4 and Annex III)
- What data basis will be used? (see 4, 6 and Annex III)
- What preparatory work by the countries and organisations will be chosen to be taken into account?
- What methods are already being used by the countries to evaluate reductions?
- Are the reductions based on loads and/or concentrations? (see 7)
- At what intervals should progress towards target achievement be reviewed after the ad hoc expert group has concluded its work? (see 8)

3. Selection of indicator substances

In order to document the reduction, by at least 30% overall compared to the 2016-2018 period, in the influx of micropollutants into waters from the three emission areas wastewater treatment plants, industry and agriculture, relevant and representative substances, known as indicator substances, are required for each emission area.

In a first step, selection criteria were defined for indicator substances (see 3.1). Secondly, a list of representative substances for the three emission areas was drawn up (see 3.2). Indicator substances were then chosen from this comprehensive list based on the agreed criteria.

3.1 Criteria for selecting indicator substances

The following criteria – subdivided into hard and soft criteria – were defined by EG MICROMIN for the selection of indicator substances.

Hard criteria:

(H1) Consideration of individual substances from different origins and areas of application which can be attributed to the emission areas wastewater treatment plants, industry and agriculture as sources

(H2) Exclusion of substances that are only relevant at local level (taking account of regional cultivation patterns in the case of agriculture)

(H3) Concentration range of measured values: easily measured in 2016-2018 (measurability of reduction, e. g. three times higher than limit of quantification)

(H4) Load: it must be possible to calculate load reduction based on concentration and discharge; this does not apply to agriculture

(H5) Relevance for goals of drinking water production and/or aquatic ecosystems

(H6) Standardised methods of analysis or other validated analysis techniques available (e. g. Federal Institute of Hydrology, BfG, method for suspended particulate matter)

(H7) Manageable analysis costs or standard in Rhine Monitoring Programme (i. e. substance is already measured)

(H8) In case of additional analyses: Substances can be measured in as few “analysis steps” as possible (saving on costs and logistics)

Additional soft (*weiche*) criteria:

(W1) Consideration of monitoring and indicator substances from the federal states and countries to review the need for more extensive treatment in wastewater treatment plants

(W2) Substances that are measured in untreated water for drinking water production (= identified as persistent and mobile)

(W3) Consideration of international and national findings on water pollution

(W4) Substances which cannot be removed using natural drinking water processing methods

(W5) Availability of data on ecotoxicology and relevance for drinking water would be advantageous

(W6) PMT substances (persistent, mobile, toxic)

(W7) Expectation that the measures recommended by ICPR will lead to a reduction in the selected substances (ICPR technical report no. 253)

(W8) Additional measures (under criterion W7) lead to a reduction in influx of other selected substances into surface waters

(W9) Plant protection products are permitted in at least one of the countries in the Rhine catchment area or are still in the waiting period (prescribed period of time between application of a plant protection product and subsequent harvest) and are primarily used in agriculture

(W10) Plant protection product is susceptible to drift, run off and drainage

3.2 Selection procedure for indicator substances

In the selection of indicator substances, proposals were discussed in several stages. Tests carried out in the water phase and on suspended particulate matter (see 6) are to be taken into account.

The selected substances for the three emission areas are listed in Annex I (A to C).

The starting point was a basic list of substances comprising the new and old list of Rhine substances (ICPR technical report no. 266 and no. 242, in German, French or Dutch), the check list and substances included in the Rhine Monitoring Programme – Chemical Component 2021 to 2026 (ICPR technical report no. 265, in German, French or Dutch). Because the basic list does not contain enough relevant substances for each of the three emission areas, other information sources were drawn on e. g. national lists of substances and the expertise of the EG MICROMIN members (see figure 1). Using this comprehensive list of substances (initial list) and defined criteria (see 3.1), lists of indicator substances were compiled for the emission areas wastewater treatment plants and industry (see 3.2.1 and 3.2.2).

As the approach for the emission area agriculture is different from the approach used for wastewater treatment plants and industry, the list of indicator substances for agriculture was, for a limited period, addressed separately by selected members of EG MICROMIN (see 3.2.3).

Substances that did not meet the criteria outlined in 3.1 were excluded from selection as an indicator substance; they will be presented again and added to the list once the criteria have been met (see 3.1 and 3.2). Substances that are relevant according to the criteria but for which there was no measurement data for the reference period 2016-2018 and which cannot be reliably measured in the water phase, were, in so far as permitted by the analysis methods, included in the suspended particulate matter monitoring programme (see 6 and Annex I.D).

Some of the substances cannot be clearly allocated to one emission area and were therefore allocated to all three emission areas (see 3.3).

The lists of indicator substances remain dynamic: substances that are no longer relevant can be deleted and new substances added.

During the regular reviews of the substance lists every three years, a substance can be delisted on the basis of an expert judgement, for example, if during the review period its measurements were always under the limit of quantification and there is no knowledge of a change in the influx situation or, in particular for indicator substances for the emission area agriculture, evaluation benchmarks were not exceeded after the reference period 2016-2018. However, delisting should only be possible after a certain period of time (the current proposal is delisting for the first time after 9 years i. e. 2029) as substances that have not been detected in a long time can also recur (e. g. atrazine). A decision on whether substances may be deleted can only be made on the basis of reliable data and interim reports, and after 2029.

It will be possible to add new substances from 2024 until 2034 at the latest. This deadline is proposed to facilitate statistical evaluation. Details on the further working steps should be agreed from 2034. The impacts of adding substances after the deadline – also in terms of progress towards the reduction target – will be further examined in 2024 as part of the first interim report (see 7). EG SMON will review the data situation of the substances on the tentative list for Rhine 2040 and, if necessary, make proposals for corresponding measurements.

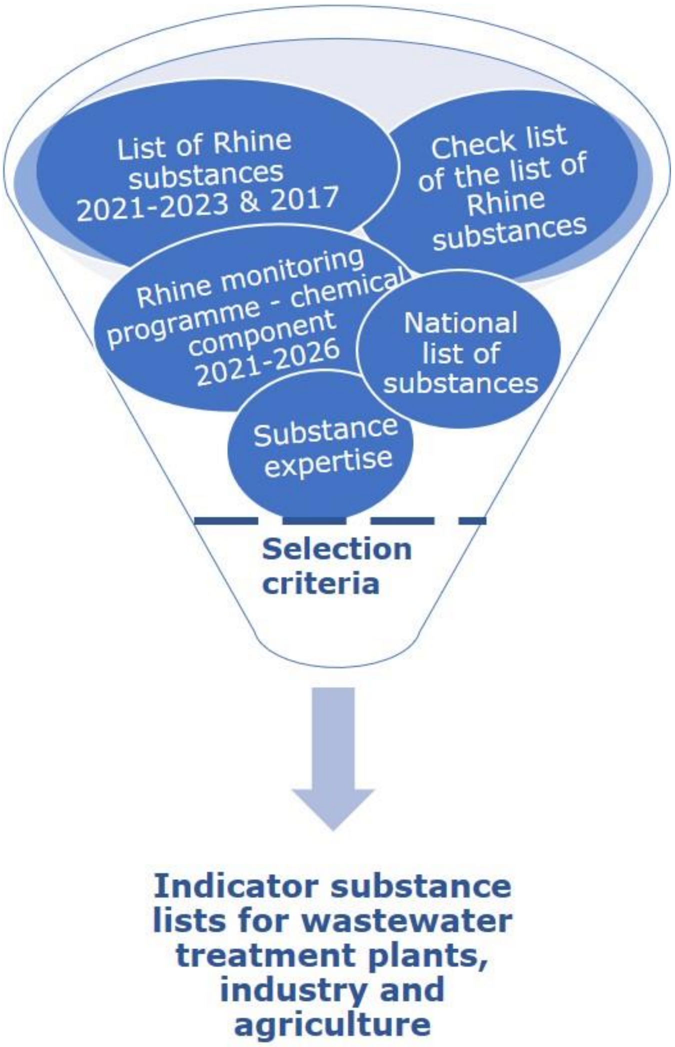

Figure 1: Selection procedure for indicator substances

Details of the procedures for the three emission areas are described in 3.2.1, 3.2.2 and 3.2.3.

3.2.1 Wastewater treatment plants

A basic list of substances (see 3.2) was compiled and used as a starting point for selecting indicator substances which are considered representative for municipal wastewater and currently discharged via wastewater treatment plant effluent. The basic list was supplemented with substances used in Switzerland, Germany and the Netherlands in order to ascertain whether more extensive purification is necessary to eliminate organic micropollutants from wastewater in wastewater treatment plants and monitor performance after construction. By also including these substances, it will be possible in future to establish a connection between the degree of reduction of these substances in the Rhine and more extensive treatment of municipal wastewater in the Rhine catchment area. Alongside these and substances already included in the basic list, expert judgement was drawn on to add further substances that occur in municipal wastewater and are discharged via wastewater treatment plant effluent. A particular focus was on whether a substance is representative of a substance group. Pharmaceutical residues, sweeteners, biocidal products and flame retardants were among the substances considered. It was also examined whether municipal wastewater is the emission source for other important substances, for example, potential priority substances under the EU Water Framework Directive (WFD). Discussions also raised the point that the substitution of individual substances e. g. from the sweeteners or radiocontrast agent substance groups, can lead to a reduction of one substance from the group, but cause an increase in another substance from the same group. It was therefore decided to include several substances from one group as indicators in order to avoid such an effect.

A decisive factor was good measurability of the substances in the Rhine and its tributaries (see criterion H3, 3.1) at the designated ICPR Rhine monitoring stations; additional, specific criteria for municipal wastewater as an emission source were not necessary. For this purpose, it was reviewed whether the substances were measured at these ICPR monitoring stations, whether the measurement data falls significantly above the limit of quantification and whether a usable data set for the reference period 2016-2018 is available.

3.2.2 Industry

The indicator substances were checked against the list of substances of the Special Chemistry Monitoring Programme 2017 (ICPR technical report no. 257) for conformity and allocated to different sectors of industry. A decisive factor was good measurability of the substances in the Rhine and its tributaries at the designated ICPR Rhine monitoring stations (see criterion H3, 3.1).

Industrial chemicals were assigned to sectors of industry in two stages.

First, information on the production and application of the chemicals was researched in different databases. The following databases were used:

- IGS-OW (information system for hazardous substances in surface waters) of the North Rhine-Westphalia Office of Nature, Environment and Consumer Protection (LANUV): https://igsow.lanuv.nrw.de/igs_ow (registration required, in German only)
- IGS (information system for hazardous substances) of the North Rhine-Westphalia Office of Nature, Environment and Consumer Protection (LANUV): https://igsvtu.lanuv.nrw.de/igs80s/Suche?scope=776005e466a0cc00 (in German only)
- PubChem (open chemistry database at the National Institutes of Health (NIH)) of the U.S. National Library of Medicine: https://pubchem.ncbi.nlm.nih.gov/
- Substance databases of the European Chemicals Agency (ECHA): https://echa.europa.eu/de/home
- OECD eChemPortal (The Global Portal to Information on Chemical Substances): https://www.echemportal.org/echemportal/

In some cases, links provided on these websites were also used e. g. to the U.S. EPA (United States Environmental Protection Agency), UNEP (United Nations Environment Programme), Environment and Climate Change Canada and ChemSec (International

Chemical Secretariat). Wikipedia was consulted in exceptional cases where sufficient information was not available elsewhere.

At the same time, the extent to which specific industrial sectors can be identified as a source for the substances was also examined. In accordance with Annex I to the Industrial Emissions Directive (2010/75/EU), industrial activities are categorised as follows, with further subcategories:

(1) Energy industries

(2) Production and processing of metals

(3) Mineral industry

(4) Chemical industry (including plastics, dyes and pigments, fertilisers, plant protection products or biocides, pharmaceutical products, photography industry, biotechnology)

(5) Waste management

(6) Other activities (including paper or cardboard, pre-treatment or dyeing of textile fibre or textiles, production of food or feed, intensive rearing of poultry or pigs, preservation of wood and wood products)

Under the IED, the production of fertilisers, plant protection products and biocides on an industrial scale is allocated to the chemical industry. The Directive does not take into account the potential use of these substances in the agricultural sector (as an emission source). The IED only considers the production of certain substances, the use of these substances/groups of substances is addressed in other regulations.

In line with this, these groups of substances were initially allocated to the chemical industry as a producing industrial sector. The agricultural sector was understood as a "user" of these substances. The user side is addressed in 3.2.3 below.

3.2.3 Agriculture

A collection of substances fulfilling one or several of the following criteria was taken as the starting point (herbicides, fungicides and insecticides as well as the known mobile transformation products of some active substances):

- Substances of the Rhine Monitoring Programme – Chemical Component 2021-2026 (ICPR technical report no. 265, in German, French or Dutch)
- Findings of the Rhine water quality reports 2015-2016 (ICPR technical report no. 251, in German, French or Dutch) and/or 2017-2018 (ICPR technical report no. 281, in German, French or Dutch)
- Substances for which there are documented findings in the Rhine in the RIWA report 2018 and/or in the 2018 ARW reports
- Substances measured in water samples taken along the Rhine (at Weil am Rhein, Koblenz and Bimmen) (e. g. Boulard et al. 2018, Hermes et al. 2018)
- Active substances of plant protection products sold in high quantities in Germany in 2015 (herbicides > 500 t, fungicides > 400 t, insecticides > 30 t)

Substances which the countries now no longer approve, or which will lose approval in the near future and thus be banned from use, were deleted from the comprehensive list of substances.

While concentrations in the Rhine are highly diluted and thus largely below the limit of quantification for routine analysis, substances used in agriculture exceed the quality standards, primarily in smaller catchment areas of the Rhine tributaries (see 7.2 and Annex I.C). It was therefore decided that in the first monitoring period, the focus would be on tributaries and smaller water bodies in the Rhine catchment areas rather than the

Rhine itself (see 4.2 and Annex III.B). This will make it possible to measure and assess influxes near their place of origin. In addition, substances which national monitoring programmes found to be conspicuous in small catchment areas were added to the list, alongside substances for which, on the basis of an expert judgement, there is sound reason to expect the substance to become more significant in future.

Lastly, the selection of indicator substances for agriculture also took into account whether, based on existing measurement data and experience, the measured concentrations can be expected to exceed eco(toxico)logical water quality standards or quality standards for the object of protection drinking water (see Annex I.C). It is only under this condition that the reduction can be quantified. This procedure is directly connected to the evaluation approach for the emission area agriculture (see 7.2) which is based on exceedances of eco(toxico)logical water quality standards or drinking water quality standards (Sum Standard Exceedances (SNO) method which determines by how much total concentrations exceed quality standards).

For the emission area agriculture, a dynamic list of indicator substances means that it has to be updated when a new benchmark is established for a substance (see 7.2). In terms of delisting, in particular for agricultural indicator substances, it must be borne in mind that a substance can be delisted not only if measurements are below the limit of quantification, but also if evaluation benchmarks are not exceeded after the reference period.

Substances that are difficult to analyse in the water phase have not currently been included as indicator substances in the list for the emission area agriculture but have been added to the Rhine 2040 tentative list (see 3.3).

3.3 Selection of substances for the Rhine 2040 tentative list

For the first reporting period (see 8), a number of potential indicator substances were deleted from the initial list for indicator substances as, for example, too little data was available for the reference period 2016-2018. During the review of the substance lists after three years (also corresponds to the review cycle of the Rhine Monitoring Programme – Chemical Component, first review 2023), these substances should also be reviewed and a new decision taken on whether to include them as indicator substances for one of the three emission areas. An overview of the candidate substances can be found in Annex II.

4. Monitoring station selection

To get as comprehensive an overview of the river's catchment area as possible, the reduction of micropollutant influxes for the emission areas wastewater treatment plants and industry will be monitored at existing monitoring stations in the main stream of the Rhine and estuaries of selected tributaries (see 4.1 and Annex III.A). These monitoring stations are less suitable for the emission area agriculture as, due to dilution, plant protection products in the Rhine can only be detected in very low concentrations, meaning it is no longer possible to make a statement on the progress towards target achievement for agriculture. To monitor and evaluate a reduction in agricultural influxes, it is therefore necessary first and foremost to include smaller watercourses in the Rhine catchment area in monitoring activities. For this reason, a separate monitoring station selection procedure was followed for agriculture (see 4.2 and Annex III.B).

Furthermore, the objects of protection aquatic ecosystems and drinking water production were taken into account in the selection of monitoring stations for the emission area agriculture (see 4.2). This was not explicitly done for the monitoring stations for wastewater treatment plants and industry; however, these two objects of protection are expressly served by the ICPR main monitoring stations (see 4.1), included in the framework of the International Warning and Alarm Plan (IWAP) (ICPR technical report no. 256, in German, French and Dutch).

4.1 Wastewater treatment plants and industry

The ICPR main monitoring stations have the highest density of monitoring data for the indicator substances selected for wastewater treatment plants and industry. To maximise potential synergies with the reporting of EG SMON, the following monitoring stations in the main stream of the Rhine will be used to take samples in the water phase: Weil am Rhein, Karlsruhe-Lauterbourg, Koblenz (Rhine), Koblenz (Moselle), Bimmen, Lobith and Maassluis. The ICPR main monitoring stations Rekingen and Kampen cannot be considered due to insufficient data (at Kampen: in the 2016-2018 reference period).

In addition to these ICPR main monitoring stations, further monitoring stations were designated for the emission areas wastewater treatment plants and industry (including tributaries): Brugg (Aare, Switzerland), Mannheim (Neckar, Germany), Bischofsheim (Main, Germany), mouth of the river Lippe near Wesel (Germany) and Nieuwegein (the Netherlands). The delegations carry out measurements and statistical evaluations for these additional monitoring stations (see Table 4). Overall aggregation of the data can be undertaken by EG SMON. See section 8 for reporting.

An overview map of the selected monitoring stations can be found in Annex III.A.

It must be pointed out that the reduction of micropollutants in the Rhine catchment area cannot be clearly attributed to an emission area at all locations and is not always representative of the entire catchment area. This is because of the different Rhine tributaries and branches of the Rhine in the Delta Rhine downstream of Bimmen/Lobith on the German-Dutch border. The values measured at the Dutch monitoring stations Maassluis and Nieuwegein will therefore not reflect the reduction of micropollutants in the entire Delta Rhine area. However, both monitoring stations can present the possible reduction of loads and concentrations and the effectiveness of measures, as already explained in section 1.

4.2 Agriculture

The following criteria were used to select monitoring stations for the emission area agriculture:

(1) The agricultural influence is marked and the influence of other pressures is comparatively low (< 50%).

(2) The monitoring stations are distributed across small, medium-sized and large catchment areas, with a focus on small catchment areas.

(3) Exceedances of quality standards for the selected indicator substances have already been detected and continue to be expected at these monitoring stations (see Annex I.C).

(4) The monitoring stations will be available on a long-term basis and belong to an existing monitoring network (*note: it cannot be 100% guaranteed that the monitoring stations will continue to be operated up until 2040, as in Switzerland and the Netherlands agreements with operators only apply for a few years at a time*).

(5) The reference period is 2016-2018 (*note: the use of a later reference period is also possible in justified exceptional cases*).

(6) Each monitoring station will cover, in so far as possible, the influence of different agricultural crops.

For this emission area, Switzerland has selected 6 monitoring stations, Germany 10, France 4 and the Netherlands 16.

The Netherlands has created an Excel template to harmonise evaluation by the countries (see 8).

An overview map of the selected monitoring stations can be found in Annex III.B.

5. Monitoring requirements

The following gives an overview of the monitoring specifications for indicator substances for wastewater treatment plants and industry (see 5.1) and agriculture (see 5.2). Annexes I and III are the authoritative basis.

The methods of analysis must meet the quality requirements of Directive 2009/90/EC. The analysis must be performed by laboratories that are equipped with a quality management system pursuant to DIN EN ISO/IEC 17025 and regularly demonstrate their competence to carry out the analysis through participation in interlaboratory comparisons.

5.1 Monitoring wastewater treatment plants and industry

The relevant specifications under the Rhine Monitoring Programme – Chemical Component 2021-2026 (ICPR technical report no. 265, in German, French and Dutch) are taken as a basis for monitoring indicator substances for the emission areas wastewater treatment plants and industry. The following key points on sampling techniques and measurement frequency are highlighted here:

5.1.1 Sampling techniques

With the exception of the Swiss monitoring stations and those of the BfG, the Rhine Monitoring Programme – Chemical Component is currently only collecting random samples at the main monitoring stations. As the review of progress on the reduction target for micropollutants from wastewater treatment plants and industry is based on load calculation (see 7), the goal should be to switch to composite sampling in future in order to further improve the data reliability of the main ICPR monitoring stations.

Analytes that are insufficiently stable or that exhibit sorption effects must continue to be studied in random samples.

The annual sampling calendars are compiled by EG SMON and can be obtained from the ICPR secretariat.

5.1.2 Measurement frequency

A standard measurement frequency of 13 measurements a year for each monitoring station was laid down.

Measurement frequency should be increased if substance concentrations show a broad margin of fluctuation or if there are other technically justifiable reasons.

5.2 Monitoring agriculture

The following provides an overview of sampling techniques and measurement frequency for the emission area agriculture. The criteria for this area are determined by the evaluation method selected for the agriculture sector, the SNO method (see 3.2, 7.2).

5.2.1 Sampling techniques

The countries use different sampling techniques. Both random and composite samples are collected. Due to the often seasonal application, taking isolated random samples at longer intervals (generally every four weeks) is less suitable for monitoring dynamic, often rain-driven influxes such as those from agricultural plant protection products, or for calculating trends. Continuous composite sampling or complex event-based sampling provide a much more accurate picture of the pollution arising from agricultural plant protection products.

That being said, if the SNO method is used to calculate the trend, the choice of sampling technique makes no difference as long as the sample is consistently collected at a monitoring station in the same way.

5.2.2 Measurement frequency

The SNO method prescribes measurements of at least 10 substances with eco(toxico)logical water quality standards. The current list for emission area agriculture comprises 26 substances (see Annex I.C).

The goal should be a standard sampling frequency of at least once a month at all monitoring stations. Where this is not possible, a minimum measurement frequency of four times in the growing season and twice in the runoff period is necessary (see Table 1).

Table 1: Overview of measurement frequency in agriculture

Standard measurement frequency	Annually, 12x per year
Recommended sampling months	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12
Where this is not possible:	
Minimum measurement frequency	Annually, at least 6x per year
Sampling months for minimum measurement frequency	4, 5, 6, 7, 8, 10

6. Supplementary monitoring programme – suspended particulate matter

A number of studies have demonstrated that highly sensitive trend analyses can be obtained by examining composite samples of suspended particulate matter for a broad range of micropollutants (e. g. Boulard et al., 2020[1]; Brand et al., 2018[2]; Nagorka & Koschorreck, 2020[3]; Rüdel et al., 2013[4]; Wick et al., 2016[5]). In light of that, the annual composite samples of suspended particulate matter from the Rhine stored in the German Environmental Specimen Bank (UPB) are also studied and analysed with regard to micropollutant reduction (see 3.2).

6.1 Sampling locations and frequency

By analysing the annual composite samples of suspended particulate matter stored at the UPB, long-term trends in selected analytes can be identified for three locations along the Rhine (Weil am Rhein, Rh-km 174; Koblenz, Rh-km 590.3 and Bimmen, Rh-km 865). Over a one-month period, the BfG collects suspended particulate matter at each monitoring station using sedimentation boxes. It is then combined at the UPB into annual composite samples and stored there at < -150°C. To ensure comparability, samples are collected and processed consistently in line with standard protocols (Ricking et al., 2017[6]). The German Environment Agency (UBA) has confirmed that the UPB can provide suitable samples.

6.2 Trend analysis

A non-commercial UBA software tool (LOESS-Trend, version 1.1, based on Microsoft Excel) has proven effective for compiling linear and non-linear trend statistics. The tool applies a locally weighted scatterplot smoother (LOESS, with a fixed seven-year timeframe) based on annual concentrations data. It then tests for significance of linear and non-linear trends using analysis of variance (ANOVA) in line with the approach of Fryer and Nicholson (1999[7]). Starting with suspended particulate matter samples from 2016, the first reliable trends can be expected as early as 2023. However, the practicality and usefulness of applying a higher temporal resolution (e. g. three-monthly composite samples) and further software tools (e. g. *Trendanalist*; https://www.amo-nl.com/software/trendanalist) are also being examined. The samples are analysed in threefold determination and regularly classified to ensure quality, retrieval and precision. Depending on analytical resources, it may be possible to extend the retrospective

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[4] Rüdel, H.; Böhmer, W.; Müller, M.; Fliedner, A.; Ricking, M.; Teubner, D.; Schröter-Kermani, C. (2013). Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: Results from the German Environmental Specimen Bank. Chemosphere 91, 1517–1524.

[5] Wick, A.; Jacobs, B.; Kunkel, U.; Heininger, P.; Ternes, T.A. (2016). Benzotriazole UV stabilizers in sediments, suspended particulate matter and fish of German rivers: New insights into occurrence, time trends and persistency. Environ.Pollut.212, 401-412.

[6] Ricking, M.; Keller, M.; Heininger, P.; Körner, A. (2017). Richtlinie zur Probenahme und Probenbearbeitung – Schwebstoff. https://www.umweltprobenbank.de/upb_static/fck/download/SOP_UPB_Schwebstoffe_V_4.0.3.pdf

[7] Fryer, R.J., Nicholson, M.D., (1999). Using smoothers for comprehensive assessments of contaminant time series in marine biota. Ices J. Mar. Sci. 56/779-790.

analysis back to 2005, and thus further increase the statistical reliability of the trend analysis.

6.3 Substance spectrum and analytical methods

Based on expert judgements, a broad spectrum of around 50 micropollutants was selected for monitoring suspended particulate matter. These substances cover a wide range of physicochemical properties and areas of application (see Annex I.D). They represent the three emission areas selected for micropollutants:

a) municipal wastewater treatment plants (e. g. pharmaceuticals and biocides)

b) industrial emissions (e. g. phosphonium compounds)

c) (diffuse) influxes from agriculture (plant protection products)

Up to 20 additional optional micropollutants can be added to the monitoring programme if measurements in 2022 show that (a) the concentrations of these substances in samples of suspended particulate matter from 2016, 2017 and 2018 exceed the limit of quantification by at least a factor of 5, and (b) validated methods are available.

The substance spectrum may change over the years, as some substances are replaced and new substances are brought onto the market. If literature and identification through non-target analyses indicate that substances previously not considered may be especially relevant for assessing trend development, these substances can potentially be added to the spectrum at a later stage and analysed retrospectively in the samples of suspended particulate matter stored at the UPB.

To complete the holistic monitoring approach, the suspended particulate matter is also analysed using high-resolution mass spectrometry. The use of a database study (Jewell et al., 2019[8]), which draws on a BfG in-house spectra database comprising over 1,000 micropollutants, allows a wide variety of micropollutants to be screened and where relevant integrated into the quantitative trend monitoring.

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[8] Jewell, K.S.; Kunkel, U.; Ehlig, B.; Thron, F.; Schlüsener, M.; Dietrich, C.; Wick, A.; Ternes, T.A. (2019). Comparing mass, retention time and tandem mass spectra as criteria for the automated screening of small molecules in aqueous environmental samples analyzed by liquid chromatography/quadrupole time-of-flight tandem mass spectrometry. Rapid Commun. Mass Spectrom. 34:e8541.

7. Evaluating influx reduction

The goal is to use the collected data to obtain an overview of the reduction of micropollutant influxes into the Rhine from the three emission areas in comparison to the 2016-2018 period. The evaluation approach for wastewater treatment plants and industry differed from that taken for the emission area agriculture.

Emission areas wastewater treatment plants and industry

The review of progress towards the reduction target for emission areas wastewater treatment plants and industry was based mainly on load calculation (see 7.1). However, this approach needs to bear in mind that only random samples are currently being collected at many monitoring stations. The higher degree of uncertainty which arises when calculating loads using random samples must be factored into the evaluation of the results (see 5.1.1).

Evaluation is generally carried out for each substance and at each monitoring station. The method ultimately used for the overall evaluation can only be decided at a later stage, once initial results are available. The following gives a brief overview of possible methods for wastewater treatment plants and industry which were discussed in EG MICROMIN.

One possibility is an **overall evaluation** based on the sum of the loads of all substances at all monitoring stations (by adding together the total load of each monitoring station).

To evaluate the potential threat to the objects of protection drinking water production and aquatic ecosystems, a supplementary concentration analysis may also be necessary. The drawback to the approach described is that it rules out an eco(toxico)logical evaluation because it does not also consider the properties of the relevant indicator substances. The continued use of this approach must be reviewed in future.

Emission area agriculture

The emission area agriculture was looked at separately, as the influx situation here is very different to that of the emission areas wastewater treatment plants and industry (see 4.2). Often, load calculations at agricultural locations in smaller water bodies are not possible because of a lack of flow data. At the Rhine monitoring stations, on the other hand, dilution effects mean that concentrations of most plant protection products are generally below the limit of quantification.

In light of this, an **evaluation approach** based on concentration levels and exceedance of benchmarks (see 7.2) was selected for agriculture. Aquatic ecosystems and drinking water production were the objects of protection selected for analysis. The evaluation approach for agriculture is essentially already an evaluation of all indicator substances for agriculture for each monitoring station. To obtain the **overall evaluation** of the Rhine catchment area, findings from all monitoring stations must be totalled up (see 7.2).

Impact of changes to the substance lists

Indicator substances deleted from the list of substances before 2040 (see 3.2) are factored into the overall evaluation proportionately. However, the same 30% reduction target cannot apply to substances that are added to the list of indicator substances up to 2034. Instead, for example, their influx reduction target should be a proportion of the 30% target in keeping with the date the substance was added to the list. Current knowledge indicates that substances can only be added to the list up to 2034, because measurements covering a minimum period of time are required to carry out a trend analysis. The initial interim report in 2024, when substances are expected to be added to the list for the first time, will also examine how these substances can be included in the evaluation methods used up to that time.

7.1 Evaluation approach for wastewater treatment plants and industry

Based on influx load calculations (kg/day), the micropollutant reduction in the emission areas wastewater treatment plants and industry is evaluated with the *Trendanalist* programme that has been used for many years in the Netherlands. The following is a brief overview of this method, a detailed description can be found in Annex IV.

Trendanalist enables the size and direction of the trend to be determined and the statistical significance checked. As *Trendanalist* was designed with environmental research in mind, it can take specific properties of surface water quality variables into account. For example, a non-normal probability distribution (whether or not due to outliers), autocorrelation, seasonal effects, observations below the limit of quantification and missing measured values.

A load reduction of 30% in 20 years corresponds to an annual average reduction of 1.5%. It therefore stands to reason that monitoring the temporal trend of the load is a good way to ascertain whether measures to reduce emissions have been successful and effective.

An annual load reduction of at least 1.5% is needed to ensure with sufficient statistical reliability (significance) that the influx reduction target of 30% will be achieved by 2040, provided the efforts undertaken are maintained.

To secure the quality of results across different data sets, the data sets must fulfil certain basic requirements. The following data selection criteria have been laid down for the use of *Trendanalist*: The load in random samples is determined using the measured concentration and daily average discharge of the calendar day (24-hour period) of the sampling. For composite samples, the daily average discharge of the calendar day on which the composite samples were collected is used. If a composite sample covers a period of several calendar days, the daily average discharge of these calendar days is used.

The target load reduction is determined relative to the reference period 2016-2018. The median of all observations in the period 2016-2018 is laid down as a reference value. The median is taken because water quality observations are generally non-normally distributed (skewed). Where distribution is skewed, the median gives a better description of the water quality because it is less sensitive to outliers than the arithmetic mean. For substances with a normal distribution, the median is equal to the mean. In these cases, too, the choice of the median leads to valid results.

Projecting target achievement

There are two ways to determine whether measures are on track for meeting the reduction target. Firstly, by calculating the relative annual trend (% per year), and secondly, by calculating the load reduction achieved as a percentage of the reference value 2016-2018. As both results are important, it is proposed that they both be presented and the overall result illustrated in a colour chart (see 8, Table 3).

To visualise the probability of target achievement (see Table 2) in the reporting period, a system of symbols to assess the reduction (ticks, exclamation marks, crosses) is proposed:

- Tick: the reduction achieved is ≥ 30%.

- Exclamation mark: the reduction achieved is < 30%, but this parameter will meet the specified target by 2040 if efforts are maintained at the same level.
- Cross: the reduction achieved is < 30% or the load has increased; this parameter will not meet the specified target by 2040 if efforts are maintained at the same level.

Table 2 demonstrates this symbols-based assessment. Taking the period 2016-2020 as an example, the table shows calculations according to the proposed method for different substances from the emission areas wastewater treatment plants and industry. No evaluation is undertaken if the available data is insufficient (less than five years) or if too many values are below the limit of quantification (above 30%).

The substance lists are reviewed every three years and substances are added or delisted (see 3.2). Provided that the collated data meets the basic requirements, new substances can also be included in the evaluation. Calculating the reference value requires three years of data as a basis for determining the median. At least five years of data enables a trend analysis to be carried out and the direction of the trend determined. If all conditions are met, the relative trend can be calculated.

Table 2: Example trend analysis of the substances at Lobith monitoring station for the period 2016-2020.

Group	Parameter	Reduction target achieved?	Reduction or increase achieved (% total)	Relative trend (%/year)	Statistical significance	Years considered	Findings < limit of quantification (%)
Industry	1,4-Dioxane	✓	-76	-15,2	*	5	5
UWWTP[1]	Acesulfame-K	✓	-73	-14,5	*	5	
Industry	Methyl-tertiary-butyl ether (MTBE)	✓	-72	-14,4	*	5	9
UWWTP	Iopamidol	✓	-64	-12,9		5	
UWWTP	Hydrochlorothiazide	✓	-63	-12,7	*	5	
UWWTP	Gabapentin	✓	-55	-11,0	*	5	
UWWTP	Metformin	✓	-52	-10,3	*	5	
Industry	Ethylendiaminetetraacetic acid (EDTA)	✓	-41	-8,1	*	5	
UWWTP	Amidotrizoic acid	✓	-38	-7,6	*	5	
Industry	1,3,5-triazine-2,4,6-triamine (melamine)	!	-26	-5,1	*	5	
UWWTP	Iopromide	!	-22	-4,5		5	
UWWTP	Iomeprol	!	-21	-4,1		5	
UWWTP	Diclofenac	!	-15	-3,0		5	
UWWTP	Benzotriazole	!	-13	-2,6		5	
UWWTP	Metoprolol	!	-11	-2,2		5	
UWWTP	Carbamazepine	!	-8	-1,6		5	2
Industry	Nitrilotriacetic acid (NTA)	✗	13	2,7		5	9
UWWTP	Iohexol	✗	25	4,9		5	
UWWTP	Sucralose	✗	67	13,4	*	5	
UWWTP	Candesartan	No assessment				4	
UWWTP	Clarithromycin	No assessment				5	55

[1] urban waste water treatment plant

NB: "No assessment" is indicated if the number of years with available data is too small (< 5 years) or the proportion of findings < limit of quantification is too high (> 30 %).

7.2 Evaluation approach for agriculture

Concentrations of micropollutants originating in agriculture often fluctuate widely in surface waters. Peak concentrations in smaller water bodies are especially problematic. By the time they reach the main stream of the Rhine, these substances are usually already heavily diluted. The evaluation therefore focuses primarily on smaller watercourses in the Rhine catchment area (see 3.2.3, 4.2 and Annex III.B). The possibility of including the main stream of the Rhine can also be reviewed.

In the Netherlands, eco(toxico)logical impacts (environmental pollution) of plant protection products are assessed using the SNO method based on exceedance of eco(toxico)logical water quality standards[9]. This SNO method is also proposed for the agriculture monitoring stations in the Rhine catchment area.

The sum of exceedances (SNO) describes the extent to which quality standards for all measured substances are exceeded at a monitoring station at a specific point in time.

The method assumes a linear relationship between the environmental pollution and the extent of the exceedance.

The SNO method is based on a *distance-to-target approach* – i. e. the relative difference between the measured value and the target value

$$\text{distance} - \text{to} - \text{target} = \frac{current - target}{target}$$

Here, ‘distance-to-target’ denotes how far the measured concentration (‘current’) of a substance exceeds the eco(toxico)logical water quality standard (‘target’).

Exceedances of quality standards (NO) and hence the level of environmental pollution are first determined for each substance and then added together for each individual monitoring station. The total NO can subsequently be aggregated for each year and for all monitoring stations.

The resulting sum of the exceedances (SNO) is calculated as follows:

A) Calculation of NO (exceedance of standard) value per monitoring station (location), date and substance:

- If measured value < LOQ and LOQ > quality standard: no calculation
- If measured value < LOQ and LOQ <= quality standard: concentration = 0
- Calculation of NO value:

$$\text{NO}_{\text{substance 1, location 1, date 1}} = \frac{\text{concentration}_{\text{substance 1, location 1, date 1}} - \text{quality standard}_{\text{substance 1}}}{\text{quality standard}_{\text{substance 1}}}$$

Key:

- LOQ = limit of quantification
- Quality standard = eco(toxico)logical water quality standard or D3 value (if “Article 7 water body” according to the Water Framework Directive) (see Annex I.C)

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[9] Peijnenburg, W. J. G. M., H. A. den Hollander, R. Luttik, D. van de Meent & D. de Zwart (2000). Ontwikkeling en toepassing van een Milieukwaliteitsindicator Bestrijdingsmiddelen. RIVM Bericht 607880 002, https://www.rivm.nl/bibliotheek/rapporten/607880002.pdf;
Bestrijdingsmiddelen en waterkwaliteit, G.R de Snoo, M.G. Vijver (2012). Universiteit Leiden, Centrum voor Milieuwetenschappen, ISBN 978-90-5191-170-1, http://www.leidenuniv.nl/cml/ssp/publications/bestrijdingsmiddelen_en_waterkwaliteit.pdf;
Atlas bestrijdingsmiddelen in oppervlaktewater, Universiteit Leiden, Centrum voor Milieuwetenschappen, Royal HaskoningDHV.

- NO = extent of exceedance of standard per substance (per location, per date)
- Measured values below limit of quantification (< LOQ) with an LOQ higher than the quality standard (LOQ > quality standard) are not considered, even though the actual concentration may have been higher than the quality standard
- For measured values below the limit of quantification (< LOQ) with a limit of quantification lower than or equal to the quality standard (LOQ ≤ quality standard), the value 0 is taken for the SNO calculation
- If NO <= 0: NO = 0

This method leads to measurements which are given as below the limit of quantification but in which the actual (unknown) concentrations lie between the quality standard and the limit of quantification, thus ensuring that the SNO value is lowered, since these measurements are factored in with NO = 0 (see above). This ensures that, while the SNO value potentially underestimates the actual environmental pollution, only measured loads are factored into the calculation and no potential “false positives”.

B) Calculating the SNO per location and date for all substances:

- At least 10 substances, if the number of substances is < 10: no calculation
- Calculation of total exceedances (SNO) for all substances:

$$\mathrm{SNO}_{\text{all substances, location 1, date 1}} = \sum_{\text{x=1}}^{\text{number of substances}} \mathrm{NO}_{\text{substance x, location 1, date 1}}$$

- e. g.: 50 measured substances at location 1 on date 1: max. 50 NO values

Key:

- SNO = total values of standard exceedances of all substances
- If NO <= 0: NO = 0
- At least 10 substances for which a quality standard exists must be measured. No SNO is calculated if less than 10 substances with a quality standard are measured in a sample.

This produces one SNO value per sample (location, date). To reduce outlier effects, the 90th percentile of the individual SNO values is used to aggregate all samples from a location to an annual SNO value.

C) Calculating the aggregated SNO per location for all dates per year and all substances:

- Calculation of 90th percentile (P90) of all SNO values for the year from each location:

$$\mathrm{SNO}_{\text{all substances, location 1, year}} = \sum_{y=1}^{number\ of\ dates} P90\left[\mathrm{SNO}_{\text{all substances, location 1, date y}}\right]$$

- e. g. 6 measurements of 50 substances at location 1 per year: max. 6 SNO values
- This gives the aggregated SNO value per year and location.
- The SNO values of all locations can be represented on a map.

Finally, an SNO annual average is calculated for the aggregated SNO values of all locations.

D) Calculating the SNO average for all locations per year and for all substances:

- Calculating all SNO values based on the SNO values determined for all locations:

$$\mathrm{SNO}_{\text{all substances, all locations, year}} = \frac{\left[\sum_{z=1}^{\text{number of locations}} \mathrm{SNO}_{\text{all substances, location z, year}}\right]}{\text{no. of locations}}$$

- The SNO values determined per year and for all locations can be represented in a trend graph.

To determine progress towards the target, the three-year average of the review period can be compared with the three-year average of the reference period.

For the emission area agriculture, the two objects of protection aquatic ecosystems and drinking water production are considered and the SNO method applied. In the case of drinking water production this method is only used for “Article 7 water bodies” under the Water Framework Directive, i. e. water bodies from which drinking water is actually abstracted. For these water bodies, the D3 value[10] of North Rhine-Westphalia (Germany) applies; this is generally based on the Drinking Water Ordinance (TrinkwV) or the UBA health advisory levels. The more stringent value is used to calculate the SNO.

Existing eco(toxico)logical water quality standards should be applied in the following order of priority - first the quality standard (1), then (2) or (3), depending on availability:

(1) Quality standards (specified by law) in a country in the Rhine catchment area (annual average), based on the latest environmental quality standard (EQS) values or on chronic quality criteria, derived in accordance with EU Guidance document no. 27 (see Annex I.C)

(2) Maximum permissible concentration (MPC) values of the Netherlands (to be applied to all individual samples, no annual average)

(3) German regulatory acceptable concentration (RAC) values[11] (to be applied to all individual samples, no annual average)

The trend is calculated using current quality standards. This means that the trend must be recalculated retroactively if a quality standard is changed (cf. SNO method).

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[10] Drinking water-specific target value derived in North Rhine-Westphalia. The value ensures that drinking water consumption is safe for life from a human-toxicological perspective. Further information can be obtained by the North Rhine-Westphalia Office of Nature, Environment and Consumer Protection (https://www.lanuv.nrw.de/).

[11] Further information in the German National Action Plan on Sustainable Use of Plant Protection Products (NAP): https://www.nap-pflanzenschutz.de/en/.

8. Reporting and communication of data

The BfG collects and reviews data for the **emission areas wastewater treatment plants and industry** at selected ICPR main monitoring stations. The respective delegations perform the task for the other monitoring stations. Overall aggregation of the data can be undertaken by EG SMON (see 4.1). Data collection, validation and trend analysis are carried out annually and the results documented and communicated using an internal table. The period 2016-2018 was laid down as a data basis.

For the **emission area agriculture**, each delegation analyses the data from their own monitoring stations. Each country aggregates and analyses the data using a uniform Excel template (see 4.2). Their findings are documented and communicated annually.

Overall evaluation and reporting for the three emission areas are carried out by selected members of the Working Group Water Quality/Emissions (WG S) and published every three years in an ICPR technical report. The first report will be published in 2024 for the years 2021, 2022 and 2023.

The interim reports will cover the following elements:

- Trends in concentrations and loads of indicator substances for wastewater treatment plants and industry, per monitoring station (colour chart of selected monitoring stations or heat map, see Table 3) and overall evaluation
- Analysis of more ambitious targets (reduction > 50/70%)
- Trend analysis of selected substances at selected monitoring stations (see Table 2)
- SNO for Rhine catchment area for agriculture indicator substances
- Review of the list of substances and possible inclusion of further substances from the Rhine 2040 tentative list
- The first report should also review the suitability of the monitoring stations for the evaluation methods.

The final report will be published in 2040.

The visualisation of the overall results will be presented in a colour chart (see Table 3).

Table 3: Colour chart visualisation of overall results

Colour	**Change wastewater treatment plants/industry**	**Change agriculture**
green	Reduction ≥ 30%	SNO ≤ 0.7 SNO reference period
yellow	Reduction < 30%	SNO > 0.7 SNO reference period
red	No reduction or increase	SNO reference period or no reduction or increase

9. Conclusion and outlook

In the Rhine 2040 programme it was agreed that the influx of micropollutants into waters is to be reduced by at least 30%. This technical report specifies the monitoring to be carried out to facilitate a facts-based review of the target at regular intervals and defines an evaluation system for reduction across the three emission areas wastewater treatment plants, industry and agriculture.

EG MICROMIN, that was tasked with developing this system, has now concluded its work and has been disbanded. In future, the WG S will review the reduction target and substance lists with the support of its expert groups (see ICPR-mandates 2022-2027).

A dynamic substance list was compiled for each of the three emission areas. In addition, a separate evaluation approach was used for agriculture, as the influx situation for this emission area is very different to that of wastewater treatment plants and industry.

Evaluation is generally carried out for each substance and monitoring station. How the overall evaluation will ultimately be carried out can only be decided at a later stage once initial results are available.

Data collection, validation and trend analysis are performed annually and the results documented and communicated using an internal table. The period 2016-2018 was laid down as a data basis. A first public report is planned for 2024 and a final report for 2040.

Evaluation of the results will review to what extent existing findings can be supplemented with information from other sources such as climate projections or the German National Action Plan on Sustainable Use of Plant Protection Products. The evaluation also considers measures at source and other emission-reducing measures, e. g. those implemented during application. This should also take into account the future EU Regulation on statistics on agricultural input and output (SAIO Regulation) on the use of plant protection products in the individual EU member states.

Groundwater pollution was not included in the work of EG MICROMIN, which focussed – also in light of the other tasks of WG S and the available data – on surface water pollution and on establishing a system to evaluate this with a view to reducing influxes. An evaluation of the procedure must examine whether the focus should be expanded in future.

Eco(toxico)logical effects are only considered for the emission area agriculture at present but could be looked at for emission areas wastewater treatment plants and industry as well, for instance using the SNO method.

Moreover, in future a toxicity index could be defined for each monitoring station. There are a number of different methods for doing this, including the msPAF method (multi substance potentially affected value[12]). Using this tool, the toxic pressure of the substances, substance groups and complete substance mixtures can be calculated based on the monitoring data.

The extent to which results from non-target analysis or effect-based methods can be considered will also be examined.

The possibility of considering the effects of mixtures in future reporting will be reviewed, either as part of or following the first assessment for the 2024 interim report.

Once initial experiences with measurements and their evaluation have been gathered, a decision will be taken on holding a workshop with participation of the countries to discuss open questions, such as whether sampling is precise enough and how toxic pressure can be considered alongside substance loads.

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[12] Dekker, E., J. Slootweg, R. Koopman, L. Osté & L. Posthuma (2021). Protocol gebruik rekentool Chemie-spoor SFT2. Achtergronddocument beschikbare kennis bij de sleutelfactor Toxiciteit. Versie 1, 30 november 2021. KIWK-Toxiciteit Notitie. Amersfoort, the Netherlands. Kennis Impuls Water Kwaliteit.

Annexes

I. Selection of indicator substances

The procedure for selecting indicator substances (I.A to I.C) is described in section 3.2.

(A) Wastewater treatment plants

Substance name	CAS registry number	Application
Acesulfame	55589-62-3	artificial sweetener
Benzotriazole	95-14-7	corrosion inhibitor
Candesartan	139481-59-7	ACE-inhibitor (antihypertensive)
Carbamazepine	298-46-4	antiepileptic
Carbendazim	10605-21-7	biocide/fungicide
Clarithromycin	81103-11-9	antibiotic (macrolide)
Diatrizoate/Amidotrizoic acid	117-96-4	X-ray contrast agent
Diclofenac	15307-86-5	antiphlogistic
Gabapentin	60142-96-3	antiepileptic
Hydrochlorothiazide	58-93-5	diuretic
Ibuprofen	15687-27-1	antiphlogistic
Iohexol	66108-95-0	X-ray contrast agent
Iomeprol	78649-41-9	X-ray contrast agent
Iopamidol	60166-93-0	X-ray contrast agent
Iopromide	73334-07-3	X-ray contrast agent
Metformin	657-24-9	antidiabetic agent
Methylbenzotriazole (Sum 4- and 5-Methylbenzotriazole)	- // 136-85-6	corrosion inhibitor
Metoprolol	37350-58-6	beta blocker
Sucralose	56038-13-2	artificial sweetener
Sulfamethoxazole	723-46-6	antibiotic (sulfonamide)
Venlafaxine	93413-69-5	psychiatric drug (antidepressant)

(B) Industry

Substance name	CAS registry number	Application	Industrial sector (according to IED)*
1,4-Dioxane	123-91-1	solvent	(4) chemical industry (6) other activities
EDTA (Ethylenediaminetetraacetic acid)	60-00-4	complexing agent	(2) production and processing of metals (4) chemical industry (6) other activities
Glyme (Di-, Tri-, Tetra-)	111-96-6 112-49-2 143-24-8	solvent	(4) chemical industry (6) other activities
Melamine	108-78-1	various (melamine resins, pastes, glues)	(3) mineral industry (4) chemical industry (6) other activities
MTBE (Methyl tertiary-butyl ether)	1634-04-4	solvent	(4) chemical industry
NTA (Nitrilotriacetic acid)	139-13-9	complexing agent	(2) production and processing of metals (4) chemical industry (6) other activities
PFBA (Perfluorobutanoic acid)	375-22-4	PFAS	(2) production and processing of metals (4) chemical industry
PFBS (Perfluorobutanesulfonic acid)	375-73-5	PFAS	(4) chemical industry (6) other activities
PFOA (Perfluorooctanoic acid)	335-67-1	PFAS	(4) chemical industry (6) other activities
PFOS (Perfluorooctanesulfonic acid)	1763-23-1	PFAS	(2) production and processing of metals (4) chemical industry (6) other activities
TPPO (Triphenylphosphine oxide, old: Triphenylphosphane oxide)	791-28-6	intermediate of Wittig synthesis	(4) chemical industry

* IED: Industrial Emissions Directive (2010/75/EU)

(C) Agriculture

Substance name	CAS registry number	Application	EQS value* [µg/l] (year, country)	D3 value** [µg/l]
Herbicides				
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7	orchards, arable crops (cereal)	0,6 (2016, CH)	0,1
AMPA *(only for protected good drinking water)*	1066-51-9	arable crops, viticulture, orchards *(TP of glyphosate)*	/	1
Chlortoluron	15545-48-9	arable crops (cereals)	0,6 (2016, NL)	0,1
Desethylterbuthylazine	30125-63-4	arable crops (maize) *(TP of terbuthylazine)*	0,25 (2016, NL)	0,1
Diflufenican	83164-33-4	arable crops (cereals)	0,01 (2018, CH)	0,1
Dimethachlor	50563-36-5	arable crops (oil seed rape)	0,12 (2019, CH)	0,1
Dimethenamid	87674-68-8	arable crops	0,26 (2019, CH)	0,1
Flufenacet	142459-58-3	arable crops (maize, cereals)	0,048 (2018, CH)	0,1
Glyphosate *(only for protected good drinking water)*	1071-83-6	arable crops, viticulture, orchards	/	0,1
MCPA (2-methyl-4-chlorophenoxyacetic acid)	94-74-6	orchards, arable crops (cereal)	0,66 (2016, CH)	0,1
Metamitron	41394-05-2	arable crops (sugar beet)	4 (2016, CH)	0,1
Metazachlor	67129-08-2	arable crops (oil seed rape)	0,02 (2015, CH)	0,1
Metazachlor ethane sulfonic acid (Metazachlor ESA) *(only for protected good drinking water)*	172960-62-2	arable crops (oil seed rape) *(TP of metazachlor)*	/	3
Metazachlor oxanilic acid (Metazachlor OXA) *(only for protected good drinking water)*	1231244-60-2	arable crops (oil seed rape) *(TP of metazachlor)*	/	3
Metolachlor	51218-45-2	arable crops (maize)	0,69 (2016, CH)	0,1
Metolachlor ethane sulfonic acid (Metolachlor ESA) *(only for protected good drinking water)*	171118-09-5	arable crops (maize) *(TP of metolachlor)*	/	3
Metolachlor oxanilic acid (Metolachlor OXA) *(only for protected good drinking water)*	152019-73-3	arable crops (maize) *(TP of metolachlor)*	/	3
Metribuzin	21087-64-9	arable crops (potato, cereals)	0,058 (2016, CH)	0,1
Nicosulfuron	111991-09-4	arable crops (maize)	0,0087 (2016, CH)	0,1
Propyzamide	23950-56-5	arable crops (oil seed rape)	0,063 (2018, CH)	0,1
Prosulfocarb	52888-80-9	arable crops (potato, cereals)	0,55 (2013, NL)	0,1
Terbuthylazine	5915-41-3	arable crops (maize)	0,32 (2020, NL)	0,1

Table continued on next page.

Continuation:

Fungicides				
Azoxystrobin	131860-33-8	arable crops (cereals)	0,2 (2017, NL)	0,1
Tebuconazole	107534-96-3	orchards, viticulture, arable crops (cereals, oil seed rape)	0,24 (2016, CH)	0,1
Insecticides				
Pirimicarb	23103-98-2	arable crops (cereals)	0,09 (2016, CH)	0,1
Thiacloprid	111988-49-9	orchards, arable crops	0,01 (2016, CH)	0,1

* EQS value: Annual average/chronic EQS based on the most recent EQS values according to the requirements of EU Guidance Document No. 27.

** year: year of the derivation of the EQS value

*** D3 value: Drinking water-specific target value derived in NRW. This value ensures that drinking water consumption is safe for life from a human toxicologic perspective.

(D) Supplementary monitoring programme – suspended particulate matter

Further information on the supplementary monitoring programme – suspended particulate matter can be found in section 6.

Substance name	CAS registry number	Application	Emission source (mainly)*
Herbicides			
Flufenacet	142459-58-3	herbicide	agriculture
Metazachlor	67129-08-2	herbicide	agriculture
Metolachlor	51218-45-2	herbicide	agriculture
Pendimethalin	40487-42-1	herbicide	agriculture
Prosulfocarb	52888-80-9	herbicide	agriculture
Terbuthylazine	5915-41-3	herbicide	agriculture
2-Hydroxyterbuthylazine	66753-07-9	TP of terbuthylazine	agriculture
Desethylterbuthylazine	30125-63-4	TP of terbuthylazine	agriculture
Fungicides			
Chlorothalonil	1897-45-6	fungicide	agriculture
Chlorthalonil Metabolit R417888	1418094-02-95	TP of Chlorthalonil	agriculture
Epoxiconazol	133855-98-8	fungicide	agriculture
Fenpropimorph	67564-91-4	fungicide	agriculture
Prochloraz	67747-09-5	fungicide	agriculture
Prothioconazole	178928-70-6	fungicide	agriculture
Prothioconazol-desthio	120983-64-4	TP of Prothioconazol	agriculture
Tebuconazol	107534-96-3	fungicide	agriculture
Biocides			
DEET	134-62-3	biocide/repellant	UWWTP, agriculture
Propiconazole	60207-90-1	biocide/fungicide	UWWTP, agriculture
Terbutryn	886-50-0	biocide/herbicide	UWWTP, agriculture
Triclosan	3380-34-5	biocide/bactericide	UWWTP, agriculture
Pharmaceuticals and human metabolites			
Amisulpride	71675-85-9	psychiatric drug (antidepressant)	UWWTP
Cetirizine	83881-51-0	antihistamine	UWWTP
Citalopram	59729-33-8	psychiatric drug	UWWTP
Desmethylcitalopram	62498-67-3	metabolite of citalopram	UWWTP
Clarithromycin	81103-11-9	antibiotic (macrolide)	UWWTP
Fexofenadine	83799-24-0	antihistamine	UWWTP
Flecainide	54143-55-4	antiarrhythmic agent	UWWTP
Fluoxetine	54910-89-3	psychiatric drug (antidepressant)	UWWTP
Lamotrigine	84057-84-1	antiepileptic	UWWTP
Lidocaine	137-58-6	local anesthetic	UWWTP
Metoprolol	37350-58-6	beta blocker	UWWTP
Sitagliptin	486460-32-6	antidiabetic	UWWTP
Sotalol	3930-20-9	beta blocker	UWWTP
Sulpiride	15676-16-1	psychiatric drug (neuroleptic, antidepressant)	UWWTP
Telmisartan	144701-48-4	ACE-inhibitor (antihypertensive)	UWWTP
Trimethoprim	738-70-5	antibiotic	UWWTP
Venlafaxine	93413-69-5	psychiatric drug (antidepressant)	UWWTP
O-Desmethylvenlafaxine	93413-62-8	metabolite/TP of venlafaxin	UWWTP
UV-filter substances			
Octocrylen	6197-30-4	UV sunscreen agent	industry
UV-234	70321-86-7	Phenolbenzotriazol UV filter	industry
UV-326	3896-11-5	Phenolbenzotriazol UV filter	industry
UV-327	3864-99-1	Phenolbenzotriazol UV filter	industry
UV-328	25973-55-1	Phenolbenzotriazol UV filter	industry
UV-329	3147-75-9	Phenolbenzotriazol UV filter	industry

Table continued on next page.

Continuation:

Flame retardants and plastizisers			
Bisphenol-A	80-05-7	monomer of plastics and epoxy resins	industry
DEHP, Bis(2-ethylhexyl)phthalate	117-81-7	plastiziser	industry
DIBP, Di-isobutylphthalate	84-69-5	plastiziser	industry
TCEP, Tris(2-chloro ethyl)phosphate	115-96-8	organo phosphorous flame retardant	industry
TCPP, Tris(2-chloro-1-methylethyl)phosphate	13674-87-8	organo phosphorous flame retardant	industry
TDCP, Tris(2-chloro-1-(chloromethyl)ethyl)phosphate	13674-87-8	organo phosphorous flame retardant	industry
TiBP, Tri-isobutylphosphate	126-71-6	organo phosphorous flame retardant	industry
TnBP, Tri-n-butylphosphate	126-73-8	organo phosphorous flame retardant	industry
Perfluorinated alkyl substances (PFAS)			
PFOA	335-67-1	PFAS	industry
PFOS	1763-23-1	PFAS	industry
TOP-Assay			industry
Quaternary phosphonium compounds (QPCs)			
Ethyltriphenylphosphonium	198488-16-3	intermediate of Wittig synthesis	industry
Methoxymethyltriphenyl-phosphonium		intermediate of Wittig synthesis	industry
Methyltriphenylphosphonium	15912-74-0	intermediate of Wittig synthesis	industry
Quaternary ammonia compounds (QACs)			
Benzyldimethyldodecylammonium		biocide/bactericide	agriculture
Denatonium	3734-33-6	bitterant	industry
Dimethyldioctylammonium		biocide/bactericide	agriculture
Dimethyldecyloctylammonium		biocide/bactericide	agriculture
Tetrabutylammonium		diverse	industry
Further substances			
4- and 5-Methylbenzotriazole	29878-31-7 and 136-85-6	corrosion inhibitor	UWWTP
Benzotriazole	95-14-7	corrosion inhibitor	UWWTP
Nonlyphenol	25154-52-3		industry

* UWWTP: urban wastewater treatment plant

Legend: Yellow ("optional")
Will be included if a) compounds at least a factor of 5 above the limit of quantification (LOQ) are detected in samples from 2016, 2017 and 2018 and b) integration in validated methods is possible (checked within 2022).

II. Selection of substances for Rhine 2040 tentative list

Section 3.3 contains a description of the selection of substances for the Rhine 2040 tentative list. The intervals at which the selection of indicator substances is reviewed is outlined in section 8.

Substance name	CAS registry number	Application	Emission source (mainly)*
1,7-Dinaphthalinsulfonic acid	85-47-2	production colourants	industry
2,2,6,6-Tretamethyl-4-piperidione	167078-06-0	UV stabilizers	industry
2-Naphthalinsulfonic acid	120-18-3	intermediate production direct colourants, reactive colourants	industry
Amisulprid	71675-85-9	psychiatric drug (antidepressant)	UWWTP
Azithromycin	83905-01-5	antibiotic (macrolide)	UWWTP
Bezafibrat	41859-67-0	Cholesterol lowering agent	UWWTP
Butylpyrrolidin	767-10-2	intermediate, solvent	industry
Ciprofloxacin	85721-33-1	antibiotic	UWWTP
Citalopram	59729-33-8	psychiatric drug	UWWTP
DCD (Dicyanodiamide)	461-58-5	nitrification inhibitor, catalyst	industry
Diphenylphosphine oxide	4559-70-0	intermediate of Wittig synthesis	industry
Erythromycin	114-07-8	antibiotic (macrolide)	UWWTP
Foramsulfuron	173159-57-4	herbicide	agriculture
Guanylurea	141-83-3	TP of metformin	UWWTP
Irbesartan	138402-11-6	ACE-inhibitor (antihypertensive)	UWWTP
Lamotrigine	84057-84-1	antiepileptic	UWWTP
Mecoprop	93-65-2	biocide/herbicide	UWWTP
Oxipurinol	2465-59-0	active metabolite of allopurinol	UWWTP
Phosphoric acid triethyl ester (TEP)	83588-59-4	catalyst	industry
Propranolol	525-66-6	beta blocker	UWWTP
Pyrethroid			suspended matter (additional)
Sitagliptin	486460-32-6	antidiabetic agent	UWWTP
Sotalol	3930-20-9	beta blocker	UWWTP
TFA (Trifluoroacetic acid)	76-05-1	PFAS	UWWTP, industry, agriculture
TMDD (Surfynol 104) (2,4,7,9-Tetramethyl-5-decin-4,7-diol)	126-86-3	foam inhibitor	industry
Tramadol	27203-92-5	analgesic	UWWTP
Triacetonamin (TAA)	826-36-8	stabiliser for polymers	industry
Triclosan	3380-34-5	biocide/bactericide	UWWTP
Trimethoprim	738-70-5	antibiotic	UWWTP

* UWWTP: urban wastewater treatment plant

III. Overview of monitoring station selection

Section 4 outlines the procedure for selecting monitoring stations.

(A) Wastewater treatment plants and industry

Table 4: Selected monitoring stations and parties responsible for taking samples and analysing samples

Monitoring station	**Responsibility sampling**	**Responsibility data analysis**
Brugg/Aare	CH	CH
Weil am Rhein	CH/DE-BW	BfG
Karlsruhe-Lauterbourg	DE-BW	BfG
Mannheim/Neckar	DE-BW	DE
Bischofsheim/Main	DE-HE	DE
Koblenz/Rhine	BfG	BfG
Koblenz/Moselle	BfG	BfG
Mouth of the river Lippe near Wesel	DE-NRW	DE
Bimmen	DE-NRW	NL
Lobith	NL	NL
Nieuwegein	RIWA-Rijn	RIWA-Rijn
Maassluis	NL	BfG

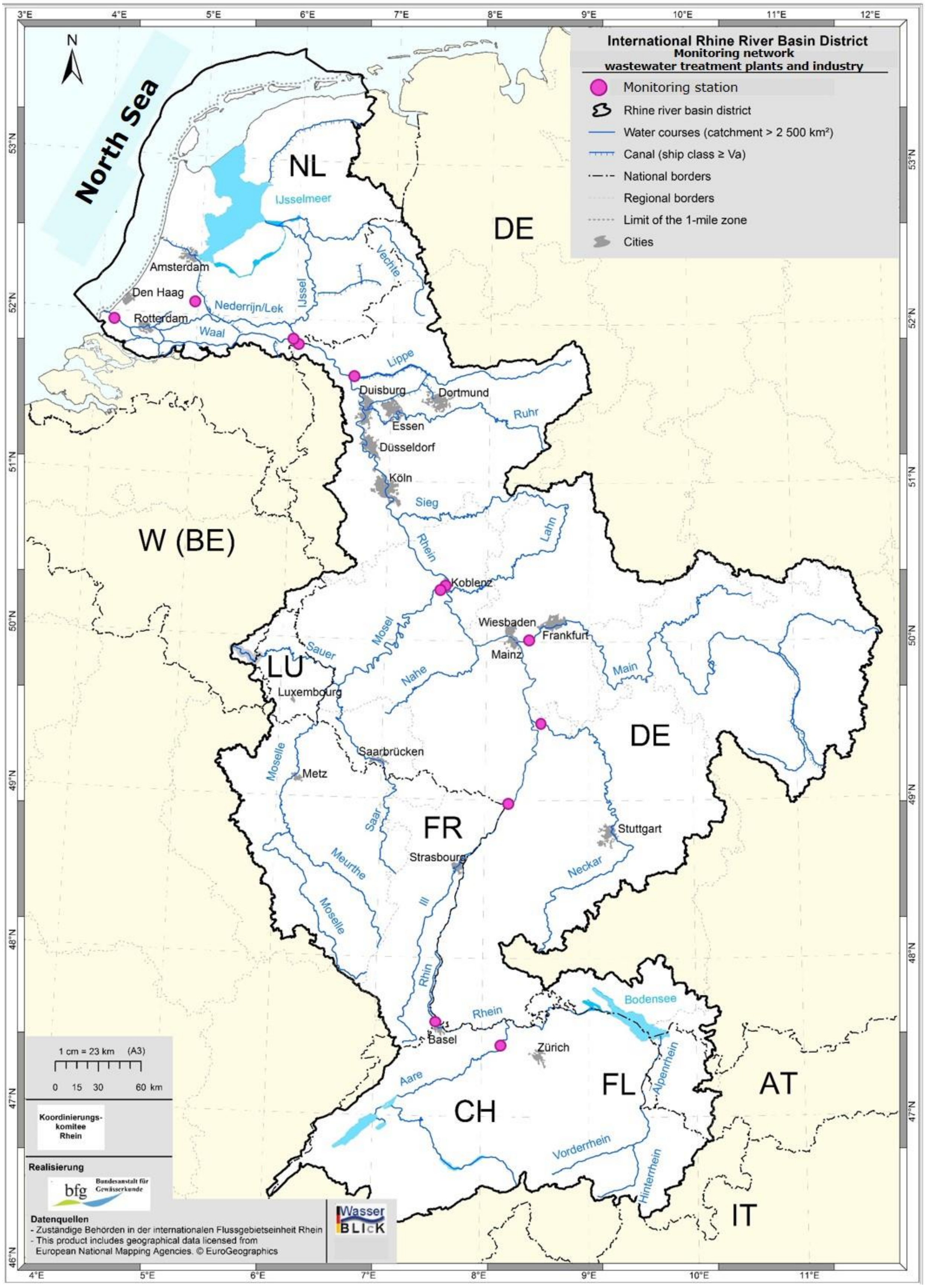


Figure 2: Network of monitoring stations for the emission areas wastewater treatment plants and industry

(B) Agriculture

More detailed information on the network of monitoring stations for the emission area agriculture can be requested from the ICPR secretariat.

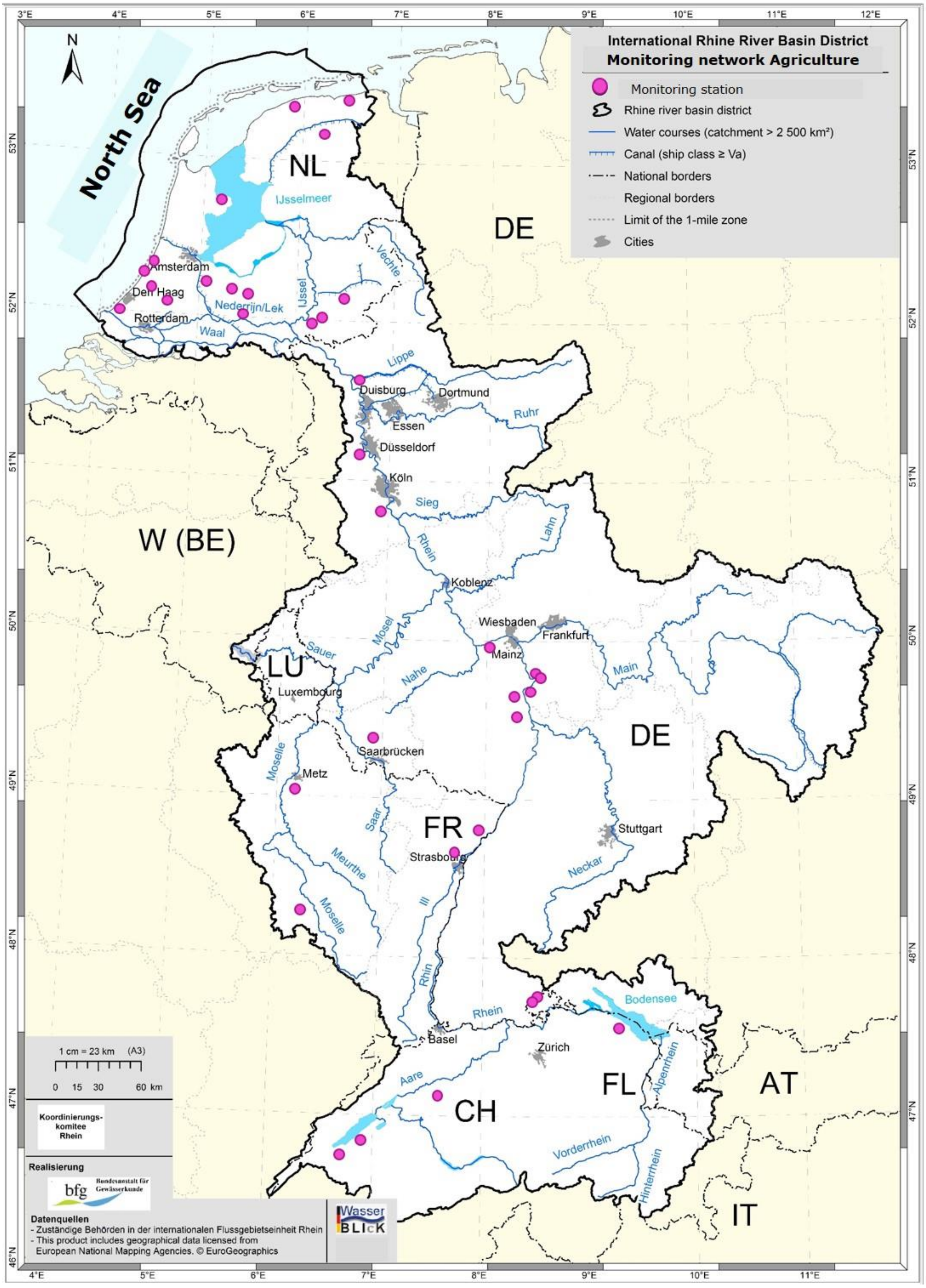


Figure 3: Network of monitoring stations for the emission area agriculture

IV. Evaluation approach for wastewater treatment plants and industry

To determine the successful execution of the declaration of the 2020 Rhine Ministerial Conference, a few operational choices will have to be made. As it was determined that the micropollutant emissions are difficult to monitor directly, it was decided that the load (kg/day) will be used as a proxy. Considering that a reduction of 30% in 20 years equals, on average, 1.5% per year it becomes apparent that monitoring the trend development of the load over time is a suitable way to determine the successful implementation of emissions reducing measures.

If the load reduction is shown to be at least or larger than 1.5% per year with sufficient statistical confidence one can be assured that the emission reduction target of 30% will be met by 2040, provided efforts made are maintained.

To determine the size and direction of the trend and test its statistical significance, it is proposed to use the *Trendanalist* programme [by Baggelaar and Van der Meulen, 2019]. *Trendanalist* has been in use for many years by water authorities and drinking water suppliers in the Netherlands for monitoring water quality by time series analysis. Below is a description of the programme and how it performs the trend analysis, followed by a proposal on how to use the programme to monitor the 30% reduction target. Finally, a proposal on how to present the results in a condensed manner is included.

Trend analysis with *Trendanalist*

Various statistical techniques have been implemented using *Trendanalist*; tests based on four linear modelling techniques (e. g. the Box-Jenkins modelling) and Mann-Kendall tests (with or without autocorrelation and seasonal effects). This allows the programme to flexibly take account of the special characteristics that often typify measurement series, such as non-normal probability distributions (whether due to outliers), seasonal effects, autocorrelation, missing measured values and values below the limit of quantification.

The term trend here means a permanent or semi-permanent change in the level of a time series over a time horizon of at least a few years. Seasonal changes and short-term calamities are therefore not included.

To be able to objectively determine whether a time series shows a trend, statistical trend analysis is performed using the *Trendanalist* programme. The statistical trend analysis comprises two parts per analysed series, namely:

i. trend detection, leading to an (objective) statement on the presence or absence of a statistically significant trend

ii. trend quantification, leading to an estimate of the magnitude of the trend (expressed as change per year)

Trendanalist tests for a monotonic trend, i. e. for a predominant decrease or increase from the starting point of the series be this in the form of a linear, convex or concave change. Testing shall be two-sided, i. e. testing for a change whether it is a decrease or an increase, with 95% confidence.

Trendanalist has been especially developed for environmental research and can therefore also take account of the specific properties of surface water quality variables. Depending on the properties of the time series in question, the programme applies the trend detection test and corresponding trend estimator that are best suited to these properties. The steps that are followed are graphically represented in a flow chart, see Figure 1.

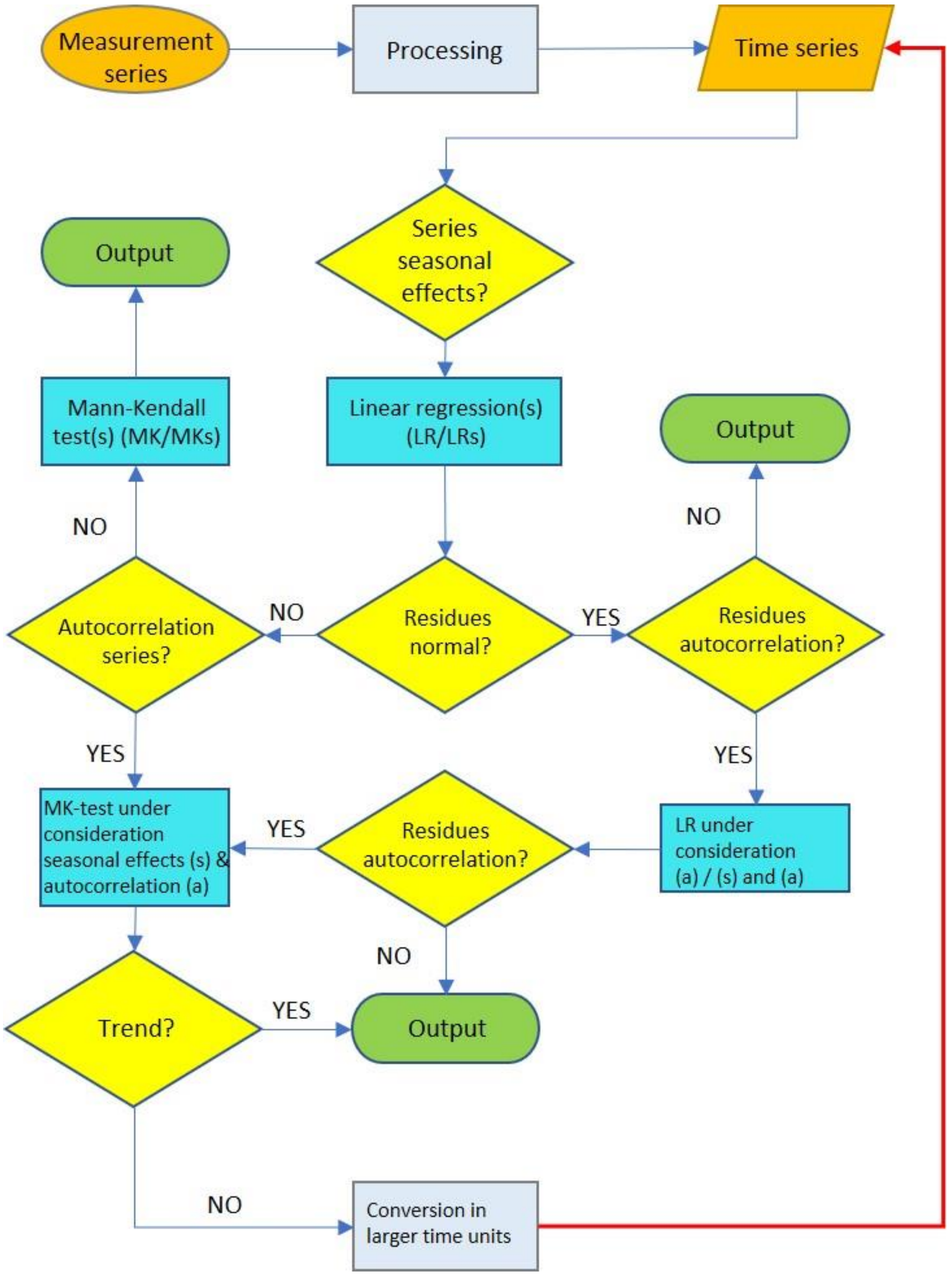


Figure 1: Flow chart showing the selection procedure that *Trendanalist* automatically follows for each data set. The different parts of the selection procedure are: orange ellipse = input, orange parallelogram = processed input, light blue rectangle = action, yellow diamond = decision moment, blue rectangle = trend test, green ellipse = output. Trend tests: LR = linear regression, MK = Mann-Kendall test, s = taking seasonal effects into account, a = taking autocorrelation into account, sa = taking seasonal effects and autocorrelation into account

Measurement series of environmental variables are rarely directly suitable for trend analysis, due to outliers, changes in measurement frequency, missing values or values below the limit of quantification. Therefore, the *Trendanalist* performs a pre-processing step by first checking each measurement series for such characteristics and based on the available suitable measurement values, converts them into a time series. This time series can consist of time units of four weeks, calendar months, two months, quarters, trimesters, half years or one year. The conversion of a measurement series to a time series shall be done by replacing all the values of the measurement series that fall within the time unit of the time series with their median.

Based on the time series characteristics, the internal expert system can choose from six trend detection tests and four trend estimators comprising three tests based on the linear regression test and three tests based on the Mann-Kendall test, the distribution-free equivalent of the linear regression test. The tests can also take seasonal effects and/or autocorrelation into account.

In the case of non-normality, distribution-free methods are considered, as they are superior to parametric methods, even with small deviations from normality and they are also not or hardly affected by outliers. The selection procedure and subsequent trend analysis are objectified in such a way that they can be carried out fully automatically. This is important in view of the large number of time series that monitoring networks can contain.

This flexibility allows for customisation and the application of the most appropriate trend test and trend estimator for each time series. This results in greater distinctiveness when testing for trend and more accuracy when estimating the trend. This ensures that the information present in the measurement series – which often required a great deal of effort in terms of sampling and analysis – is used to the best possible effect.

If a time series is tested for trend using the linear regression test, the trend is estimated as the linear regression slope and if it is tested using the Mann-Kendall test, the trend is estimated as the Theil slope [Theil, 1950; Sen, 1968]. The latter is the median of all individual slopes between the individual values in the time series and can thus be understood as a distribution-free trend estimator, which is resistant to the influence of extremes.

Data format *Trendanalist*

Trendanalist is available as a stand-alone application for Windows. Individual and group licences for the use of *Trendanalist* are offered for companies or agencies that manage their own networks.

Trendanalist reads measurement series saved as a text file (ASCII format). The extension of the file name must be: '.tai', '.csv', '.dia' and '.riw'.

The standard input file for *Trendanalist* has the extension '.tai', an abbreviation of 'Trendanalist input'. Such files have to be constructed as follows:

- Measuring location: x-coordinate; y-coordinate; parameter name; date; time; measured value; unit of measurement
- Optional are y-coordinate, y-coordinate (Dutch national triangle coordinates) and time
- The fields are separated by a tab or a semi-colon (';'), the decimal separator is a point ('.')

Below is an example of a standard *Trendanalist* input file with the extension '.tai'. In this example, the fields are separated by a tab:

Example1	252491	473930	Cd	8-4-2021	11:40	0,32	µg/l
Example1	252491	473930	Cd	26-5-2021	11:30	0,25	µg/l
Example1	252491	473930	Cd	10-6-2021	9:40	0,28	µg/l
Example1	252491	473930	Cd	7-7-2021	11:50	<0,1	µg/l

Further specifications:

- If a measurement value is preceded by a '<' sign, the measurement value is interpreted as a value below the limit of quantification.
- Measured values may be missing. The relevant field is then empty.
- The file may contain several measurement series.

Operational choices

The application of *Trendanalist* described above leaves a lot of room for making operational choices. To guarantee unambiguity of the test results across different data sets, a number of proposals for preconditions are submitted which the data sets must meet. In *Trendanalist*, too, choices can be laid down in advance. The influence of these choices is limited in some cases and larger in others. Nevertheless, confidence in the test result hinges on an unambiguous execution as much as possible, regardless of the origin of the data. If, due to circumstances, it is not possible to comply with these preconditions and operational choices, it is still possible to carry out an assessment, possibly with less statistical eloquence. It is then up to the users or rapporteurs to decide whether to accept the test result. In that case, the deviation and why the result is accepted are described.

Determination of load

The load is calculated as the product of the concentration (e. g. µg/l) and the discharge (m/s^3). Preferably, it shall be expressed in kg/day (kg/24 h). In case of sampling, the measured concentration and the daily average discharge of the calendar day (24-hour period) of sampling are used to calculate the load. The discharge is often measured at high frequency, but the exact time of collection of a sample from which the concentration is determined is not always recorded, therefore the daily average discharge is chosen. For composite samples, the daily average discharge of the calendar day is used on which the composite sample was taken. Where a composite sample is collected covering a time period starting before midnight (00:00 hrs) and ending after midnight, the load shall be calculated using the average discharge for the two calendar days in question.

There are locations where, for example due to weir management, discharge may be 0 m/s^3 at any given time. In that case, the calculated load over this sampling period is also 0 kg/day. This is a different situation from when the measured concentration is below the limit of quantification or reporting limit.

Determination of reference load

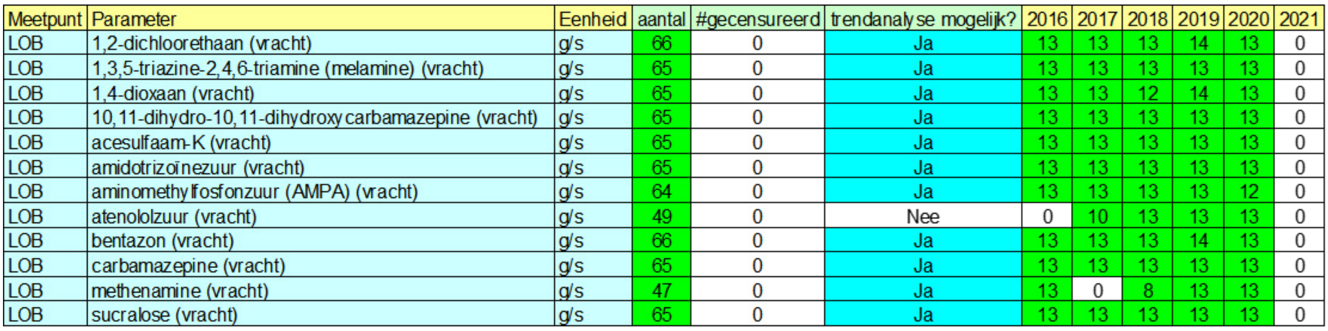
In accordance with the reduction target formulated by the 2020 Rhine Ministerial Conference, the load reduction achieved is determined as a fraction of the load in the period 2016-2018. The median of all observations in the period 2016-2018 is chosen as the reference value. The median is chosen because water quality observations are generally non-normally (skewed) distributed. In the case of a skewed distribution, the median gives a better description of the water quality, as it is less sensitive to outliers for example, due to calamities. For substances with a normal distribution, the median is equal to the mean, in which case the choice for the median is also valid. For substances with a measurement series starting after 2016 see 'Adding new substances'.

Boundary conditions for data set

Starting year: To determine the statistically tested slope, it is suggested that the data set should include data from at least five measurement years. These measurement years start in 2016 at the earliest. Substances can be added to the reduction target programme later. The first fully completed measurement year then forms the start of the data series to be tested, see 'Adding new substances'.

Measurement series and frequency: As a minimum requirement for performing the test, it is suggested that the measurement series cover at least five calendar years and that in each quarter at least two measurements be available. This requirement is lower than the proposed measurement programme, but it does make it possible to perform the test if, due to circumstances, less measurement data has been collected than foreseen. *Trendanalist* analyses the measurement series and produces a so-called 'measurement density matrix', see Table 1. This shows how many values each measurement series contains per year. Therefore, this overview can be consulted when assessing the completeness of the data set.

Table 1: Section of measurement density matrix produced by *Trendanalist*. The green columns show the total number of data per measurement series (column 'aantal') and the number of measurement values per year (columns '2016' to '2021') (example).



Meetpunt	Parameter	Eenheid	aantal	#gecensureerd	trendanalyse mogelijk?	2016	2017	2018	2019	2020	2021
LOB	1,2-dichloorethaan (vracht)	g/s	66	0	Ja	13	13	13	14	13	0
LOB	1,3,5-triazine-2,4,6-triamine (melamine) (vracht)	g/s	65	0	Ja	13	13	13	13	13	0
LOB	1,4-dioxaan (vracht)	g/s	65	0	Ja	13	13	12	14	13	0
LOB	10,11-dihydro-10,11-dihydroxycarbamazepine (vracht)	g/s	65	0	Ja	13	13	13	13	13	0
LOB	acesulfaam-K (vracht)	g/s	65	0	Ja	13	13	13	13	13	0
LOB	amidotrizoïnezuur (vracht)	g/s	65	0	Ja	13	13	13	13	13	0
LOB	aminomethylfosfonzuur (AMPA) (vracht)	g/s	64	0	Ja	13	13	13	13	12	0
LOB	atenololzuur (vracht)	g/s	49	0	Nee	0	10	13	13	13	0
LOB	bentazon (vracht)	g/s	66	0	Ja	13	13	13	14	13	0
LOB	carbamazepine (vracht)	g/s	65	0	Ja	13	13	13	13	13	0
LOB	methenamine (vracht)	g/s	47	0	Ja	13	0	8	13	13	0
LOB	sucralose (vracht)	g/s	65	0	Ja	13	13	13	13	13	0

Values below the limit of quantification: It is to be expected that at some point the measured values will fall below the limit of quantification or reporting limit. On the one hand, not all substances will have a high initial load or concentration at all locations. On the other hand, it is conceivable that with the improvement of water quality, the loads and concentrations may drop below the limit of quantification or reporting limit. It is therefore suggested that the test should only be carried out if no more than 30% of the values in the measurement series are below the limit of quantification (or reporting limit). It is conceivable that for some substances the initial level at some locations will be close to the limit of quantification. In this case, if the fraction of values below the limit of quantification exceeds 30%, the judgement "target achieved" can be made, even if this series is insufficient for trend analysis because of the number of values below the limit of quantification. If in the course of time the limit of quantification or reporting limit threshold decreases and the measurement series again contains less than 30% of censored values, the assessment can still be resumed.

Processing values below the limit of quantification

It is common practice that observations below the limit of quantification (or reporting limit) are generally converted to half the value of the limit of quantification or reporting limit for further processing e. g. averaging or risk estimation. However, since loads are now looked at, a special situation arises. As the discharge increases during a flood event, the concentration of a parameter may decrease proportionally due to dilution. If the measured value then drops below the limit of quantification or reporting limit and is replaced by half of the value of the limit of quantification or reporting limit, this value in combination with a very high discharge would be used in the load calculation. As a result, the load at high discharge would become disproportionately high and could influence the result of the trend determination. This problem becomes more significant as loads and concentrations decrease over time as water quality improves.

For this reason, it was decided to replace the loads based on data below the limit of quantification with the value 0. An additional advantage is that in doing so, false trends resulting from the improvement of determination or reporting limits are avoided. It is reasonable to assume that over the 20-year period of the work plan, analytical techniques will continue to improve and limits of quantification or reporting limits will decrease. In the case of replacing data below the limit of quantification with half the limit of quantification or reporting limit, one would detect a trend that is only caused by the lower limit of quantification or reporting and not by the improved water quality. Furthermore, this choice of using zero values is similar to the SNO method (see 7.2).

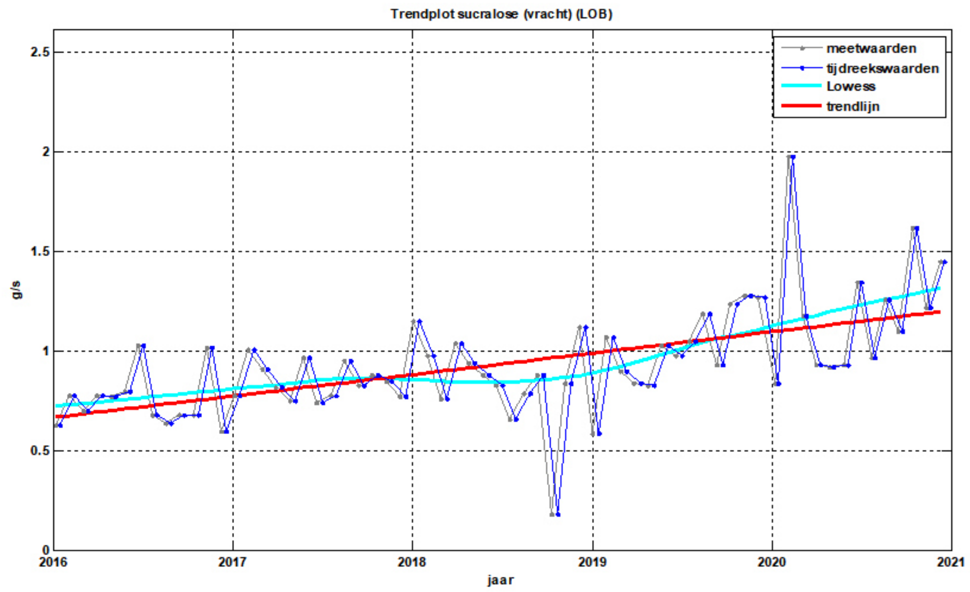
Target range assessment

Formally, on the basis of the declaration of the 2020 Rhine Ministerial Conference, it would be possible to compare the reference load for the period 2016-2018 with the median load for the period 2038-2040 in order to check whether the reduction target has been achieved. If necessary, this comparison could also be carried out in the interim in order to see whether the target is on course to be achieved. This approach has the disadvantage that only a limited set of available data is used over the entire period. Trend analysis using all the available data gives a statistically more robust statement and visual inspection of the graphs also makes it possible to quickly identify any deviations, thus providing more information than just the judgment "target achieved/not achieved".

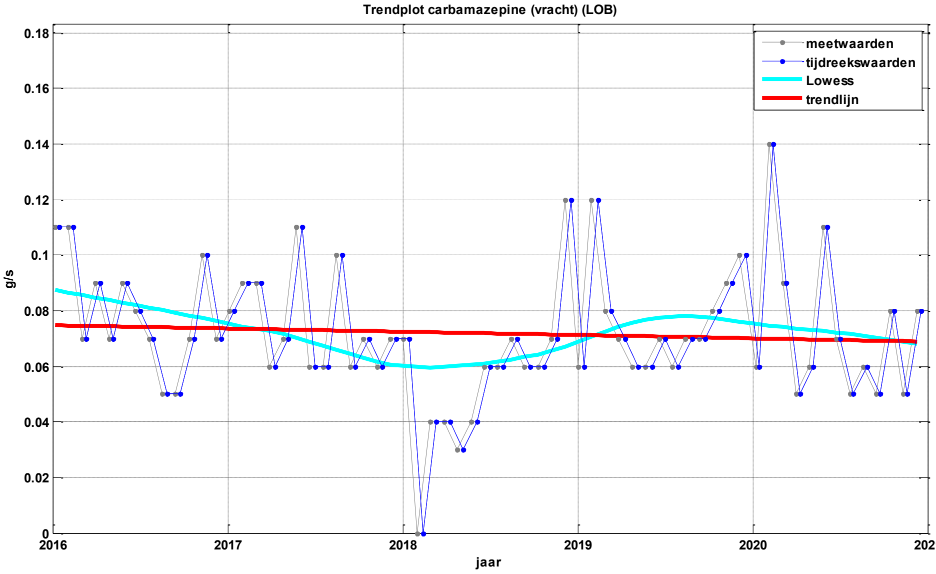
Determining the slope of the trend line and the relative trend: For the reason mentioned above, it is proposed to test whether the reduction target is met by using the slope of the trend line of the measurement series and the reference load. From this, the annual percentage change compared to the reference load can be determined, i. e. the relative trend per year. Assuming that the objective is to reduce the load of a parameter by 30% over a period of no more than 20 years, it can also be stated that the load must decrease by 1.5% annually compared to the reference load from the starting period. Every parameter with a reduction of more than or equal to 1.5% will, all other things being equal, achieve the target within the specified time. Naturally, there will be substances that are reduced by more than 1.5% per year, these will reach the target sooner and may be eligible for reassessment for a higher reduction target. This is in line with the ambition of the 2020 Rhine Ministerial Conference to increase the reduction target in the interim. For parameter loads, which decrease by less than 1.5% per year, stagnate or even increase, additional measures will be required. The trend analysis may also provide an early warning if this analysis is carried out continuously during the period 2020-2040.

By determining the slope of the trend line, its statistical significance can also be determined. It goes without saying that in the absence of sufficient statistical significance, the calculated slope may be the result of chance. Even more so, it means that this slope may change direction in subsequent years due to one or a few added measurement values. This is particularly noticeable for small slopes. The statistical significance of the trend makes it clear whether a result is robust or determined by coincidence. It is conceivable that measurement series show a reduction of 1.5% or more that is ultimately insignificant. In that case, the next measurement year may have a noticeable influence on the result in the following years.

The *Trendanalist* programme can perform trend analysis and display the results in the form of tables and graphs. Two examples of such graphs are shown below (see Figure 2). These graphs can provide additional insight into the measurement series and the calculated trend.




Resultaat LR-toets is
Oordeel = grote trend
De geschatte trend = 0.10722 eenheden per jaar.




Resultaat LRsa-toets is
Oordeel = geen trend
De geschatte trend = -0.0011812 eenheden per jaar.

Figure 2: Two examples of trend plots generated by *Trendanalist*. In each plot, the determined (overall) trend line (red line) and the local trend (at the measuring site) (bluish line) are shown. Below each plot, the slope of the trend is shown.

Determination of target outcome: By determining the relative trend, it is easy to test in the interim to what extent the reduction target has been met. The realised relative change is determined by calculating the product of the relative trend per year and the number of years in the measurement series. If this value is less than or equal to -30%, one can conclude that the reduction target has already been met. When the trend is significant, it can also be concluded with sufficient statistical certainty that the target has been met.

Length of measurement series

The trend analysis is carried out on measurement series of at least five years. In most cases, this period is the minimum required to be able to make a statistically significant statement. During the period 2020-2040, data from each subsequent year will be added to this measurement series to assess the slope and target range. However, as the measurement series grows longer, the trend will become less and less sensitive to changes in water quality, whether better or worse. In particular, when measures are implemented late in the work plan period, it is possible that the trend line lags behind the actual reduction. In that case, in addition, the trend can also be calculated over a shorter period of time to get a better insight into the reduction as a result of the measures and whether the reduction target has been reached. Even then, the recommendation is to use no less than five years of data to determine the slope of the trend, see also 'Special situations: Discontinuity'.

Assessment and visualisation of the results

As mentioned earlier, there are two ways to determine the level of progress made towards achieving the set reduction target: by calculating the relative trend or by calculating the relative change achieved so far. Both results have their value, and it is therefore suggested presenting both and visualising the result by symbols. Because these results are determined for a large number of substances and locations, a table format seems the most appropriate, possibly supplemented by bar charts. Substances that show sufficient relative load reduction will, under unchanged conditions, easily meet the target and require little attention. Substances exhibiting insufficient relative load reduction can be inspected visually on a case by case basis. Depending on the additional information this provides, graphs of these substances (or a selection of representative substances) can be added to the report to highlight these substances.

By ordering the substances in order of relative trend from negative to positive percentage, substances with the highest annual reduction are listed at the top and substances with the lowest reduction or increase are listed at the bottom. The symbols of these values make it possible to assess large numbers of substances and locations at a glance. If the result is significant, this can be indicated with the * symbol. Whether or not the reduction target has been met in the interim can be indicated by the relative change achieved so far and visualised by means of a symbol.

Symbols

For visualising the target coverage or the achieved relative change over the reporting period, it is suggested using symbols (tick, exclamation mark and cross) based on the value.

- Tick: The reduction achieved is ≥ 30%.
- Exclamation mark: The reduction achieved is < 30%, but with unchanged effort this parameter will reach its target by 2040.
- Cross: The reduction achieved is < 30% or there is an increase and with unchanged effort this parameter will not reach its target by 2040.

An example for the proposed symbols is presented in section 7.1, Table 2.

As more reporting periods are added for a location, a picture emerges of the extent to which the reduction target has been achieved for a large number of substances.

Adding new substances

It is to be expected that during the work plan period new substances will emerge that also qualify for an emission reduction target. Provided the data collected fulfils the preconditions set, it is possible to include these substances in the assessment. To calculate the reference value, three years of data must be available from which the median can be determined. On the basis of at least five years of data, a trend analysis can be carried out to determine the slope of the trend. Subsequently, the relative trend can be calculated. This can also be evaluated according to the criteria as described in 'Assessment and visualisation of the results', regardless of the starting year of the new measurement series.

Special situations

The proposed method tries to treat all measurement series in a uniform way as much as possible to be able to perform an unambiguous assessment for a large number of parameters and locations. However, in doing so, one must not lose sight of the objective, which is to determine the reduction of emissions by at least 30% compared to the period 2016-2018. Special situations are conceivable that require extra attention to prevent the intended improvement (or possibly also a deterioration) from not being noticed in time.

Discontinuity: The proposed method is mainly aimed at establishing a gradual (monotonous) improvement in water quality. However, it is conceivable that, due to local circumstances, an incremental improvement is realised, for example by expanding an urban wastewater treatment plant (UWWTP) with a 4th purification step. In that case, it may be that the improvement realised is not immediately noticed in the trend analysis and that the determination of the achievement of the target also lags behind the reality. It is therefore useful to compare the result of the trend analysis with expectations based on measures taken to avoid realised improvements not being noticed. Similarly, a gradual deterioration might not be noticed in time and it remains necessary to critically examine individual measurement series.

Peak shaving: It was noted earlier that water quality data is in general not normally distributed and that for this reason the median is the better variable to choose as the reference load. An additional advantage is that the reference load is less influenced by (particularly upward) outliers. However, this can also be a disadvantage, e. g. when an emission reduction is achieved by modifying a discharge permit. If the new permit imposes stricter requirements on peak discharges (outliers upwards), this improvement will be less well noticed if the median is chosen for the test. Assuming one has knowledge of such a measure, one may choose to perform the assessment for this parameter using the mean.