



**Review report of Agri-
Drinking Water quality
Indicators and
IT/sensor techniques,
on farm level, study
site and drinking water
source**

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EXECUTIVE SUMMARY

I. BACKGROUND AND OBJECTIVES

The present report is written as part of Work Package 3 (WP3) of the FAIRWAY project. The main objective of WP3 is identifying, selecting and prioritizing transparent and data-driven indicators for monitoring of the impacts of agriculture activities on drinking water quality, referred as Agri-Drinking Water Indicators (ADWIs). ADWIs are intended to assist agricultural consultancy, therefore, they should be appealing and understandable for farmers. On a larger scale, ADWIs are intended to support central and local administration and policy-makers, water companies in analysing the situation of diffuse pollution and selecting measures to protect drinking water resources.

The ADWIs are developed by 1) reviewing/identifying relevant pre-existing indicators (e. g., Agri-Environmental Indicators of the European Commission); 2) quantitatively and conceptually evaluating the identified indicators using compiled data of 13 case study sites of FAIRWAY; and 3) selecting/prioritizing ADWIs that are suitable for assessing the effects of agriculture measures on mitigating diffuse pollution of drinking water quality.

According to the proposal, the ADWIs are defined within the DPSIR-framework (Driving forces – Pressure – State – Impact – Response). However, this framework does not have a domain to reflect the variability of hydrogeochemical settings among the case study sites, which may govern the cause-effect relations between the agriculture activities – including mitigation measures – and drinking water quality. Therefore, in WP3, a new domain called Link is introduced. In WP3, we focus on nitrate and pesticide release from the agricultural system (Driving force and Pressure indicators), the transport and fate of nitrate and pesticides in the hydrogeological system (Link indicator) and the quality of the drinking water (State/Impact indicator).

This document reports the results of the first step of the ADWIs development: *Reviews on ADWIs, participatory monitoring, and IT/sensor techniques*.

II. THE DPSLIR FRAMEWORK

The DPSIR model is defined as “causal framework for the description of interactions between society and the environment”. It was adopted by the European Environment Agency (EEA 2018). According to its terminology, social and economic developments (Driving forces, D), exert Pressures (P) on the environment and, as a consequence, the State (S) of the environment changes. This leads to Impacts (I) on ecosystems, human health and society, which may elicit a societal Response (R) that feeds back on Driving forces, on State or on Impacts via various mitigations, adaptations or curative actions (Smeets and Weterings, 1999; Gabrielsen and Bosch, 2003).

According to the FAIRWAY proposal for WP3, ADWIs are to be defined within the DPSIR-framework. The adjusted **DPSLIR**-framework contains a new element, the Link Indicator (Table II-1).

Table II-1: Interpretations of the DPS(L)IR framework for Agri-environmental indicators (AEIs) and Agri-drinking water indicators (ADWIs)

| Domain | Description*) | AEI interpretation**) | ADWI interpretation |
|----------------------|--|---|--|
| Driving force | "Social, demographic, and economic developments in societies and the corresponding changes in the lifestyle and overall levels of consumption and production patterns" * | "the state and evolution of regional farming system in relation to input use, land use, and management practices" | Social, demographic, and economic demands for clean drinking water and the corresponding changes of the agricultural system in relation to input use, land use, and management practices |
| Pressure | "Developments in release of substances (emissions), physical and biological agents, the use of resources and land" | "harmful and beneficial processes attribute to agriculture" | Inputs of nitrate and pesticides from the agricultural system to the hydrogeological system |
| State | "Quantity and quality of physical phenomena, biological phenomena, and chemical phenomena" | "the state of different natural and semi-natural resources in rural area" | Quality of drinking water resources |
| Link | Natural and anthropogenic processes of transport and evolution of nitrate and pesticides in natural systems (from farm fields to water abstraction points) | - | Natural and anthropogenic processes of transport and evolution of nitrate and pesticides in the hydrogeochemical system |
| Impact | "Relevance of changes in the state of environment" | "the share of agriculture, as a sector, to undesirable changes in the state of the environment resources and its effective contribution to the preservation/enhancement of other environmental resources" | Public health concerns and regulatory compliances |
| Response | "Groups and individuals in society and government attempt to prevent, compensate, ameliorate, or adapt to changes in the state of environment" | "Societal, market, and policy responses that influence production systems and agriculture practices" | Implementation of mitigation measures |

*(Stanners et al., 2007); **(EEA, 2005)

III. AGRI-DRINKING WATER INDICATORS (ADWIs)

Agri-environmental indicators (AEI), as developed by OECD and Eurostat, are implemented and further developed for the monitoring and evaluation of the negative and positive impacts of agricultural activities on the environment. AEIs are used on European/national level (28 AEI are listed in fact sheets related to COM final 0508/2006 (Eurostat, 2018). The AEI are applied e. g. to evaluate/benchmark the transcript of EU-legislation at Member State level), on regional level (to monitor the impact of agriculture on environment, identify hotspots or focus subjects and areas for the agricultural advisory service) and on farm level (as decision aid tool for the farmer) (Figure III-1).

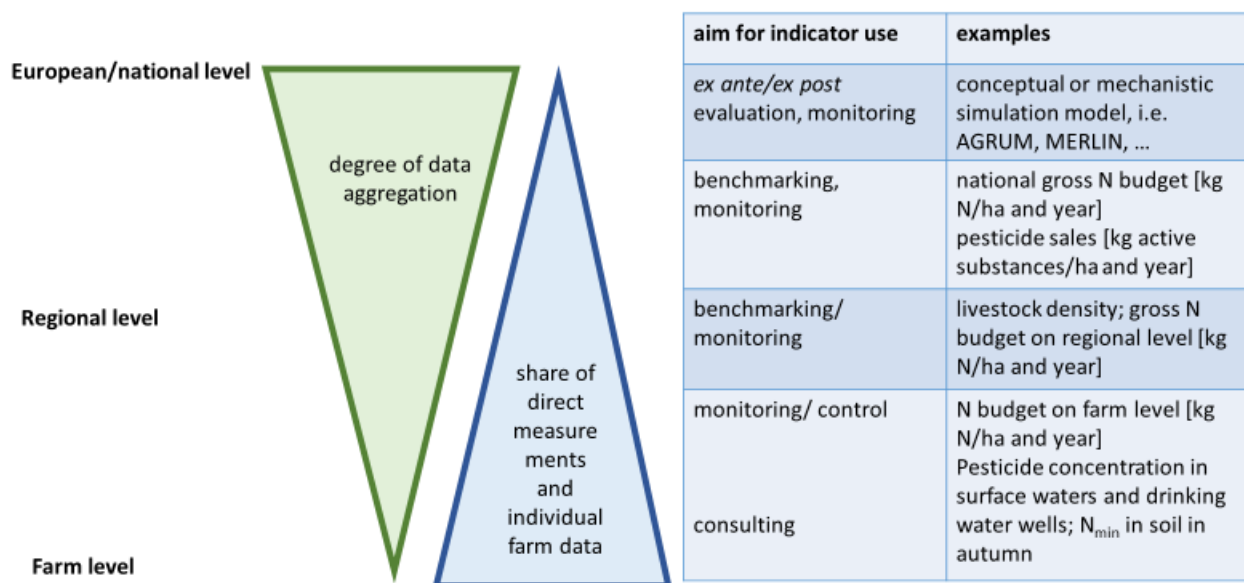


Figure III-1: Deduction and statistical evaluation of AEI: degree of aggregation and individualisation in relation to operation level of indicator necessary

Agri-drinking water indicators (ADWIs) to be developed in FAIRWAY are defined as indicators for the quality of drinking water. As drinking water may be produced from groundwater or surface water, ADWIs aim at the quality of both. As done for the 28 harmonised AEI (COM 2006, Eurostat 2018), we classified all ADWIs, which the case studies reported (FAIRWAY Milestone 3-1) into the adjusted DPSLIR framework (Table III-1). We added further ADWIs according to a literature review. The ADWIs listed in the table may work as indicators by themselves or they are elements of compound indicators. Indicators for both, nitrates and pesticides, are listed in the same table, in order to avoid redundancy as far as possible.

IV. PRIORITISATION OF AGRI-DRINKING WATER INDICATORS

All ADWIs discussed are listed in Table III-1, i. e. those being subject of the survey among the case studies, those proposed by the case study leaders to be included in a further evaluation and those which, according to a literature review, are used for pesticide and nitrate monitoring/risk assessment. From the number of indicators listed and further explained in chapter 5 of the report, it can be deduced, that indicators which act in the agricultural sector as Driving forces and as Pressure indicators, are far more numerous than State respectively Impact indicators. The large number of agricultural Driving forces and Pressure ADWIs also explains, that from this part of the DPSLIR-model, many factors may influence water pollution. State indicators which are used for the evaluation of the water quality are on the contrary far more standardised, like the water quality standards they are supposed to monitor.

A prioritisation of ADWI is therefore above all necessary for the Driving forces and Pressure indicators in the agricultural sector, in order to focus on the most **significant, prevalent, effective and easy to use indicators**.

The survey on ADWIs already used in case studies and the most promising indicators discussed in chapter 5 lead to a first weighting of indicators. The result is listed in Table IV-1. On the right part of the table, three columns show the evaluation of a survey among FAIRWAY case studies about data availability in order to calculate ADWI (this survey was carried out for FAIRWAY Milestone 3-1).

Answers would also indicate the resolution in space, in which data can be delivered from the case studies (at plot, farm or regional/larger scale).

In Table IV-1, ADWI for which data can be supplied by the case studies are marked in orange. ADWI for which data can (possibly) not be supplied by case studies are marked in blue. These data may possibly not be used in certain or all case studies, or the parameter was not included in the questionnaire of Milestone 3-1.

Case studies do not seem to collect specific data on the use of single pesticides/active substances. However, from parameters on total use or from general indices, no link can be drawn to the parameter at sink level (e. g. pesticide analyses of raw water). Indicators, for which data are not readily available in the case studies may be calculated, in case these data are freely available from other data sources. One example is the use of pesticides, which may be deduced from local cropping patterns and from usage data reported from the member states according to Regulation (EC) No 1185/2009. The next step towards prioritisation will be done in FAIRWAY using data of catchments in the case studies. For this reason, data are requested from the case studies.

Table III-1: ADWIs in the DPSLIR framework

| Domain | Subdomain | Chapter | Indicators category |
|----------------|----------------------------------|---------|--|
| Impact | Societal and economic demands | | Demands for clean drinking water*) |
| | | | Population density*) |
| | | | Cost for drinking water production*) |
| Driving forces | Resource management and planning | 5.1.1 | Land use (planning) <ul style="list-style-type: none"> - Land use/land cover (i.e. winter wheat surface evolution) - Land use change (grassland->arable land) |
| | | 5.1.2 | (Water protection planning) |
| | | 5.1.3 | Agricultural preconditions <ul style="list-style-type: none"> • Climatic conditions <ul style="list-style-type: none"> - precipitation - temperature - wind |
| | | | <ul style="list-style-type: none"> • Soil properities <ul style="list-style-type: none"> - soil type - organic carbon - clay content - top soil bulk density - field capacity • Topography <ul style="list-style-type: none"> - susceptibility to erosion and compaction |
| | Farm management | 5.2.1 | Farming standards <ul style="list-style-type: none"> - organic/conventional |
| | | 5.2.2 | Farming Intensity <ul style="list-style-type: none"> - crop yield |
| | | 5.2.3 | Farm management <ul style="list-style-type: none"> - cropping patterns - catch crop use - method of soil cultivation/tillage practice - soil cover - cropping systems |
| | | 5.2.4 | N-fertilisation <ul style="list-style-type: none"> - Livestock density - Livestock excretion - Types of organic fertilisers - plant availability of organic bound N - Manure applied in autumn - Animals out of pasture |

| Domain | Subdomain | Chapter | Indicators category |
|------------------|-------------------------|---------|--|
| | | | <ul style="list-style-type: none"> - Organic fertilisation/ha; organic fertilisation/crop*ha - Mineral fertilisation/ha; mineral fertilisation/crop*ha - Total fertilisation/ha; total fertilisation/crop*ha - Timing of fertiliser application - Splitting/frequency of fertiliser application - Application techniques for fertilisers |
| | | 5.2.5 | Pesticide application <ul style="list-style-type: none"> - Type of Pesticides - Chemical properties - Consumption of pesticides - Application of pesticides/ha (active substances; most frequently used pesticides; most persistent or most toxic pesticides) - Application of pesticides/ha*crop (active substances; most frequently used pesticides; most persistent or most toxic pesticides) - Timing of pesticide application - Splitting/frequency - Application techniques for pesticides |
| | Trends | 5.3.1 | Intensification/Extensification |
| | | 5.3.2 | Specialisation |
| | | | |
| Pressure | Leaching | 5.5.1 | Leaching quantity <ul style="list-style-type: none"> - Depth of water table - Drainage index (DI) - Exchange frequency (EF) |
| | | 5.5.2 | Nitrogen in soil water <ul style="list-style-type: none"> - After harvest soil nitrate - Autumn soil nitrate - Spring soil nitrate - Soil water potential and nitrate content in soil solution |
| | | 5.5.3 | Pesticides in soil water |
| | Surface water pollution | 5.6.1 | Indicators for nitrogen and pesticides in surface water |
| | Point sources | 5.7.1 | Point source of nitrates and pesticides |
| | Aerial immission | 5.8.1 | Pesticide drift |
| | | 5.8.2 | Deposition of nitrogen |
| | N-Efficiency | 5.9 | Nitrogen budgets |
| State/ Impact | Water quality | 6.1 | Concentrations in water |
| | | 6.2 | Concentration trends |
| | Regulatory compliances | 6.3 | Frequency of exceedance of water quality standards |
| Link | Catchment typology | 7.1 | Catchment typology |
| | Lag time | 7.2.1 | Recharging rate |
| | | 7.2.2 | Water age |
| | Source tracer | 7.3.1 | Nitrate Isotope indicators |
| | | 7.3.2 | Point source of pesticide |
| | Vulnerability | 7.4.1 | Nitrate vulnerability |
| | | 7.4.2 | Pesticide vulnerability |
| | Leaching risk | 7.5.1 | Nitrogen leaching risk indicators |
| | | 7.5.2 | Pesticide leaching risk indicators |

*) Indicator not discussed in this report

Table IV-1: Ranking of ADWI according to significance and prevalence based on a survey carried in WP 3 of FAIRWAY

| Subindicator of ADWIs | Prevalance: evaluation of data availability in case studies (number of times mentioned) | | |
|--|---|------------|----------------|
| | Plot scale | Farm scale | Regional scale |
| Land use/land cover | 6 | 2 | 5 |
| Land use change | | | |
| Legislation | | | |
| Precipitation/evapotranspiration | 2 | 2 | 12 |
| Temperature | | | |
| Wind | | | |
| Soil type | 5 | 1 | 4 |
| Organic carbon | | | |
| Organic/conventional | 1 | 7 | 1 |
| (Average) crop yield | 1 | 7 | 1 |
| Cropping patterns | | | |
| Method of soil cultivation/tillage practice | | | |
| Soil cover | | | |
| Livestock density (LU/ha /yr on an area of reference) | 3 | 7 | 4 |
| Livestock excretion (kg N/ha/yr on an area of reference) | 1 | 5 | 1 |
| Organic fertilisation/ha; organic fertilisation/crop*ha | 2 | 6 | 0 |
| Mineral fertilisation/ha; mineral fertilisation/crop*ha | 4 | 4 | 6 |
| Total fertilisation/ha; total fertilisation/crop*ha | 2 | 7 | 2 |
| Type of Pesticides | | | |
| Chemical properties | | | |
| Consumption of pesticides | | | |
| Application of pesticides/ha (active substances; frequently used; most persistent/toxic) | 2 | 6 | 0 |
| Application of pesticides/ha*crop (active substances; frequently used; most persistent or toxic) | | | |
| Timing of pesticide application | | | |
| Splitting/frequency of pesticide application | | | |
| Nitrates in soil water | 4 | 1 | 2 |
| Pesticides in soil water | | | |
| Nitrogen leaching risk indicators | | | |
| Pesticide leaching risk indicators | | | |
| Surface transport of nitrogen and pesticides (with soil/fertiliser particles) | | | |
| Pesticide Drift | | | |
| Volatile N-compounds | | | |
| Nitrate: grazing animals near surface waters, farmyard, storage facilities | | | |
| Pesticides: farmyard, pesticide storage facilities | | | |
| Annual average nitrate concentration (mg NO ₃ /l) | 4 | 1 | 8 |
| Concentration trend analysis | | | |
| Frequency of exceedance quality standards (%) | 2 | 0 | 8 |
| Nitrogen maximal concentration in drinking water collection points | 3 | 0 | 8 |
| Catchment typology and dominant flowpath | | | |
| N stable isotopes | | | |
| Number of substances that exceed water quality standards at least once the year | 4 | 0 | 7 |
| Maximum concentration by substance (if >0.1 µg/l) in drinking water collection points | 4 | 0 | 7 |
| Frequency of exceedance quality standards in the drinking water (percentage of the number of samples where the 'drinking water' standard is exceeded) by substance | 4 | 0 | 6 |
| Vulnerability assessment maps of aquifer and surface water | 2 | 0 | 7 |

V. FURTHER PRIORITISATION AND EVALUATION OF AGRI-DRINKING WATER INDICATORS

In order to further drive forward the prioritisation of the selected ADWIs in FAIRWAY, we intend to connect ADWIs from the agricultural and the water work side, using statistical methods. We also intend to further investigate on the Link indicator, especially how this ADWI fits in between the other indicators. We intend to examine

- the feasibility of indicators calculation,
- the link between indicators, and
- the relevance of some indicators, as statistical calculations give the mathematical expression for the link that exists between them.

For this purpose, a database of ADWI-data on catchments-level will be established by collecting data from the FAIRWAY-case studies. Preparatory work has been carried out, using the Voulzie case study, in order to specify the data request to the case studies. Statistical analyses of data of the Voulzie case study showed, that the spring discharge time series can be rather well explained by the evolution of the recharge of the year before. The first attempt to build this database enabled the calculations of indicators as well as the first links between Pressure indicators and State indicators. Finding the proper, statistically based link between agricultural Driving forces and Pressure indicators and the State/impact indicators might supply ADWIs on a reliable basis.

VI. IT-/SENSOR- AND AUTOMATIC SAMPLER TECHNIQUES FOR PESTICIDE AND NITRATE SAMPLING

Monitoring has evolved considerably over the past ten years and even more in recent years. There are broad avenues for innovation and, as part of the FAIRWAY project, a review of in situ monitoring methods has been achieved, in accordance with the chapter on participatory monitoring. Many methods can also be applied in the laboratory. A review showed that many tools (some are prototypes) and methods are being developed to improve measures for both nitrates and pesticides. The developed methods are based e. g. on optical sensors and paper based sensors. These tools make it possible to improve the confidence in the measurement while improving the analytic capacities of the devices (limits of measurements and types of molecules). In addition, relays with smartphones can be developed to facilitate the reading of the results and to trust them.

VII. PARTICIPATIVE Monitoring: Involvement of Citizens

Participatory monitoring, although old in its concept, has become much more developed during the last decades. Several types of participative monitoring systems can be characterised in relation to the intended goal of the promotor. Participatory monitoring initiatives can often be considered successful as they allow measurement of phenomena at frequencies and locations that are not reachable by a team of researchers alone. On the other hand, associated difficulties have been identified. First, it is not always easy to find the right number of participants to complete a large program, some "site-specific" programs may be canceled due to lack of participants. Moreover, in our field of water and environment, participatory programs can only hope to change behaviors if educational tasks have been planned in the projects. Lastly, participatory monitoring programs generally only work with a coherent method to analyse the data (computer infrastructure and/or scientific manpower) that must be anticipated. If the educational tasks and IT tasks are taken into account, participatory monitoring programs are not necessary less expensive than the institutional programs.

The review of in situ monitoring tools in development (even prototypical) suggests possibilities of access to increasingly simple and robust tools or new probes attached to smartphones. Thanks to these tools, some problems, such as the lack of participants and some analysis bias, could be resolved.

VIII. CONCLUSIONS

From a survey among the FAIRWAY case studies (Milestone MS3-1) on indicator use and from the present review report the following aspects can be deduced:

- Regarding the two kinds of pollutants – nitrates and pesticides – frame conditions are quite different:
 - Nitrate is one single substance, being mobilised and immobilised, leached, transported by runoff and emitted. It is essential for plant growth and omnipresent, even under “natural” conditions.
 - On the contrary, around 250 so called “active substances” of pesticides are authorised by EFSA. Placement on the market of pesticide product needs national approval. They may only consist of the registered active substances registered on EU-level, pure or in mixture, and of additives, for a better handling of the pesticide. Pesticides are supposed to be – to the greatest possible extent - harmless. They are supposed to degrade or at least to be absorbed by the soil matrix, but not to leach into groundwaters. Improper handling may however lead to runoff or drift and therefore to pollution of surface waters.
- ADWI are useful on all levels: at farm level as an aid in farmer’s consultation, at local or even national level as an evaluation and monitoring tool for administration work and for policy-makers.
- As more aggregated data show less standard deviation than the single datasets, correlation of ADWI with water quality could be stronger between data on a regional level than on farm level.
- ADWIs which act in the agricultural sector as Driving forces and as Pressure indicators are far more numerous than State respectively Impact indicators; this indicates, how many factors from the agricultural side may influence water pollution. State indicators which are used for the evaluation of the water quality are – on the contrary – far more standardised, like the water quality standards they are supposed to monitor.
- Aim, size and structure of the different case studies are different, and so are the ADWIs in use. very few ADWIs are uniformly used throughout Europe.
 - Common indicators on nitrate risk in use are rather simple statistics on fertiliser use, animal density or yield, but also N-budgets are applied.
 - Pesticide risk indicators in use are compound/composite indicators, like the Treatment Frequency Index and Pesticide Load Index.
- Concerning pesticides, the DPSLIR-model can only be used, if data on the Driving force and Pressure side on the use of specific pesticides are available and can be linked to the State/impact side. Since a regional differentiated data compilation of application data and a consequential estimation of the pesticide inputs is missing, pesticides found in drinking water can only sporadically be related to application data (SRU, 2016).
- Correlation analysis with data of the test site showed, that the compound/composite indicators (field budget or Cassis-N surplus) were not the ones with the best correlation: budgets calculate N-losses from the root zone, and therefore do not take into account the N-losses in the unsaturated zone beneath the root zone (this is the reason why we introduce the Link indicator for the DPSLIR-framework). Composite indicators may show a low relative sensitivity for changing conditions (Buczko and Kuchenbuch, 2010).
- Calibration and validation of ADWIs against field data is of high importance (Buczko and Kuchenbuch, 2010a).

- The data acquisition scale may be a problem, because readily available data categories at the national level are difficult to access at the local level. Due to uncertainties related to the new regulation on data protection (EU 2016/679), but also due to a tightening of fertiliser legislation in some member states, questions on confidentiality of farm data arise in conjunction with the survey.

1. INTRODUCTION

1.1 OBJECTIVES, DELIVERABLES AND ORGANISATION OF THE REPORT

The present report has been written in the context of the Work Package 3 (WP3) of the FAIRWAY project. Aim in WP3 is to prioritise and evaluate data-driven indicators for the monitoring of the impact of agricultural activities on drinking water quality, referred to as Agri-Drinking Water Indicators (ADWIs). ADWIs are designed to assess the probability of water pollution due to nitrates and pesticides and to evaluate the dimension of it, for a defined water resource in an easily understandable way even in a complex context.

In the context of the FAIRWAY project, ADWIs development in WP3 is closely related to work conducted in WP4 and WP5:

- WP4 assesses the effectiveness of measures to reduce the agricultural impacts on drinking water resources, and
- WP5 assists stakeholders in their decision-making process of finding the best measures to reduce pollution of drinking water e.g. by using decision support systems.

WP3 is indirectly related to all other Work Packages within FAIRWAY for example:

- to test and analyse data which is coming from case studies (WP2) and use the indicators for Multiactor platforms of the different case studies
- to evaluate the implementation of EU directives and policies by national, regional and local authorities as well as measures beyond policies (WP6),
- to discuss and the role of indicators in EU policy making (WP/), a task emphasised by EU-Policy makers, and
- to communicate the results of monitoring and evaluation (WP8).

Agri-environmental indicators have been widely used on the EU level i. a. to monitor the Common Agricultural Policy and European environmental status. However, given the complex system and linkage of different agricultural production systems as well as different settings and specific characteristics in hydrological systems, the overall aim of this report is to develop a range of indicators that analyse in depth the relation between agricultural inputs of nitrate and pesticides and the impact on drinking water quality as this is an aspect so far only broadly addressed within agri-environmental indicators.

Using the ADWIs, stakeholders on the different activity levels may better understand the characteristics of the system such as sources, pathways, and transit time of nitrates and pesticides from the farmlands to their drinking water resources. We address agricultural practices and frame conditions for livestock and arable farming including horticulture with influence on the pollution of surface and groundwater as resources for drinking water by nitrates and pesticides. The understanding of pollution pathways is a precondition for setting the time-scales of implementation and evaluation of mitigation measures.

The operational scale of ADWIs may on one hand be the source area of a drinking water resource e. g. catchment or abstraction area. On the other hand, a more regional approach may be appropriate, in order to obtain an overview of the situation of a region or in a member state. This will affect the data requirements: while farm data are appropriate for analysing the catchment scale, also (free available) datasources with aggregated data may be used for the regional approach.

Therefore, according to function, target group and operational scale, data quality and composition of ADWIs may differ considerably.

To best explain the background, the selection and the prioritisation of ADWIs in this report we proceed as follows:

Chapter 2 starts with providing background information (statistics, approval/registration procedure, registration procedure, environmental impact) on pesticides and nitrates and their relation to drinking water. Furthermore, we briefly summarise theoretical aspects of indicator development. It covers definitions of agri-environmental indicators, explains a framework for indicator application (the Driving forces – Pressure – State – Impact-Response (DPSIR) framework), and related EU legislation. In Chapter 3, we conceptually describe the agri-hydrogeologic system and cycles of nitrate and pesticides in the system. We explain the pathways of pesticides and nitrates from their use in agriculture to ground- and surface water. Then, the ADWIs are connected to the context of the developed DPSLIR framework. We mainly focus on driving force/pressure and state/impact indicators. Additionally, we introduce link indicators: these are indicators that describe how nitrate and pesticides leave the agriculture system by leaching or runoff (pressure) and move on soil surface or through the hydrogeological system (link) to drinking water resources (state/impact). In Chapter 4 we define the ADWIs according to the FAIRWAY-approach within the newly introduced DPSLIR framework. Then, we review the agricultural driving force and pressure indicators in Chapter 5, state/impact indicators in chapter 6 and the link indicators in Chapter 7. A first prioritisation of ADWIs is presented in Chapter 8. Chapter 9 mainly focusses of future work, how a further prioritisation and evaluation of ADWIs will be transacted. Methods are presented using the example of the French case study. The report is completed by Chapter 10 on IT-/sensor- and automatic sampler techniques and Chapter 11 on participative monitoring.

The work on the deduction of ADWIs is still in progress. Consequently, the report presents a review on relevant definitions, methods and indicators as well as some background information. The report also reflects the work status, with a first prioritisation of indicators and the perspective on further prioritisation and evaluation.

This report concerns the FAIRWAY deliverable D 3.1: “Review report of Agri-Drinking Water quality Indicators and IT/sensor techniques, on farm level, study site and drinking water source”.

2. BACKGROUND INFORMATION

2.1 NITRATES

Nitrates are intermediate products in the nitrogen cycle (see Chapter 3.3). As ions in soil water they are the most prevalent form of nitrogen being uptaken by plants.

2.1.1 Nitrogen statistics

Nitrogen containing fertilisers are the most used fertilisers in Europe (Eurostat, 2018). EU-wide, mineral nitrogen consumption as fertiliser in 2015 amounted to 11,362,000 tons, which equals an average of 75 kg N/ha utilised agricultural area (UAA) (Netherlands: 137 kg N/ha UAA; Romania: 28 kg N/ha UAA) (Eurostat, 2018). This figure does not include nitrogen from organic fertilisers, such as farmyard manure, compost, digestate or sewage sludge.

Total number of livestock in the EU amounted to 130,319,600 livestock units (LU) in 2013, which equals 73.8 LU/ha UAA (Netherlands: 359 LU/ha UAA; Bulgaria: 20.6 LU/ha UAA) (Eurostat, 2018; Statistisches Bundesamt, 2015). Per rough estimation¹ this corresponds to an extra N input to 7,300,000 tons or approximately 42 N/ha UAA.

The gross N budget amounted in 2015 to 51 kg N/ha UAA (Cyprus: 194 kg N/ha UAA²; Netherlands: 189 kg N/ha UAA; Romania: 9 kg N/ha UAA) (Eurostat, 2018). The result of the budget is always positive but varies largely between Member States with an intensive animal and plant production and those, where extensive agriculture dominates. The budget surplus indicates nitrogen losses into air (as ammonia, nitrous oxide, nitrogen oxides and dinitrogen) and water (as nitrate) (see 1.4.1).

The figures cited above show, on the European average, a nitrogen import on the field as mineral and organic fertilisers (including grazing) of 117 kg N/ha UAA and an export by crops of 66 kg N/ha.

2.1.2 Registration/placing on the market of fertilisers

Commercial mineral fertilisers, chelating agents, nitrification and urease inhibitors (and liming materials) are subject to the European fertiliser regulation 2003/2003. The regulation lists authorised types of EC fertilisers, including method of production, minimum concentration of plant nutrient and form and solubilities of nutrients. Regulation 2003/2003 contains an open list of approved fertilisers, which is continuously amended, in order to add new fertiliser types, categories or improved analytical methods (EC, 2003). Amendments are effectuated upon application of a Member State and the fertiliser industry affected. There is no registration of organic fertilisers on the European level up to now, but the Commission plans a complex regulation system within the framework of “circular economy”. The European Parliament’s Internal Market Committee (IMCO) voted in July 2017 on amendments to the Fertiliser Regulation and suggested it be expanded in order to open the European market to more products such as organic fertilisers (Euroactiv, 2017).

On Member State level, there already exists legislation on the placement on the market of organic fertilisers (i.e. compost, digestate, manure).

2.1.3 Data requirements

The Nitrates Directive (91/676/EEG) was adopted in 1991 to protect waters against agriculturally derived N pollution. WFD (2000/60/EG) was passed in 2000 to protect European waters in order to reach “good status” objectives for water bodies throughout the EU.

¹ 1 LU equals roughly 0.8 “fertiliser units” of 70 kg N/year (Ifulg, 2018)

² Due to data quality issues

Member States are required for the implementation of the Nitrates Directive to (i) establish monitoring networks in order to identify polluted or threatened waters; (ii) establish a voluntary code of good agricultural practice; (iii) allocate all land that drains into polluted waters as nitrate vulnerable zones (NVZ); (iv) establish mandatory action programmes within NVZ and (v) review the action programmes and NVZ boundaries every four years. In this connection, Member States have to report the quality of their surface and groundwater. Additionally, Member States have to report on their national action programmes. Impact assessment of the action programme measures may require Member States to provide information on the following elements:

- Total number of farmers, and farmers with livestock, total land (km²)
- Agricultural land (km²)
- Agricultural land available for application of manure (km²)
- Permanent pasture
- Permanent crops
- Annual contribution of mineral and organic forms of N (kg N/ha)
- Annual use of mineral and organic N (kilotonnes)
- Nitrogen discharge into the environment from agriculture, urban wastewater and industry (Oenema et al., 2011).

2.2 PESTICIDES

Pesticides are substances that are meant to control pests, including weeds. The term pesticide includes all of the following: herbicide, insecticides (which may include insect growth regulators, termiticides, etc.) nematocide, molluscicide, piscicide, avicide, rodenticide, bactericide, insect repellent, animal repellent, antimicrobial, fungicide, disinfectant (antimicrobial), and sanitizer (<https://en.wikipedia.org/wiki/Pesticide>).

2.2.1 Pesticide statistics

A regulation on the reporting duties of the Member States to the EU on statistical usage data of plant protection products (Regulation (EC) No 1185/2009) was published in 2009. This regulation contains details of the requirements in all Member States for pesticide statistics and reports on the progress of the implementation of the Framework Directive on the Sustainable Use of Pesticides (FDSUP). All Member States have to collect sales and usage data to provide insights into the amount of pesticides sold and applied per crop and area. Statistics regulation (EC) No 1185/2009 requires, that the nationally sold annual weight (kg) of all active substances listed in its Annex III are collected under certain major groups and product categories.

Required usage data for pesticides refer to representative crops (selected by Member State) within a one-year reference period and a 5-year reporting. Key pieces of data required are the quantity (kg) of each substance used on each crop, and the area (ha) treated with each substance. Usage data to be reported include pesticide consumption, pesticide characteristics, soil characteristics, application rates, application timings and mitigation measures.

Table 2.1 shows the pesticide sales per hectare (UAA minus permanent grassland) as total and split into the different types of pesticides, in kg of active ingredient per hectare, for each of the 28 European Member States and as European average. Pesticides are used in far smaller quantities than fertilisers: on the European average, pesticide sales amount to 3.18 kg/ha [UAA minus permanent grassland], of which fungicides and bactericides take the largest share with almost 1.39 kg/ha [UAA minus permanent grassland], herbicides and similar type of substances take a share of 1.05 kg/ha [UAA minus permanent grassland]. For this indicator, areas of permanent grassland are subtracted from UAA, as pesticides are not regularly applied on grassland, which is mostly used as

feedstuff for animals. It is noticeable, that some Member States have reported sales of active substances far over the European average: these are Belgium, Cyprus, Italy, Malta, the Netherlands, Portugal, Slovenia and Spain (Eurostat 2018, 2018b). In most of these cases, the sales of fungicides and bactericides, herbicides and related products (active ingredients) are elevated in comparison to the European average.

However, the quantity of active substances sold does neither gives clear information on the toxicity of the pesticides used, nor on their persistence or on other chemical characteristics. Therefore, an interpretation towards the intensity of pesticide use is difficult and may include the following factors:

- range of pesticides being approved for the zonal market of a Member state. This varies probably a lot and may depend on the market size: in small markets it may be less interesting for pesticide producers to register new products: there, more of the older products may still be in use. Those products are generally applied in higher concentration per hectare as products being put on the market recently,
- climatic distinctions,
- cropping patterns/range of crops being cultivated,
- intensity of crop production.

2.2.2 Registration/marketing licence for pesticides

A two-step approval procedure for pesticides is obligatory in the EU. As first step, the placement of pesticides (=plant protection products) on the market is subject of the Regulation (EC) No 1107/2009. The central authorisation of the so called “active substances” of the pesticides is at the request of a Member State pronounced by European Food Safety Authority (EFSA) and approved by the European Commission. Application papers are confidential. Every active ingredient has to run through a complex admission system, before it can be developed as pesticide and provided to the user. An industrial company starts the process with the submission of an application of approval of a new active substance to an EU Member State. The application includes supporting scientific information and studies, including pesticide fate modelling for defined scenarios. The Member State evaluates the application. Subsequently, the European Food Safety Authority EFSA peer reviews the Member State’s assessment of the active substance. On the basis of EFSA's review, the European Commission and the Members States decide whether to authorise the active substance. Active substances are approved for a period of 10 years. Industry has to apply for the renewal of the approval.

In a second step, a company applies to a Member State to put a pesticide containing an approved substance on the market. The Member State assesses the approval and puts forward a proposal for specific Maximum Residue Levels (MRL). If the proposed MRL is covered by existing legislation, the application is submitted to the EC. The EC decides whether to accept the proposed MRL; if it does, the Member State can authorise the pesticide for a defined usage zone (EFSA, 2018).

The pesticide then can be brought to the market. The Member States are required to monitor pesticide use and pesticide residues in food. The Framework Directive on the Sustainable Use of Pesticides (FDSUP) (2009/128/EC) contains requirements on training provision of pesticide advisors and spray operators, and the testing of spray equipment. This directive is implemented by the Member States in National Action Plans.

Table 2.1: Sales of pesticides in 2016 in the EU in total and per Member State and per type of pesticide (in kg of active ingredient per ha [UAA – permanent grassland]) (Eurostat 2018, 2018b)

| GEO/CROPS | fungicides and bactericides | herbicides, haulm destructors and moss killers | insecticides and acaricides | molluscicide | plant growth regulators | other plant protection products | total pesticides |
|-------------------------|------------------------------------|---|------------------------------------|---------------------|--------------------------------|--|-------------------------|
| EU-28 | 1.39 | 1.05 | 0.31 | 0.01 | 0.11 | 0.30 | 3.18 |
| Austria | 1.43 | 0.91 | 0.67 | 0.01 | 0.06 | 0.03 | 3.10 |
| Belgium | 3.26 | 2.59 | 0.63 | 0.02 | 0.38 | 0.92 | 7.81 |
| Bulgaria | 0.29 | 0.55 | 0.19 | 0.00 | 0.00 | 0.00 | 1.03 |
| Croatia | 0.99 | 0.78 | 0.14 | 0.00 | 0.05 | 0.01 | 1.97 |
| Cyprus | 3.25 | 1.03 | 0.99 | 0.01 | 0.00 | 0.23 | 5.51 |
| Czech Republic | 0.70 | 1.14 | 0.15 | 0.00 | 0.20 | 0.15 | 2.34 |
| Denmark | 0.17 | 0.80 | 0.02 | 0.01 | 0.08 | 0.00 | 1.08 |
| Estonia | 0.15 | 0.86 | 0.00 | 0.00 | 0.00 | 0.00 | 1.02 |
| Finland | 1.43 | 0.56 | 0.01 | 0.00 | 0.04 | 0.01 | 2.04 |
| France | 1.61 | 1.52 | 0.18 | 0.04 | 0.16 | 0.13 | 3.64 |
| Germany | 1.01 | 1.26 | 1.29 | 0.02 | 0.32 | 0.01 | 3.92 |
| Greece | 0.55 | 0.54 | 0.28 | 0.00 | 0.03 | 0.04 | 1.45 |
| Hungary | 0.84 | 1.00 | 0.18 | 0.00 | 0.04 | 0.07 | 2.14 |
| Ireland | 1.33 | 5.01 | 0.07 | 0.03 | 0.48 | 0.07 | 7.00 |
| Italy | 4.01 | 0.82 | 0.22 | 0.01 | 0.02 | 1.46 | 6.53 |
| Latvia | 0.20 | 0.76 | 0.02 | 0.00 | 0.34 | 0.01 | 1.33 |
| Lithuania | 0.34 | 0.66 | 0.02 | 0.00 | 0.51 | 0.00 | 1.53 |
| Luxembourg (2012, 2015) | 1.43 | 1.31 | 0.00 | 0.02 | 0.24 | 0.00 | 1.58 |
| Malta | 7.21 | 0.48 | 0.24 | 0.04 | 0.00 | 1.96 | 9.93 |
| Netherlands (2015) | 4.11 | 2.70 | 0.27 | 0.03 | 0.40 | 1.86 | 9.38 |
| Poland | 0.67 | 1.13 | 0.13 | 0.00 | 0.19 | 0.05 | 2.18 |
| Portugal | 3.11 | 1.08 | 0.44 | 0.02 | 0.00 | 0.90 | 5.56 |
| Romania | 0.50 | 0.56 | 0.08 | 0.00 | 0.05 | 0.00 | 1.20 |
| Slovakia | 0.46 | 0.77 | 0.08 | 0.00 | 0.13 | 0.06 | 1.50 |
| Slovenia | 4.27 | 1.23 | 0.20 | 0.01 | 0.01 | 0.02 | 5.74 |
| Spain | 2.24 | 0.88 | 0.43 | 0.01 | 0.01 | 0.87 | 4.44 |
| Sweden | 0.10 | 0.64 | 0.01 | 0.00 | 0.01 | 0.01 | 0.76 |
| United Kingdom | 0.88 | 1.61 | 0.06 | 0.00 | 0.00 | 0.00 | 2.55 |

FOCUS, the FORum for Co-ordination of pesticide fate models and their Use (EC, 2018b) runs a website, from which currently approved versions of simulation models and clearly defined scenarios can be obtained (for further detail, see Chapter 5.6.2.16). Both are used to calculate the concentrations of pesticides in ground- and surface water according to Regulation (EC) No 1107/2009. Furthermore, this website contains links to the reports of all FOCUS workgroups.

Standard scenarios were among other reasons introduced to facilitate a consistent scientific evaluation of the leaching potential of substances at the EU level. A Version Control Workgroup as a standing body ensures that the scenarios are updated in order to reflect scientific progress and representativeness for European conditions (EC, 2018b).

The EC website "Guidelines on Active Substances and Plant Protection Products" lists technical guidance documents under the topics physico-chemical analytical methods, efficacy, toxicity, residues, fate and behaviour and ecotoxicology (EC, 2018c).

Under the topic "fate and behaviour", an EC working document is published as Guidance Document on Persistence in Soil (DG AGRI, 2000). Under the same topic, a Guidance document on the assessment of the relevance of metabolites in Groundwater of substances regulated under the Council Directive 91/414/EEC is published (DG SANCO, 2003).

Member States are also required to adopt – on a regional or national scale – harmonized risk indicators for pesticides, although these are still under development by the EU. Until then, the Member States may use national indicators (Oenema et al., 2011).

2.2.3 Evaluation of the EU approval procedure for pesticides

There has been criticism concerning the procedure for putting pesticides on the EU market. This refers to transparency aspects, but also to the systematic approach pursued until present.

After discussions on the risk posed by the herbicide substance glyphosate and other pesticides, the EU Parliament decided in February 2018 to set up a special committee on the EU's authorisation procedure for pesticides (PEST). Task of the special committee is to assess up to 12 December 2018

- the authorisation procedure for pesticides in the EU;
- potential failures in how substances are scientifically evaluated and approved;
- the role of the Commission in renewing the glyphosate licence;
- possible conflicts of interest in the approval procedure; and
- the role of the EU agencies, and whether they are adequately staffed and financed to enable them to fulfil their obligations (EU parliament, 2018).

Element of the regular agenda is a REFIT evaluation of the EU pesticide legislation, in order to assess if the regulations meet the needs of citizens, businesses and public institutions in an efficient manner. The REFIT-evaluation is carried out by the Commission. The evaluation aims to perform an evidence-based assessment of the implementation of the regulations on pesticide and maximum residue levels and address synergies, gaps, inefficiencies and administrative burdens. According to the roadmap published by the Commission in November 2016, main evaluation criteria to be addressed in this REFIT evaluation are:

- Effectiveness of the intervention;
- Efficiency in relation to resources used;
- Relevance in relation to identified needs and problems;
- Coherence with other interventions with common objective;
- EU added value compared to what could have been achieved by Member State or international action.

The whole process including stakeholder's comments can be followed on the web page https://ec.europa.eu/food/consultations-and-feedback_en#fbk (European Commission, 2018).

2.2.4 Adjustment needs for the EFSA evaluation procedure of the environmental impact of pesticide active substances

According to the EU guideline 2009/128/EG, pesticides should have, if used properly, no negative effects on the physical health neither of human beings or animals (with the exception of the target species) nor on surface and groundwater and the rest of the environment.

However, analyses by several research teams show that the current pesticide input has considerable negative effects on terrestrial and aquatic ecosystems and biodiversity (SRU, 2016). Several countries in Europe report that groundwater has concentrations of pesticides that exceed the quality standards. About 7 % of the groundwater stations reported excessive levels for one or more Pesticide (Eurostat, 2018f).

Also surface waters showed abnormalities: nearly half of the insecticide concentrations in the European surface waters exceeded the regulatory accepted values (Stehle and Schulz, 2015).

Pesticide contamination is considered one of the reasons by which streams fail to achieve good ecological and chemical status, the main objectives of the Water Framework Directive. However, little is known on the interaction of different pesticide sources and landscape parameters and the resulting impairment of macroinvertebrate communities (Bunzel et al., 2014).

In aquatic systems, insecticides change structure (Liess and von der Ohe, 2005) biodiversity (Beketov et al., 2013) and function of aquatic biocoenoses (Schäfer et al., 2011, 2012). Worldwide, the size of populations of invertebrates has been reduced by around 45 % and the number of species sank drastically, too (Dirzo et al., 2014).

A meta-study by German, Danish and Australian universities in 2012 revealed that the current pesticide admission procedure is neither suited to meet the biodiversity targets for streaming waters nor the targets of the Water Framework Directive to establish a good ecological status of European water bodies. Their analysis showed that with concentrations that are not problematic according to the allowed standard procedures, the abundance of sensitive organisms was reduced by 27-61%, depending on how far unstressed upstream river conditions existed (Schäfer et al., 2012).

In terrestrial systems, herbicides reduce diversity and abundance of flowering plants, especially of arable herbs. This results in a loss of feed for insects and a reduced diversity of insects, not only at the border of fields (Roß-Nickoll et al., 2004; Ottermanns et al., 2010; Legrand et al., 2011; Schmitz et al., 2014; Hahn et al., 2015) but in the whole agrarian landscape. Due to the massive reduction of biomass, structures of microhabitats and feed resources, not only insects but all consumers of insects, as small mammals and birds, are affected (= feed network; Hallmann et al., 2014; Goulson, 2015; Rundlof et al., 2015; Woodcock et al., 2016; Hallmann et al., 2017; Vogel, 2017).

One reason identified is that the current admission procedures only assess the effect of single pesticides, a situation that does never occur in natural environments, where organisms are repeatedly exposed to multiple substances (Schäfer et al., 2012). Additionally, the presence of other active substances can reduce the degradation of a pesticide significantly, as was shown for the herbicide Pendimethalin, where the half-life doubled in the presence of Mancozeb (Swarcewicz and Gregorczyk, 2012).

The toxic effect of a pesticide mixture can, in comparison to the single substances, be enforced or reduced by mutual impact: the mixture can have additive, synergetic or antagonistic toxic effects as compared to the single pesticides. Moreover, the LD₅₀/LC₅₀ value for the standard reference organisms, used as toxicity indicator for terrestrial/aquatic organisms, does not allow conclusions on the effect of a pesticide on different species of an ecosystem, since the most sensitive species to a

pesticide in an ecosystem is not known³. Additionally, indirect effects such as secondary damages in the food chain are not accounted for by the LD₅₀/LC₅₀ values. Thus, the LC₅₀ value of the single substances is not suitable as indicator for the impact of pesticides on an ecosystem, although often used that way (Fent, 2013).⁴

Moreover, the standard admission procedures ignore the fact that organisms are exposed to multiple stresses in the environment which can increase their vulnerability against pesticides (Schäffer et al., 2012).

Another reason behind the adverse effects of pesticides on ecosystems are deficits in the pesticide prediction models concerning pesticide soil degradation and exposition of water bodies as well as in pesticide regulation. A Swiss monitoring-study revealed, that from a selected range of 80 pesticides applied to fields between 1995 and 2008, still 80 %, half of them metabolites, can be detected in small quantities in the soils (Bonmatin et al., 2015), although in the admission papers far shorter retention times are documented (Schäffer et al., 2018).

Risk assessments do not consider mixtures of active substances with each other or with fertilisers, sequential exposition and total load of pesticides (Schäffer et al., 2018).

Risk assessments during pesticide admission fall short of indirect effects such as loss of habitat and food resources following pesticide application. Risk assessments hardly consider multiple stress factors that add to the pesticide exposure, such as competition with less sensitive species, overfertilisation, narrowed crop rotations or consequences of climate change such as drought periods or extreme rainfall events. Many potentially affected species such as wild pollinators (bumblebees or wild bees) and amphibians are not integrated in the current risk assessments during pesticide admission tests.

The German monitoring of pesticide concentrations following the Water Framework Directive does not include all active substances relevant for the present agricultural practice and is therefore according to Schäffer et al. (2018) not suited to serve as a general representative monitoring for pesticides.

³ On the other side, a safety factor of 100 for LC₅₀ and of 10 for the no-observed-effect-concentrations (NOECs), which are used to derive the regulatory acceptable (RAC) values, was established; J. Strassemeier, Julius-Kühn-Institut.

⁴ But LC₅₀ are not the only endpoints relevant for the EFSA-registration; EC₅₀, NOECs, mesocosm studies and field studies are used to evaluate the regulatory acceptable concentration (RAC); J. Strassemeier, Julius-Kühn-Institut.

2.3 INDICATOR DEFINITION

Below, the relation between environmental, agri-environmental and agri-drinking water indicators (ADWIs), main subject of this report, is outlined.

2.3.1 Environmental Indicators

An environmental indicator is an index or a measurement endpoint used to evaluate the condition of a studied system. The term “indicator” is frequently used as a link between scientific results and policy making. Indicators are usually used to describe or extrapolate the future condition of habitats and to evaluate test whether a desired environmental condition is achieved.

Environmental indicators were developed by the Organisation for Economic Co-operation and Development (OECD) in the early 1990s. Main criteria for their selection were “policy relevance and utility for users”, “analytical soundness, and “measurability” (EAA 2014).

Indicators can be used for:

- *ex ante* evaluations of actions during the planning phase,
- *ex post* evaluation of actions at their end or implementation,
- monitoring with an alert role,
- decision support in real time to drive the system, and
- communication (Bockstaller et al., 2008).

Diferent types of indicator can be distinguished (Bockstaller et al., 2008):

- Simple indicators, based on one type of variable not directly measured, but obtained by surveys or databases. They can consist on one or a simple combination of variables and often show a poor quality of prediction.
- Indicators based on conceptual or mechanistic simulation model allow to link the predicted effect to causes. Their complexity is a major limitation to use.
- Indicators based on measurements. They are used when the focus lies on impacts and no accurate model is available. Disadvantageous are the costs.

The output of an indicator may be quantitative or qualitative, a reference value can assist in the interpretation of the individually calculated value (Bockstaller et al., 2008).

Lebacqz et al. (2013) define a typology for four kinds of indicators Table 2.2):

- means-based indicators, assessing technical means and inputs used on the farm, i. e. livestock stocking rate,
- system-state indicators, concerning the state of the farming system, i. e. post-harvest soil nitrate,
- emission-indicators related to the farm’s polluting potential, i. e. estimated farm’s loss of nitrates to ground- and surface waters and
- effect-based – measured – indicators reflecting the impact of the practices on the environment, i.e. actual nitrate concentration in ground water.

While means-based indicators are easy to implement with regard to data availability and calculation, they show a low quality of prediction of environmental impacts (van der Werf et al., 2009). Effect-based indicators, on the other hand, directly reflect environmental impact, but are difficult to implement and data collection is often more expensive and time-consuming (Lebacqz et al., 2013). System-state and emission indicators, ranging from budgets to complex model-based indicators, have an intermediate position.

Table 2.2: Description of the typology of environmental indicators and characterisation of these types, in terms of calculation method, data availability and environmental relevance, in the context of data-driven approach (Lebacqz et al., 2013, adapted from Bockstaller et al., 2008; van der Werf and Petit, 2002; van der Werf et al., 2009)

| Type | | Example | Definition | Calculation | Spatial scale*) | Data availability*) | Environmental relevance*) |
|-------------------------|------------------|--------------------------------------|---|---------------------------------------|-----------------|---------------------|---------------------------|
| Means-based indicators | | Livestock stocking rate | Agricultural practices | Single variables | P/F | ++ | – |
| Intermediate indicators | System-state | Amount of post-harvest soil nitrate | State of the farming system | Single variables, direct measurements | P/F | +/- | +/- |
| | Emissions | | Emissions of greenhouse- and acidifying gases, nutrients, pesticides into the environment and potential impacts | | | | |
| | -Nutrient budget | Farmgate nitrogen surplus | | Combination of variables | F | + | +/- |
| | -LCA*) | Eutrophication potential | | Emission factors | F+ | +/- | + |
| | -Model-based | Nitrogen leaching modeling | | Modeling | P/F/R | – | + |
| Effect-based indicators | | Nitrate concentration in groundwater | Environmental impact | Direct measurements | W/R | -- | ++ |

*) LCA life cycle analysis; P parcel level; F farm level; F+ farm level, including upstream activities (e.g., production and transport of inputs); R regional level; W watershed level; ++, +, +/-, -, -- relative degree of data availability and environmental relevance

2.3.2 Agri-Environmental Indicators (AEI)

Agri-Environment Indicators (AEI) for monitoring the integration of environmental concerns into the Common Agricultural Policy (CAP) were further developed in 2002 by the IRENA (Indicator Reporting on the Integration of Environmental Concerns into Agriculture Policy) operation. It is an indicator set used by DG Agri, DG Environment, Eurostat and Joint Research Centre, and the European Environment Agency.

IRENA was organised as a joint project of DG Agriculture and Rural Development, DG Environment, DG Joint Research Centre, Eurostat and the European Environment Agency (EEA). The purpose was to develop and compile for EU-15 the set of 35 indicators defined in COM final 0020/2000 and COM final 0144/2001 at the appropriate geographical levels and, as far as possible, on the basis of existing data sources. Using the DPSIR-model, agri-environmental relationships with respect to the topics water, land use and soil, climate change and air quality, biodiversity and landscape were developed and 28 AEI were defined for the monitoring of environmental concerns into the CAP. Several limitations remain for a number of indicators (eurostat 2018):

- deficiencies in the data sets related to certain indicators, in terms of harmonisation (e. g. farm management), or geographical coverage (e. g. water quality),
- data availability (e. g. genetic diversity or pesticide risk),
- requirement of further conceptual improvement (e. g. high nature value farmland areas).

DireDate, a project finalised in 2011 on behalf of eurostat, was run with the objective to set up a sustainable system for the collection of data sets from farms and other sources that would serve primarily European and national statisticians to calculate the 28 AEIs. The objectives of DireDate were to analyse and describe AEI data requirements, to provide recommendations for priority data collection and to analyse the feasibility for a combined data collection and processing. Methodologies for the calculation of combined indicators, i. e. the farm nutrient budget, were presented.

Certain types of data can be obtained from the Farm Structure Survey (FSS) and from the Survey on Agricultural Production Methods (SAPM), however, also individual farm data on animal feeding, animal housing, manure storage and manure application are needed for the calculation of farm nutrient budgets. Oenema (2011) pointed out, that the EU Member State systems for collection, processing and reporting of agri environmental data need increased coordination, harmonisation and streamlining throughout the whole chain.

The level, on which the AEI are used and the purpose they may be used for on these levels differs with scale:

- **European/national level:** The application of AEI enables e. g. the European Commission to evaluate/benchmark the transcript of EU-legislation at Member State level. Under the topic "Agriculture and environment (AEI)," 13 AEI are listed for the Member States, partly on NUTS 2 regional level (Eurostat, 2018c). At the national level, AEI are typically based on/calculated from existing statistical data, as it is not possible to either find detailed data or it is too expensive to start collecting them for a whole country (Niemeijer and de Groot, 2008).
- **Regional level:** AEI are used e. g. on supranational/regional/local context, to monitor the impact of agriculture on environment, identify hotspots or focus subjects and areas for the agricultural advisory service.
- **Farm level:** On farm level, the nitrogen farm budget as AEI could be used, first of all, as decision aid tool, to help farmers to adapt their cultivation practices to integrated arable farming system requirements, from one cropping year to the next (Bockstaller and Girardin, 1997). This is the case e. g. in Denmark, France, Germany, the Netherlands, Portugal and Romania. On this level, AEI are used for benchmark-purposes, too, i.e. to compare the management of the same type of farms and to focus on "low performers". Besides the calculated budget-indicators, measured indicators play a larger role for practical farm consulting. For example, the harvest N_{min} -

concentration of arable soils is a meaningful indicator for nitrate leachate in winter and contamination of ground water (Osterburg and Runge, 2007).

Figure 2.1 visualises the levels of operation of AEI in relation to the aim for their use and examples for corresponding indicators. The figure shows, that the degree of data aggregation increases with level of operation. In the other direction, the degree/proportion of individual farm data and measurements increases from European towards farm level.

As more (in time and space) aggregated data show less standard deviation than the single datasets, correlation with water quality could be stronger between AEI being deduced from data on a regional level than on farm level. This would explain, why Wick et al. (2012) found the Gross Nitrogen Budget a statistically significant predictor for groundwater nitrate concentration, while other authors (Buczko et al., 2010; Lord and Antony, 2002; Rankinen et al., 2007; Sieling and Kage, 2007) calculated less strong relationships for indicators at a smaller scale.

From the above it can be concluded, that on the different levels of operation, AEI may be the same, or they may differ in the parameters included.

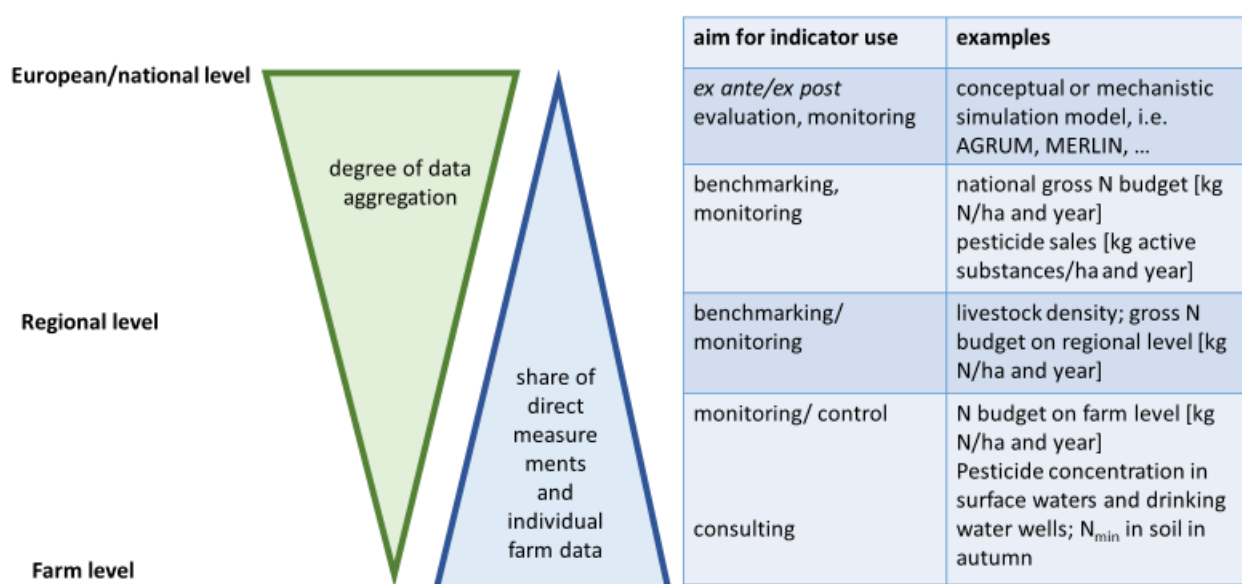


Figure 2.1: Deduction and statistical evaluation of AEI: degree of aggregation and individualisation in relation to operation level of indicator necessary

2.4 THE DPSIR FRAMEWORK

The DPSIR model is defined as “causal framework for the description of interactions between society and the environment”. Based on the PSR (pressure – state – response) model developed by OECD, it was adopted by the European Environment Agency (EEA, 2018). According to its terminology, social and economic developments (driving forces, D), exert pressures (P) on the environment and, as a consequence, the state (S) of the environment changes. This leads to impacts (I) on ecosystems, human health and society, which may elicit a societal response (R) that feeds back on driving forces, on state or on impacts via various mitigation, adaptation or curative actions (Smeets and Weterings, 1999; Gabrielsen and Bosch, 2003).

2.4.1 The DPSIR-model in the environmental context

In the agri-environmental context, the indicators of the DPSIR-model can be interpreted as follows (Gabrielsen and Bosch, 2003):

- **Driving forces** describe the social, demographic and economic developments in societies and the corresponding changes in lifestyles, overall levels of consumption and production patterns, *such as the preference for meat in diets*.
- **Pressure indicators** describe developments in emissions, the release of physical and biological agents and the use of resources including land by human activities. As result, a variety of natural processes lead to changes in environmental conditions, *i.e. in an increase in ammonia emissions or in nitrogen deposition in natural habitats*.
- **State indicators** give a description of the quantity and quality of physical, biological and chemical phenomena, *such as the concentration of nitrates in surface- and groundwaters*.
- **Impact indicators** show the impacts on the functions of the environment, *such as human health and quality of ecosystem, resources availability, losses of manufactured capital, and biodiversity*.
- **Response indicators** refer to responses by society, as well as government attempts to prevent, compensate, ameliorate or adapt to changes in the state of the environment. *The reduction of meat consumption as societal response* can be regarded as negative driving force, since prevailing trends in consumption and production patterns are redirecting. Other responses may be to increase the efficiency of agricultural production, *i.e. nitrogen efficiency in plant production*.

Table A1 in the annex lists the 28 European AEI and shows how they are embedded in the DPSIR framework (Eurostat, 2018).

2.4.2 Application of the DPSIR model in different contexts and levels

The DPSIR model is used on different contexts and scales.

- **European/national level:** The data on national level behind each of the 28 AEI are listed in fact sheets related to COM final 0508/2006 (Eurostat, 2018). On the European level and in relation to water quality, there are quite a few approved AEI which work as driving forces, but only some AEI function as pressure and risk indicators with focus on water quality: Nitrate pollution and Pesticide pollution (Table Annex 1 and Figure 2.2). While the indicator “Gross nitrogen budget” is well defined, although further implementation might be necessary, the indicator “Pesticide risk” needs further development: The conceptual and, where appropriate, modelling framework underpinning this indicator needs to be developed (COM, 2016; Eurostat, 2018).
- **Regional level:** Breaking down the regulations of the WFD on the level of river basin management/ground water bodies, the DPSIR-model can be applied to explain the mechanisms of the transformation of the Directive on this regional level. Certain targets, like water quality indicators, have to be met at this level. These AEI are also used for monitoring and control purposes.
- **Farm level:** The DPSIR-model can also be applied on farm level. The compliance with national fertilising legislation, for example in Germany, has to be proven by setting up a net nitrogen soil (surface) budget; since the beginning of 2018, for intensive animal breeding farms, a gross nitrogen farmgate budget is compulsory, too. The result of these budgets, on farm level, serve as proof of “good agricultural practice”, the compliance with the rules of the nitrates directive and the fertilising legislation, also in the framework of cross compliance.

Driving forces

- Mineral fertiliser consumption
- Consumption of pesticides
- Irrigation
- Land use change (Archived)
- Cropping patterns
- Livestock patterns
- Soil cover
- Tillage practices
- Manure storage
- Intensification/extensification
- Specialisation

Pressure and Risk

- **Gross nitrogen balance**
(Archived)
- **Pesticide risk**
- Ammonia emissions
- Soil erosion

State/Impact

- **Water quality - Nitrate pollution**
- **Water quality - Pesticide pollution**
(Archived)

State/Impact

- Soil quality (Archives)
- Landscape – state and diversity (Archived)

Figure 2.2: Linkage of AEI related to Water quality on international (European level)

3. CONCEPTUAL UNDERSTANDING OF THE NITROGEN AND PESTICIDE CYCLES IN THE AGRI-HYDRO-GEOCHEMICAL SYSTEM

3.1 DEFINITIONS OF THE AGRI-HYDROGEOCHEMICAL SYSTEM

ADWIs are selected within the cycles of nitrate and pesticides in the agri-hydrogeochemical system. The driving force (D), pressure (P), state (S), and link (L) indicators are defined in the agri-hydrogeochemical system while impact (I) and response (R) are considered to be outside the system (see Figure 3.1).

The agricultural system, in the ADWI context, is physically defined by the zone between the atmosphere and the rooting depth where all the agricultural activities and reactions occur (Figure 3.1). In the agricultural system, interplay between human activities (e. g. fertiliser and pesticide use, crop production) and natural processes (e. g. nitrogen cycle, soil erosion, adsorption/desorption, denitrification) control leaching of nitrate and pesticides to the underlying hydrogeochemical system. The driving force (D) and pressure (P) indicators represent the agricultural system and the primary focus is to quantify the leaching and run off of nitrates and pesticides into the underlying hydrogeochemical system.

The hydrogeochemical system is the zone from the ground surface to the drinking water abstraction point (Figure 3.1). The hydrogeochemical system governs pathways to deliver nitrate and pesticide from the agricultural system to the drinking water abstraction point. The pathways control the transit time of pollutants, i. e. nitrate and pesticides, and biogeochemical reactions that may change the concentrations and phase of them in the hydrogeochemical system (Figure 3.1). The state (S), and link (L) indicators describe the fate, retention and transport of nitrate and pesticides in the hydrogeological system.

The waterworks system describes drinking water production processes (Figure 3.1). In the waterworks system, nitrate and pesticides in raw waters – groundwater or/and surface water – might be removed by various types and degrees of processes, depending on the water quality and technological possibilities. The state (S) indicator shows the quality of drinking water.

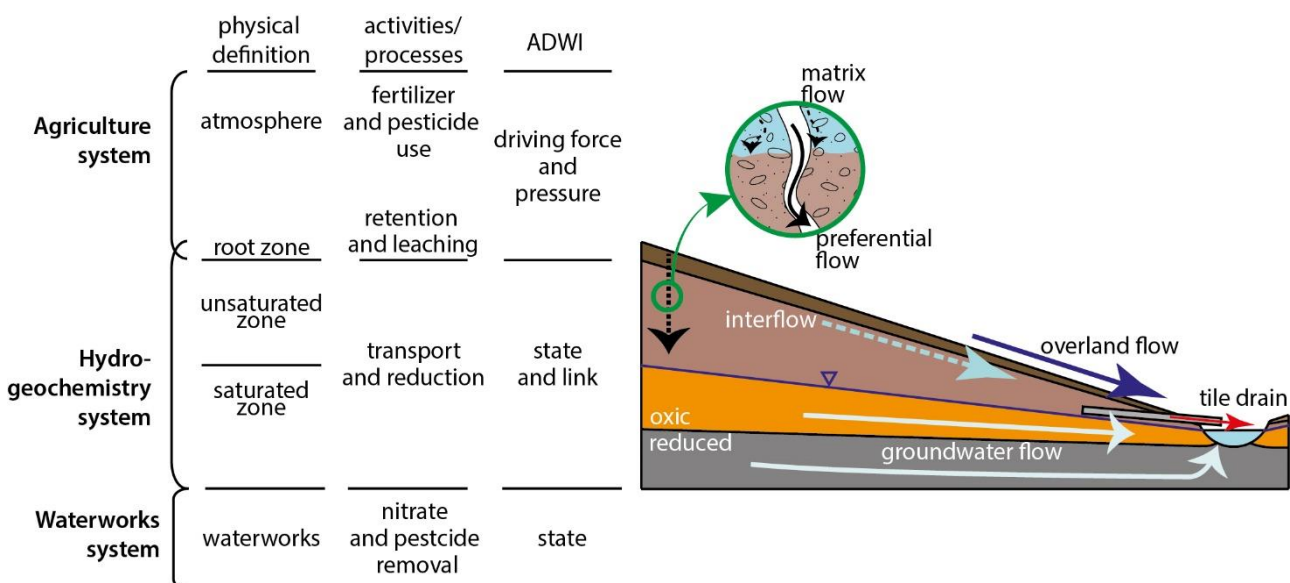


Figure 3.1: Conceptual model of the Agri-Hydrogeochemical system of ADWIs

3.2 PATHWAYS IN THE HYDROGEOCHEMICAL SYSTEM

Pathways in the hydrogeochemical system are the routes of nitrate and pesticides from the agriculture system to drinking water abstraction points. Identifying the dominant pathways are important for different reasons related to:

- 1) Planning and selection of specific agricultural mitigation measures in regard to protection of water resources as lakes, streams or groundwater taking the lack time into account,
- 2) Planning and selection of drinking water protection strategies and treatment possibilities in order to secure clean drinking water in the short and long term perspective.

Therefore, one of the key roles of the ADWIs should be identifying the dominant pathways of the hydrogeochemical system. Dominant pathways of the hydrogeochemical system are controlled by complex interplay between its hydrogeologic structure (e. g. soil type, soil thickness, soil moisture, surface topography, bedrock type, groundwater table depth, hydrogeology and hydraulic parameters) and climatic conditions (e. g. seasonality, rainfall intensity); therefore, it may spatially vary and seasonally shift.

In the context of development of ADWI, we conceptualised the pathways as follows: two pathways for groundwater and four pathways for surface waters (Table 3.1).

Two pathways for groundwater: To recharge groundwater, water primarily flows vertically via

- 1) Matrix flow pathways and/or
- 2) Preferential flow pathways (Figure 3.1).

This water eventually emerges back to the surface water.

Matrix flow is a pathway through pore spaces in the soil matrix. In the unsaturated zone, matrix flow moves uniformly with a wetting front, therefore it is also called as uniform flow. The transit time of matrix flow can be long (months to years; Table 3.1); therefore, the groundwater table and groundwater chemistry show relatively small variations and slow changes over time.

Preferential flow is a pathway via macro-pores in the soil and fractures in bedrock, bypassing a dense or less permeable matrix (Beven and Germann, 1982, Hendrickx and Flury, 2001). The macro porous spaces in soils can be created along root channels, soil fauna channels, cracks (i. e. freeze-thaw, wetting-drying), fissure, or soil pipes (Beven and Germann, 1982). Preferential flow may be transiently active; however, it can deliver a significant quantity of contaminants to groundwater quickly (hours ~ weeks; Table 3.1).

Four pathways for surface waters: Horizontal flow is the most dominant pathways for surface waters governing the transport and fate of contaminant in the systems. The horizontal flow pathways are

- 1) Overland flow,
- 2) Interflow,
- 3) Groundwater discharge and
- 4) Tile-drainage flow (Figure 3.1).

Overland flow is water flowing along the land surface directly into the stream. This occurs in some landscapes, where the groundwater table is near the land surface (peat soils) or the top soil is extremely impermeable e. g., clay rich (Figure 3.1). The transit time of overland flow is extremely short (Table 3.1) and the water will be continuously exposed to fertilisers or pesticides along the pathways. Furthermore, overland flow causes soil erosion, which may transport nitrogen and

pesticides in the particle phase. Therefore, a hydrogeologic system with overland flow is expected to be highly dynamic and vulnerable to contamination.

Interflow occurs in the unsaturated zone where infiltrated water flow laterally via preferential pathways and travel directly to the stream (Figure 3.1). Interflow may develop a localised and transiently saturated zone and water may flow relatively fast (e.g., days to weeks; Table 3.1).

Groundwater discharge is laterally groundwater flowing directly into surface waters such as streams and lakes. The transit time of groundwater to surface waters may vary but, among the four pathways to surface water, it is the slowest pathway (Table 3.1). Therefore, in a groundwater-dominated system, stream discharge and chemistry may response to the rainfall inputs slowly.

Tile-drainage may be another important pathway in clay rich soils. It may operate in a similar manner to that of interflow (Table 3.1).

Table 3.1: Definitions and qualitative transit time of pathways

| Water resource | Pathways | Definition | Transit time |
|----------------|-------------------|--|----------------------|
| Surface water | Overland flow | pathways along the land surface | very short (~hours*) |
| | Interflow | pathways through the unsaturated (or partially saturated) subsurface, mainly via soil macro-pores, fractures, or perched groundwater | short (days~weeks*) |
| | Tile drains | pathways via tile drains | short (days ~weeks*) |
| | Groundwater flow | pathways through the saturated zone | long (years~decades) |
| Groundwater | Preferential flow | Flow paths via fractures and macro-pores | short (hours~weeks) |
| | Matrix flow | Flow paths via matrix (i.e. via pore spaces) | long (years~decades) |

*) These time specifications are approximations to compare the paths to each other. These approximations are only valid when the flow of water is sufficient during wet conditions/heavy rainfall. This is not always the case. The transit time is dependent on the water flows (in this case rainfall).

3.3 NITROGEN CYCLE IN THE AGRI-HYDROGEOCHEMICAL SYSTEM

3.3.1 Input and output of N in the agri-hydrogeochemical system

N is introduced to the agri-hydrogeochemical system as fertilisers (mineral and organic fertilisers), atmospheric deposition, and biological N fixation (Figure 3.2). N is removed from the agri-hydrogeochemical system by crop and animal production, manure export, and biological denitrification (Figure 4.2).

3.3.2 Fate of N in the agri-hydrogeochemical system

N is present in soils in both mineral (e.g. nitrate or ammonium,) and organic forms (e.g. urea, crop residue, manure, soil organic matters). Some organic fertilisers (like urea) rapidly hydrolyze into ammonium after application and are therefore sometime considered as mineral fertiliser. The total N stock in soil (N_t) is almost equal to organic N (Figure 3.3). Mineral N (N_m) is readily soluble and

bioavailable, and so it can be taken up by crop. There are, however, a range of situations where the crops can not absorb all nitrogen (see Chapter 3.3.4). This may enhance leaching of nitrogen.

Organic N must be mineralised to NO_3^- or NH_4^+ first via microbial organisms to be utilised by plants and transported with water (Figure 3.2). Rates of microbial N mineralisation may depend on environmental conditions (e. g. climate) and types of organic N. For example, the mineralisation rate is higher in warm and humid climate conditions. Liquid manure with a narrow carbon/nitrogen ratio results in higher mineralisation rates than farm yard manure containing straw.

Mineral N can also be immobilised by soil micro-organisms (Figure 3.2). For example, immobilisation of mineral N occurs when cereal straw (high C/N ratio) is incorporated into the soil after harvest.

Denitrification reactions are the main pathways to remove nitrate from the agri-hydrogeochemical system as gaseous N, i. e. dinitrogen (N_2), nitrous oxide (N_2O), nitrogen oxides (NO_x). Types and rates of microbial N denitrification reactions depend on available energy source (e. g. organic carbon, pyrite) and the redox condition. Denitrification reactions occur only under the redox condition (no oxygen present). Such conditions develop mainly in the root zone layer and deep saturated zone. Denitrification also occurs in the upper part of the root zone during wet conditions (e. g. heavy rainfall).

In the soil layer, microorganisms reduce nitrate by oxidising organic carbon (Figure 3.2). In this layer, the influx of fresh organic matters from the ground surface fuel the microorganisms and the reduced condition may develop at a micro-scale.

In the reduced saturated zone, in contrast, organic matter usually is less available to fuel the microorganisms. In this layer, microorganisms use different energy sources. A coupled pyrite oxidation and nitrate reduction is one of the well-known reactions to remove nitrate in the deep saturated zone (e. g. Figure 3.2; Postma et al., 1991).

In the unsaturated zone and the oxic saturated zone, nitrate travels conservatively. In the unsaturated zone, the soil air usually contains oxygen, and the oxic groundwater is defined by the presence of detectable dissolved oxygen. Therefore, nitrate concentrations in water in the unsaturated zone and the oxic groundwater may show the similar level to that of water leached out of the root zone.

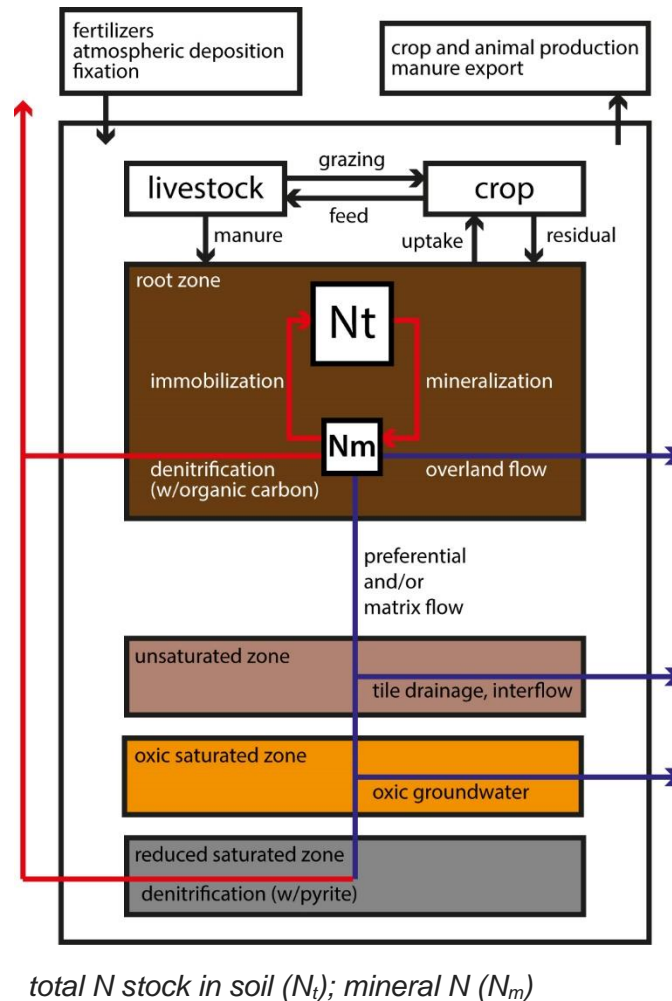


Figure 3.2: Conceptual description of the N cycles in the agri-hydrogeochemical system

3.3.3 Pathways of N in the hydrogeochemical system

Nitrates travel vertically via matrix flow and/or preferential flow in the hydrogeochemical system (Figure 3.2). For groundwater, nitrate concentrations will vary with depth. Despite intense denitrifying activities in the root zone, nitrate concentrations will be highest in the root zone due to high N input. In the unsaturated zone and oxic groundwater, nitrate concentrations in water may be similar to the concentrations in the leaching from the root zone. NO_3^- concentrations become negligible in the reduced saturated zone.

In the saturated zone or groundwater nitrate reduction occurs in a transition zone with anoxic condition often called the redox interface. Here the nitrate concentrations are lower than the concentrations in the leaching from the root zone and often nitrite is used as an indicator of anoxic nitrate-reducing conditions.

For surface water, nitrate concentrations will vary depending on the dominant pathways. The pathways through the zone between the soil surface and oxic groundwater – overland flow, interflow, tile-drainage, and oxic groundwater – will deliver nitrate while the reduced groundwater will not be a pathway of nitrate to the surface water (Figure 3.2).

3.3.4 Reasons for N leaching/runoff from the agricultural system

An important reason for the leaching of nitrates below the root zone is the fact, that in majority of soils most of the soil nitrogen (N_t) is organically bound as soil biomass (humus) and slowly released over time by microbial degradation and transformation into mineral nitrogen (N_{min}). Only the microbial biomass itself is fast degradable (N_{fast}) (Beisecker et al., 2015). The release rate of the organically bound nitrogen is linked to the microbial activity in soil: it is high under warm and humid climate conditions and low during cold and dry weather. Small changes in the climatic frame conditions lead to a relatively large alteration of the N release rate. The larger the N_t -stock in soil, the less predictable the amount of N which will mineralise during one growth season (Figure 3.3). With advancing climate change, the situation may even become worse as climate conditions become less predictable.

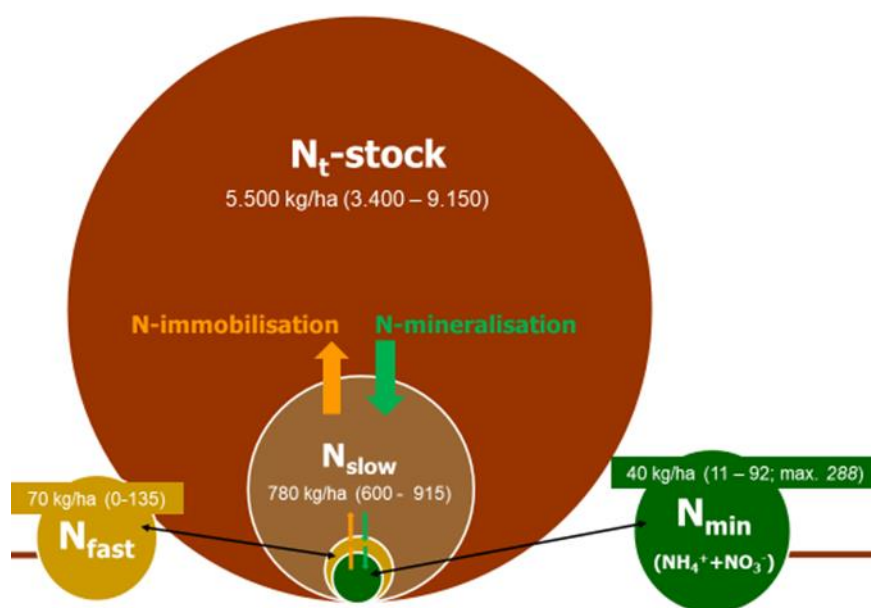


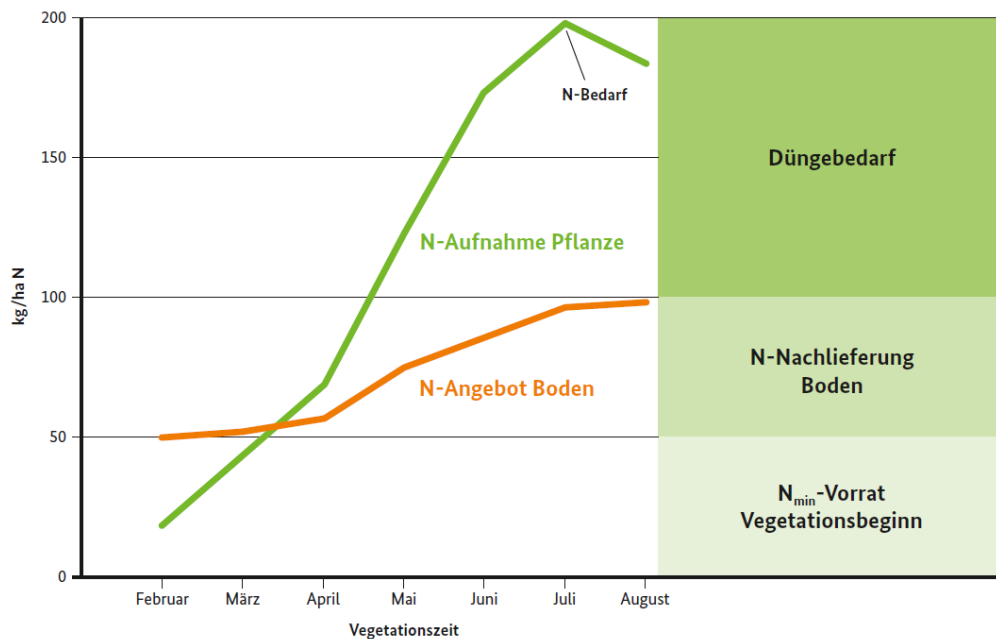
Figure 3.3: size of N-pool in soil (Beisecker et al., 2015)

N-fertiliser planning usually takes into account a certain amount of N_{min} in soil at the beginning of the vegetation period and a certain amount of mineralised nitrogen during the plant growth. The difference between plant need and this soil borne nitrogen should be met by N fertilisation (Figure 3.4). Nitrates leach out of the agricultural system due to the unpredictability of both, the plant development during the growing season and of the amount of nitrogen which will be mineralised.

A reasonable efficiency of N fertilisation (quota of N in harvested field products versus the amount of fertilised N) is around 50 to 60 % under central European conditions, which means around 40 to 50 % of the applied nitrogen is not harvested as crop product. In Denmark the N use efficiency in 2014 was around 40 % (Hansen et al, 2017). Besides the above explained factors this is due to the following reasons:

- Ammonia losses, especially if fertiliser application techniques are used which do not insert nitrogen fertilisers into the soil.
- Denitrification losses from the top soil, e. g. after application of nitrate containing fertilisers to soil rich in organic matter (high denitrification potential), such as grasslands and peat soils.
- Plant growth/development and in consequence N plant need is not exactly predictable, as it depends on a range of factors (e.g., climate, plant health etc.).
- An imbalance between nitrogen demand and supply: this may be absolute, in case nitrogen (as mineral fertiliser or manure) is applied under positive yield estimates.
- The imbalance may be relative, when nitrogen supply and plant demand do not match in course of time (due to N mineralisation or not appropriate timing of N fertilisation).

- The harvested crop contains not all fertilised N, part of it remains in roots and plant parts which remain on the field (i.e. straw, leaves).
- The type of organic fertiliser used: liquid manure or digestate with a narrow carbon/nitrogen ratio possess a higher N-release rates than solid organic fertilisers, such as compost (Gebauer and Schaaf, 2017).
- Point sources, e. g. grazing animals with access to a small stream or lake, may cause nitrogen pollution to surface waters (Bohner et al., 2007).



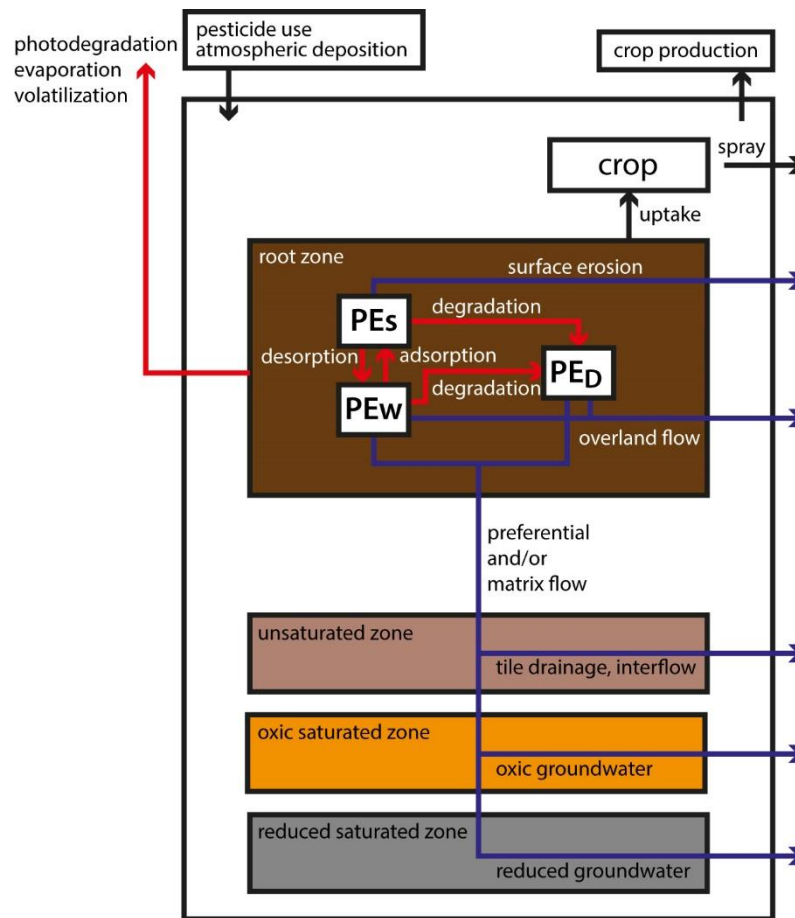
(N-Bedarf=N requirement; N-Aufnahme Pflanze=N uptake by plant; N-Angebot Boden=N available in soil; Vegetationszeit=vegetation period; Düngbedarf=fertiliser requirement; N-Nachlieferung Boden=N delivery from soil; N_{min} -Vorrat Vegetationsbeginn=Nmin stock at the beginning of the vegetation period)

Figure 3.4: Targeted N fertilisation under consideration of the plant N demand and the soil N supply (Baumgärtel, 2012, in Klages et al., 2018)

3.4 PESTICIDE CYCLE IN THE AGRI-HYDROGEOCHEMICAL SYSTEM

3.4.1 Inputs and outputs of pesticide to/from the agri-hydrogeochemical system

Pesticides are introduced to the agri-hydrogeochemical system by pesticide application, atmospheric deposition and drift (Figure 3.5). Pesticides can be removed from the agri-hydrogeochemical system by crop production (accumulation in crops); however, removal by crops may be a minor loss compared to the overall pesticide cycle (Figure 3.5).



pesticides adsorbed onto soil particles (PE_s); pesticides dissolved in water (PE_w); daughter products of pesticides (PE_D)

Figure 3.5: Conceptual description of the pesticide cycles in the agri-hydrogeochemical system

3.4.2 Fate of pesticides in the agricultural system

There are approximately 250 active substances approved by the EFSA for use in the European Commission (2018a) and these substances show a wide range of physical, chemical, and biological properties. Nitrogen, for instance, is transported predominant as nitrate in water. Pesticides, on the contrary, are transported as gas, particles, and solutes. To a less extent, pesticides can be transported via biota. In addition, pesticides undergo more complex physicochemical and biogeochemical transformation than nitrogen does.

Here, we provide a general overview of the pesticide cycle in the agri-hydrogeochemical system from the ADWI perspectives. We focus on two properties of pesticides that may control the appearance of pesticides in water: persistence (or degradability) and mobility.

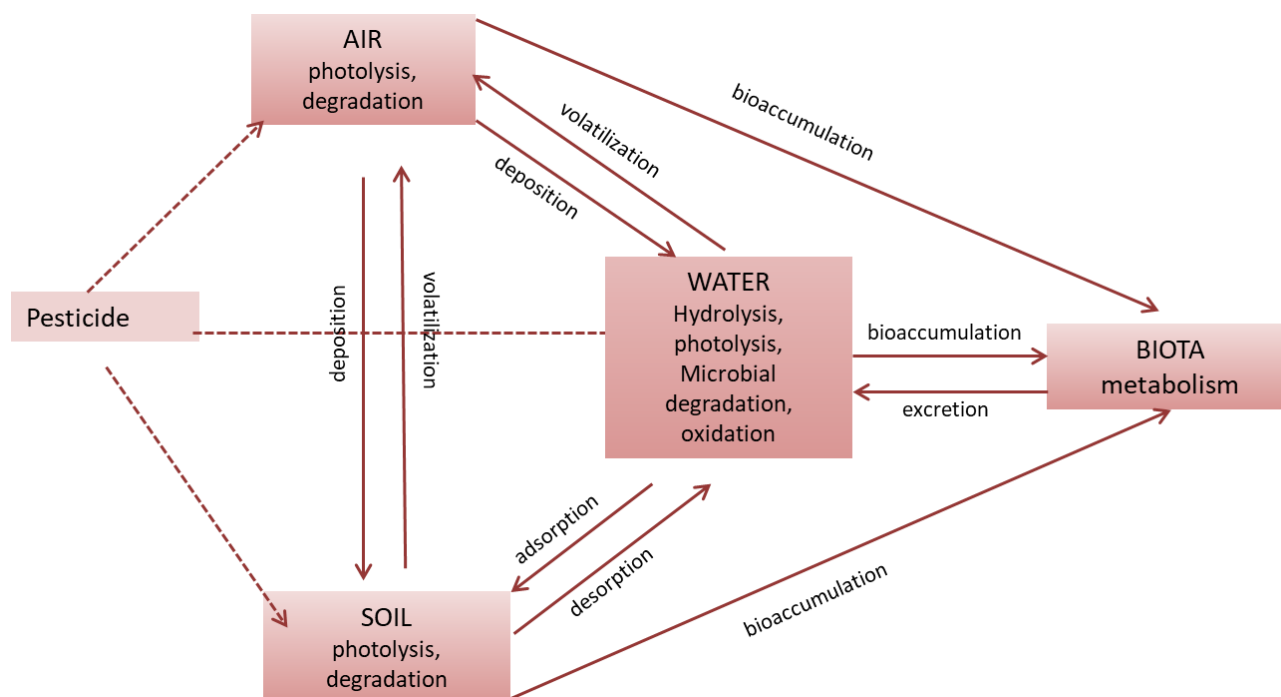


Figure 3.6: Fate of pesticides in the environment: besides transport and transfer processes between the single environmental compartments soil, air and water, transformation processes in the single compartments play a major role in pesticide degradation (Fent, 2013)

The fate of pesticides is controlled by three types of processes: transfer, transport, and degradation processes (Figure 3.6: Fent 2005; Gavrilescu, 2005). Via transfer processes, pesticides move among different environmental media such as air, soil, water and biota. In each medium, pesticides undergo different degradation processes. Transfer processes are responsible for moving pesticides from the initial sources. Persistence and mobility of a pesticide are governed by interactions between the pesticide's property and these processes.

Persistence

Persistence is degradability of a pesticide by transformation and degradation processes. Via these processes, the structure of a pesticide breaks down and its toxicity usually decreases. The physical and chemical characteristics of pesticides may be the first order control for their degradability. In general, more reactive ones (e. g., soluble, small-sized compound, aliphatic structure) are more easily degradable. Table 3.2 summarises the pesticides properties that may control the degradability of organic pesticides (Gavrilescu, 2005).

Table 3.2: Physical, chemical and structural characteristic that may control degradability of organic pesticides (modification of Table 5 from Gavrilescu, 2005)

| Properties | Degradability | |
|--------------------------------|-------------------------------|-------------------------------|
| | More easily | Less easily |
| Solubility in water | Soluble in water | Insoluble in water |
| Size | Relatively small | Relatively large |
| functional group substitutions | Fewer functional group | Many functional groups |
| Compound more oxidized | In reduced environment | In oxidized environment |
| Compound more reduced | In oxidized environment | In reduced environment |
| Created | Biologically | Chemically by man |
| Structure | Aliphatics (branch structure) | Polyaromatic (ring structure) |

The degradation processes are divided into three categories: microbial degradation, chemical degradation, and photodegradation (Gavrilescu, 2005).

Microbial degradation is the primary process to degrade pesticides in soil and water. Soil biota, such as microorganisms, bacteria and fungi may use pesticides as a source of energy or degrade pesticides while using other energy sources such as organic carbon. The rates of microbial degradation will be highest under a favorable condition for soil biota such as a warm, moist and neutral pH environment (Gavrilescu, 2005).

Chemical degradation is an abiotic process, including hydrolysis, oxidation-reduction reactions, and ionization (Gavrilescu, 2005). Pesticides can be degraded by sunlight. Photodegradation occurs not only in the air but also in the shallow soil where photons can penetrate (Gavrilescu, 2005).

Mobility

Pesticides in soils exists both as particles and as solute and the phase influences their mobility and transport mechanisms. Table 3.3 summarises the key properties of pesticides and environmental conditions that affect the mobility.

The organic carbon-water partitioning coefficient (K_{ow}) of pesticide is the ratio of the concentration of a chemical compound in the n-octanol phase to its concentration in the aqueous phase at equilibrium in a two-phase octanol/water system. K_{ow} is usually expressed as $\log K_{ow}$, which is inversely related to water solubility. It is frequently used to predict the distribution of a substance in water and soil.

It is related to the soil adsorption coefficient (K_d) which is described as:

$$K_d = \text{Concentration of compound in soil} / \text{Concentration of compound in water}$$

K_d usually varies greatly because the organic content of is extremely variable also. Nevertheless, adsorption occurs predominantly into the organic matter of the soil, therefore it is more useful to express the distribution coefficient in K_{oc} .

K_{oc} is also known as organic carbon-water partition co-efficient and is described as:

$$K_{oc} = (K_d * 100) / \% \text{ Organic carbon}$$

K_{oc} may be the most important property to determine whether a pesticide is transported as particles or as solutes (Gavrilescu, 2005). The range may not be precise though, in general, pesticides with high K_{oc} values (>100) – the herbicides trifluralin, paraquat and glyphosate – are likely adsorbed onto soil particles and lost via erosion. Such pesticides may accumulate in the soil and degrade over time releasing daughter compounds. While pesticides with intermediate K_{oc} values ($0.1 < K < 100$), which are most herbicides today, are primarily lost with water (Fawcett et al., 1994).

Water solubility may be another important property to determine how easily a pesticide can be transported in water. In general, a pesticide with water solubility of less than 1 ppm is likely to adsorb onto soil particles (Gavrilescu, 2005). If a pesticide is not persistent, because it is transformed into different forms, it will less likely be mobilised either by solutes or particles.

Soil texture, pH and organic contents may also be important environmental factors to determine the degree of adsorption of pesticides (Gavrilescu, 2005; Table 3.3). The soil texture controls the available surface areas where adsorption can occur. Soil pH affects the pesticide solubility and microbial degradation rates; consequently, the adsorption rate will change. In general, in acidic soil, a pesticide is more soluble and microbes degrade the pesticide faster. Organic matter in soil provides binding sites to pesticides and serves as energy source for microbial reactions/degradation.

Table 3.3: Key pesticide and environmental characteristics that control pesticide mobilisation (modified from Gavrilescu, 2005)

| | mobilised as solutes | mobilised as particles |
|--|-----------------------------|-------------------------------|
| Pesticide characteristics | | |
| Organic carbon-water partitioning coefficient (K_{oc}) | low | high |
| water solubility | high | low |
| persistent | high | high |
| Environmental characteristics | | |
| soil texture | low | high |
| soil pH | low | high |
| organic matter contents | low | high |

3.4.3 Pesticide cycle in the agri-hydrogeochemical system

The persistence and mobility of pesticides are mainly determined in the root zone. Below the root zone, pesticides are mainly conservatively transported. Microbes play the dominant role in degrading and transforming pesticides (Fenner et al., 2013; Gavrilescu, 2005). Although some researchers reported that microbial degradation in groundwater is potentially possible (Janniche et al., 2012), due to scarcity of energy source and nutrients, the rates of microbial degradation below the soil layer is generally insignificant compared to that in the soil layer. Therefore, once pesticides leach out of the root zone, they are redistributed without any significant transformation or degradation (Figure 3.5).

After a pesticide is applied in an agricultural field, it can be released back to the air via evaporation and volatilisation. In addition, it can be degraded by light in the shallow soil layer and be emitted to the atmosphere (Figure 3.5). Some fractions of the pesticide may accumulate in crops. Depending

on its property, the pesticide can be adsorbed onto the soil particles (PE_s in Figure 3.5) or dissolved in soil pore water (PE_w ; in Figure 3.5). Soil microbes can degrade the pesticide, producing daughter compounds (PE_D ; Figure 3.5).

3.4.4 Pathways of pesticides in the agri-hydrogeochemical system

A potential pathway of pesticides through the atmosphere is spray drift (Figure 3.5). When a pesticide is applied as spray, it can be drifted directly into the adjacent surface water especially under windy conditions (Carter, 2000).

Surface erosion is a pathway to transport pesticides that are adsorbed onto soil particles (Figure 3.5). The dissolved phase of pesticides and the daughter compounds are transported via water pathways: pesticides are transported vertically via matrix flow or/and preferential flow and laterally via overland flow, interflow, tile-drainage, and groundwater (Figure 3.5).

The application of pesticides for plant protection purposes on agricultural fields is a diffuse source (Carter, 2000). On the contrary, point sources are localised situations such as tank-filling respectively cleaning, farmyard-runoff and spills from agricultural sources, fruit washing facilities or even sewage plants (Carter, 2000). Point sources are mainly due to misuse or inadequate management. Especially after heavy precipitation events, farmyard runoffs together with field runoffs produce contamination peaks and account for most of the contaminant load of small streams. In a catchment area with individual agricultural farms scattered and no other possible contamination source present, farmyard runoff accounted for 89.8 % of pesticide contamination, especially fungicides and insecticides (Neumann et al., 2002).

Pesticides of diffuse pollution will be transported via the pathways mentioned above, depending on their properties and environmental conditions, but pesticide pollution from point sources are mostly directly transported into water (Carter, 2000). For instance, poor management of filling/cleaning facilities may result in discharge of pesticides along the impermeable surface or via pipes (Wenneker et al., 2010), acting like overland flow. Illegal discharge of pesticides will directly flow into stream or groundwater, bypassing all the pathways (Carter, 2000).

Issues following an inappropriate usage of pesticides and alternative entry paths into the environment are addressed in the EU guideline 2009/128/EG. The Member States are obliged to transform the guideline into National Action Plans, to introduce measures to protect aquatic environments (see WP 4) and to organise the education of pesticide applicants in the correct handling, disposal and cleaning of pesticide application devices.

3.4.5 Challenges in pesticide monitoring and regulation

Up to present, the pesticides that are found in the different environmental compartments can only sporadically be related to application data of the pesticides, since a regional differentiated data compilation of application data and a consequential estimation of the pesticide inputs is missing (SRU, 2016).

According to the approval procedure and a proper usage of pesticide products, no pesticide transport to surface or groundwater and no accumulation in soil should take place. However, EU-wide, a number of pesticides are detected in surface- and ground waters, the most abundant are listed in Table 3.4.

Pesticide contamination in surface waters being reported by EAA (WISE-databank, reports by Member States) are in their large majority due to substances, which are withdrawn from the market some time ago. In most sites, this is due to occasionally high quantities of pesticides contained in the water table that feeds surface water. In some sectors, also fraudulent use of pesticides had been proven (Laurent, 2015).

Table 3.4: Most abundant pesticides being detected in surface- and ground waters: number of waterbodies not achieving a good chemical status due to pesticides and number of Member States affected (EEA, 2018a; University of Heartfordshire, 2017)

| Substance | CAS- or EEA-No. | Chemical group | Type | Examples for product with AS | Introduced to the market | Current market situation | No. of WB not achieving good chemical status | No. of MS with WB not achieving good chemical states for the listed substance |
|-----------------------|-----------------|--|--|--|--------------------------|--|--|---|
| Surface waters | | | | | | | | |
| Isoproturon | 34123-59-6 | Urea derivative | Herbicide | Arelon, Azur, Alpha IPU, Alpha Isoproturon, Koala, Trump, Javelin, Javelin Gold, Protugan, Tolugan Extra | 1971 | approved EU-wide since 2003, with expection of CY, DK, EL, FI, MT; withdrawn in 2016 | 199 | 8 |
| Hexachlorhexane | 608-73-1 | Halogenated hydrocarbon, organochlorine | Insecticide, acaricide | Lindan | 1945 | on the market since 1945; according to EC 1107/2009 not approved | 120 | 11 |
| Trifluralin | 1582-09-8 | Dinitroanaline | Herbicide | Alpha Trifluralin 48EC, Ardent, Fargo Axit, Treflan, Uranus, Elancolan | 1961 | approval withdrawn in 2007 according to EC 1107/2009 | 12 | 6 |
| Chlorfenvinphos | 470-90-6 | Organophosphate | Insecticide, acaricide, veterinary substance | Vinylphate, Birlane, Steladone, Supona, Apachlor, Haptarax | 1962 | not approved | 10 | 4 |
| Atrazine | 1912-24-9 | Triazine | Herbicide | Gesapri, Fenamin, Atrazinax, Weedex, Primaze, Atratol, Radazine | 1957 | not approved | 9 | 4 |
| Simazine | 122-34-9 | Triazine | Herbicide | Sanazine, Simanex, Amizina, Eagrow, Derby | 1960 | not approved | 5 | 2 |
| Alachlor | 15972-60-8 | Chloroacetamide | Herbicide | Lasso, Alanex, Pillarzo | 1936 | not approved | 5 | 3 |
| Pentachlorphenol | 87-86-5 | Organochlorine | Insecticide, Herbicide, fungicide, molluscicide, plant growth regulator, wood preservative | | 1936 | not approved | 3 | 3 |
| Ground waters | | | | | | | | |
| Pesticides | EEA_34-01-5 | Active substances in pesticides, including their | | | | | 345 | 11 |

| Substance | CAS- or EEA-No. | Chemical group | Type | Examples for product with AS | Introduced to the market | Current market situation | No. of WB not achieving good chemical status | No. of MS with WB not achieving good chemical states for the listed substance |
|------------------------|-----------------|---|-----------------------------------|--|--------------------------|---|--|---|
| | | relevant metabolites, degradation and reaction products | | | | | | |
| Bentazone | 25057-89-0 | Benzothiazinone | Herbicide | Basagran, Zone 48, Troy 480, Herbattox, Leader, Laddox | 1972 | approved in all EU-countries | 31 | 5 |
| Atrazine | 1912-24-9 | triazine | Herbicide | Gesaprim, Fenamin, Atrazinax, Weedex, Primaze, Atratul, Radazine | 1957 | approval expired | 60 | 8 |
| Desethylatrazine | 6190-65-4 | Dealkylated atrazine metabolite | Plant growth inhibitor | | | | 69 | 5 |
| Desethylterbuthylazine | 30125-63-4 | | metabolite | | | | 34 | 4 |
| Terbuthylatrazine | 5915-41-3 | triazine | Herbicide, microbiocide, algicide | Calaris, Skirmish, Gardo Gold | 1967 | expired in DK, EE, FI, FR, LT, LV, MT, SE | 25 | 4 |
| Desisopropylatrazine | 1007-28-9 | | metabolite | | | | 16 | 4 |
| Bromacil | | Uracil | Herbicide | Hyvar X bromoacil, Borocil 1V, Cynogan, Borea, Krovar II, Urgan | 1961 | expired | 13 | 5 |
| Simazine | 122-34-9 | Triazine | Herbicide | Sanazine, Simanex, Amizina, Eagrow, Derby | ca. 1960 | expired, except for ES | 17 | 5 |
| Metholachlor | 51218-45-2 | Chloracetamide | Herbicide | Dual, Bicep, Pennant, Pimagram | 1976 | expired | 58 | 3 |
| Alachlor | 15972-60-8 | Chloracetamide | Herbicide | Lasso, Alanex, Pillarzo | 1969 | expired | 63 | 1 |
| Acetochlor | 34256-82-1 | Chloracetamide | Herbicide | Harness, Trophy, Trophee, Acentit, Guardian, Sacemid, Surpass | 1985 | expired | 32 | 1 |
| Dicamba | 24-00-9 | Benzoic acid | Herbicide | Di-Farmon R, Foundation, Prompt, Relay P, Banval | ca. 1963 | expired in MT and SE | 22 | 2 |

Using the WISE-databank, the causes of pesticide contamination of ground waters cannot be identified precisely, because obviously some of the Member States reported under a collective term, other reported the analyses of certain active substances. Most of the pesticides being reported contaminating groundwater are not any more approved by EFSA-authorities (Table 3.4).

Tauchnitz et al. (2017) investigated in the German Harz foreland pesticide concentration in soils and surface waters. In surface waters, Glyphosate, Bentazone, AMPA, Diflufenican, Tebuconazol and Terbutylazin were detected. There was no correlation between agricultural application and detection of pesticides, possibly due to pesticide use/leaching from residential areas. Agricultural activities were clearly the reason for accumulation of pesticides in soils underneath agricultural activities. Especially Glyphosate and MCPA were found in depths of nearly five meters, S-Metolachlor and Pendimethalin in around one meter depth.

Ulrich et al. (2018) report the accumulation of herbicides and their transformation products in small water bodies or catchment areas. The autumn sampling focused on the herbicides Metazachlor, Flufenacet and their transformation products – Oxalic acid and – Sulfonic acid as representatives for common pesticides in the study region.

3.5 NITRATE AND PESTICIDES IN THE WATERWORKS SYSTEM

Agriculture has a direct influence on the concentrations of nitrates and pesticides in the raw water used for drinking water production. However, the raw water, coming from either groundwater or/and surface water, might be treated at the waterworks before delivered as drinking water to the consumers. Therefore, important for the final concentration of nitrates and pesticides in drinking water is the specific water treatment procedure at the waterworks.

In Europe, drinking water is produced with different degree of treatment (Van Der Hoek et al., 2014; amended, Table 3.5):

- 1) Without treatment
- 2) With conventional treatments such as aeration and sand filtration;
- 3) With advanced treatments such as active carbon filtration, advanced oxidation process (e.g., UV/H₂O₂, ozonation), desalination; and
- 4) With combination of conventional and advanced treatments
- 5) Mixing/dilution
- 6) Excluding of polluted wells

Because nitrate is highly soluble and pesticides are persistent, the conventional treatments cannot remove them. Nitrate in water is removed via ion exchange, reverse osmosis, electrodialysis, biological/chemical/catalytic denitrification and combination among them (Kapoor et al., 1997).

The ion exchange process is running NO₃-containing raw water through exchange resins, which contain strong base anions such as Cl⁻ and HNO₃⁻; therefore, nitrate is replaced with these anions. The reverse osmosis process is filtering out ions by pushing water through a semipermeable membrane. The electrodialysis process is transferring ions in a diluted solution to a concentrated one through a membrane with a direct electric current. The biological, chemical, and catalytical denitrification processes are denitrifying nitrate by biological (e.g. microbes), chemical (e.g. Fe (II)), and catalytical (e.g. palladium-alumina; Pd-Al₂O₃) agents, respectively.

To remove pesticides in water, advanced oxidation processes, coagulation-flocculation-sedimentation, nanofiltration, and active carbon adsorption are used (Ormad et al., 2008). The advanced oxidation process is to break down pesticides into biodegradable compounds using strong oxidants such as chlorine or ozone. This process is often combined with biological treatments;

therefore, it is also called as a 'preoxidation process'. The coagulation-flocculation-sedimentation is a physical and chemical process to remove pesticides by forming larger particles so that they can easily be separated out. The nanofiltration is filtering out pesticides using a filter membrane that has extremely small pore sizes. Pesticides can be removed by adsorption on the active carbon. These techniques are often used in combination.

Table 3.5: Summary of drinking water treatment methods in Europe (modification of Table 1 in Van Der Hoek et al. 2014)

| Water process method | Groundwater | Surface |
|-----------------------------------|---|---|
| No treatment | - | - |
| Conventional treatment | Aeration and/or Rapid Sand Filtration (RSF) | Coagulation, sedimentation, and filtration (CSF) |
| Advanced treatment | Carbon filtration, advanced oxidation process, membrane desalination, ion exchange, reverse osmosis, electrodialysis, nitrification, coagulation-flocculation-sedimentation, nanofiltration | Carbon filtration, advanced oxidation process, membrane desalination, ion exchange, reverse osmosis, electrodialysis, nitrification, coagulation-flocculation-sedimentation, nanofiltration |
| Conventional + advanced treatment | Aeration and/or RSF + advanced treatment | CSF + advanced treatment |

Table 3.6: Cost of water treatments in France (Juery, 2012)

| | Treatment | Cost (€/m ³) |
|--------------|--|--------------------------|
| code1 | Water intake + disinfection | 0.05 |
| code2 | Pretreatment + coagulation/flocculation + sedimentation + sand filtration + disinfection | 0.13 |
| code3 | Pretreatment + coagulation/flocculation + sedimentation + preoxidation + sand filtration + O ₃ /activated carbon filters treatment + disinfection | 0.20 |
| code4 | Code 3 without preoxidation + biological denitrification | 0.38 |
| code5 | Pretreatment + coagulation/flocculation + sedimentation + sand filtration + disinfection+microfiltration+nanofiltration | 0.43 |
| code6 | Ultrafiltration + disinfection | 0.50 |

The level and type of water treatment of each country may depend on the quality of raw water, its financial circumstances, and strategic political decisions (WHO Regional Office for Europe, 2002). In general, advanced treatments (e. g. nanofiltration, advance oxidation process) are more expensive than the conventional treatment techniques. An example of treatment cost is shown for France in Table 3.6 (Juery, 2012). Disinfection alone costs in average 0.05 (€/m³) whereas ultrafiltration + disinfection cost in average 0.50 (€/m³) (Table 3.6). The costs of water treatment in other countries will differ from those in France (Table 3.6), because of differences in local conditons. Table 3.7 shows main types of drinking water treatments used in some countries (not specific to the case study sites) that are part of FAIRWAY (WHO Regional Office for Europe, 2002).

Table 3.7: Main types of water treatment methods for drinking water production (modification of Table 4.5 in WHO Regional Office for Europe, 2002)

| Country | Groundwater/spring water | Surface water |
|---------------------------------|--|--|
| Denmark | <ul style="list-style-type: none"> · Aeration and sand filtration | <ul style="list-style-type: none"> · Not used for drinking water supply |
| France | <ul style="list-style-type: none"> · Disinfection only · Some nitrate removal (ion exchange and biological denitrification) | <ul style="list-style-type: none"> · Chemical coagulation, advanced oxidation process, disinfection · Few waterworks with membrane technology · Some nitrate removal (ion exchange) |
| Greece | <ul style="list-style-type: none"> · Disinfection only, using chlorine · Aeration and sand filtration · Iron and manganese removal for some source · Some nitrate removal (ion exchange and biological denitrification) | <ul style="list-style-type: none"> · GAC and PAC use · Mostly chemical coagulation and disinfection · Some slow sand filtration · Removal of pesticides by granulated active carbon or O₃ with granulated active carbon |
| Germany (UBA 2016, 2018) | <ul style="list-style-type: none"> · 70 % of drinking water derives from groundwater, another 7 % is artificially enriched groundwater (Aeration), flocculation and sand filtration · In addition membrane processes and occasionally oxidation, ion exchange or activated carbon filtration · Occasionally nitrate removal by ion exchange, reverse osmosis, nanofiltration, biologic treatment or electrofiltration | <ul style="list-style-type: none"> · 16 % of drinking water is surface water, further 8 % is water treated by bank filtration · In addition flocculation, filtration, O₃ with granulated active carbon or disinfection |
| Netherlands | <ul style="list-style-type: none"> · Aeration and multistage sand filtration | <ul style="list-style-type: none"> · Extensive use of multistage treatment, including dune infiltration, coagulation, activated carbon, and disinfection with chlorine or O₃ |
| United Kingdom | <ul style="list-style-type: none"> · Disinfection only, using chlorine · Iron and manganese removal for some source · Approximately 20 waterworks with nitrate removal (ion exchange) · Removal of organics (e.g., pesticides, solvents) by O₃ and granulated active carbon | <ul style="list-style-type: none"> · Mostly chemical coagulation and disinfection · Some slow sand filtration · Removal of pesticides by granulated active carbon or O₃ with granulated active carbon |

One of the challenges of drinking water production is disinfectant by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs; e.g. Van Der Hoek et al., 2014; WHO Regional Office for Europe, 2002). Disinfection processes are intended to eliminate pathogens in drinking water (Safe Drinking Water Committee, 1980) and it is particularly important for surface water. Van Der Hoek et al. (2014) reported that nearly 88 % of drinking water production – nearly 99.99 % from surface water and more than 70 % from groundwater – in Europe employs a disinfection process. Raw water is disinfected primarily via oxidation reactions using strong oxidants

such as chlorine compounds (e. g. chlorine, hypochlorite, chlorine dioxide), ozone (O₃), UV/H₂O₂ (World Health Organisation, 2000). Although it may be a minor risk in comparison to preventing waterborn diseases (WHO Regional Office for Europe, 2002), oxidation of some pesticides during the oxidation process can produce DBPs (e. g. Adams and Randtke, 1992; Chiron et al., 2000; Huang et al., 2009; Li et al., 2016). Nitrate may indirectly play a role in producing DBPs: excessive nitrate, along with phosphorus, in raw water (i. e. surface water) can trigger algae blooms. Then, while the algae cells are destroyed at the disinfection process, DBPs can be produced as well (e. g. Huang et al., 2009; Plummer and Edzwald, 2001).

In Denmark, groundwater protection has a high priority in order to secure clean drinking water for the population provided directly from the taps in the houses. Accordingly, the Danish groundwater protection policy is based on prevention rather than treatment at the waterworks.

Water works in Germany, according to a recently conducted nationwide survey, tend to avoid the implementation of expensive treatment measures in order to reduce high nitrate concentration in drinking water (Oelmann et al., 2017). Figure 3.7 shows clearly, that the so called “Preventive measures” (consulting farmers, cooperation between farmers and water works, including – financial – support, purchase or lease of land) are far more common than the so called “Reactive measures” (mixing, avoiding, E. g. excluding the polluted well, advanced treatment).

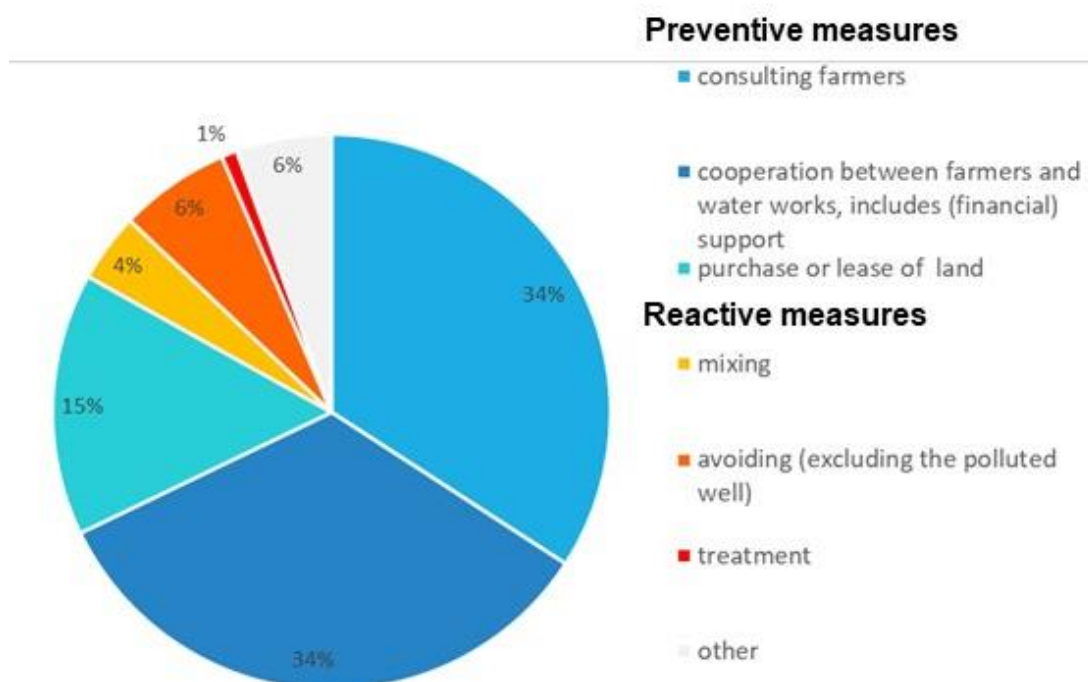


Figure 3.7: Survey among 188 German water works concerning the measures conducted in order to prevent or to treat nitrate contamination in raw water; multiple answers possible (Oelmann et al., 2017)

4. DEVELOPMENT OF FAIRWAY AGRI-DRINKING WATER QUALITY INDICATORS (ADWIs)

4.1 DEFINITION OF ADWIs

Main task of WP 3 in FAIRWAY is to develop, i. e. to prioritise and evaluate data-driven indicators which can be applied to detect, monitor or even predict the pollution of ground- and surface water by nitrates and pesticides.

Agri-environmental indicators (AEIs), as developed by OECD and Eurostat, are implemented and further developed for the monitoring and evaluation of the impacts of agricultural activities on the environment. These impacts may be negative and positive, on and off the farm. Negative impacts include pollution and degradation of soil, water and air, while positive effects include ecosystem services, such as mitigation of flood risks through the adoption of certain farming practices (OECD, 2018).

Consequently, Agri-drinking water indicators (ADWIs) to be developed in FAIRWAY may be defined as indicators for the quality of drinking water. As drinking water may be produced from ground- or surface water, ADWIs aim at the quality of both. ADWIs may be identical to AEIs, or they may be different.

4.2 DPS(L)IR FRAMEWORK

According to the FAIRWAY proposal for WP 3, ADWI shall be defined within the DPSIR-framework. Having in mind, that ADWIs may be construed as a share of AEIs, there is not much difference between the AEIs interpretation within the DPSIR-framework and the interpretation of ADWI within the DPSIR-framework. The adjusted DPSIR-framework contains a new element, the Link indicators, which will be further explained in Chapter 7 (Table 4.1).

Table 4.1: Interpretations of the DPS(L)IR framework for AEI and ADWI

| Domain | Description*) | AEI interpretation**) | ADWI interpretation |
|---------------|--|---|--|
| Driving force | "Social, demographic, and economic developments in societies and the corresponding changes in the lifestyle and overall levels of consumption and production patterns" * | "the state and evolution of regional farming system in relation to input use, land use, and management practices" | Social, demographic, and economic demands for clean drinking water and the corresponding changes of the agricultural system in relation to input use, land use, and management practices |
| Pressure | "Developments in release of substances (emissions), physical and biological agents, the use of resources and land" | "harmful and beneficial processes attribute to agriculture" | Inputs of nitrate and pesticides from the agricultural system to the hydrogeological system |
| State | "Quantity and quality of physical phenomena, biological phenomena, and chemical phenomena" | "the state of different natural and semi-natural resources in rural area" | Quality of drinking water resources |
| Link | Natural and anthropogenic processes of transport and evolution of nitrate and pesticides in natural systems (from farm fields to water abstraction points) | - | Natural and anthropogenic processes of transport and evolution of nitrate and pesticides in the hydrogeochemical system |

| | | | |
|----------|--|---|---|
| Impact | "Relevance of changes in the state of environment" | "the share of agriculture, as a sector, to undesirable changes in the state of the environment resources and its effective contribution to the preservation/enhancement of other environmental resources" | Public health concerns and regulatory compliances |
| Response | "Groups and individuals in society and government attempt to prevent, compensate, ameliorate, or adapt to changes in the state of environment" | "Societal, market, and policy responses that influence production systems and agriculture practices" | Implementation of mitigation measures |

*(Stanners et al., 2007); **(EEA, 2005)

In Table 1 in the Annex, all 28 AEI according to COM final 0508/2006 and applied on EU-level are listed (COM 2006, eurostat 2018). The AEI are allocated to domains and subdomains of the DPSIR framework. With Table 4.2, we grouped all ADWIs, which were reported to us during a survey among the in the FAIRWAY case studies and we supplemented the table with indicators according to a literature review. We finally added a further type of indicator, the Link indicator.

Table 4.2 also quotes the chapter, in which the the indicators are further discussed: ADWIs which function as Driving forces and those which indicate Pressure are further discussed in Chapter 5. State/impact indicators in Chapter 6 and the newly introduced Link indicators in Chapter 7.

Table 4.2: ADWIs in the DPSLIR framework

| Domain | Subdomain | Chapter | Indicators category |
|----------------|----------------------------------|---------|--|
| Impact | Societal and economic demands | | Demands for clean drinking water*) |
| | | | Population density*) |
| | | | Cost for drinking water production*) |
| Driving forces | Resource management and planning | 5.1.1 | Land use (planning) <ul style="list-style-type: none"> - Land use/land cover (i.e. winter wheat surface evolution) - Land use change (grassland->arable land) |
| | | 5.1.2 | (Water protection planning) |
| | | 5.1.3 | Agricultural preconditions <ul style="list-style-type: none"> • Climatic conditions <ul style="list-style-type: none"> - precipitation - temperature - wind |
| | | | <ul style="list-style-type: none"> • Soil properities <ul style="list-style-type: none"> - soil type - organic carbon - clay content - top soil bulk density - field capacity • Topography <ul style="list-style-type: none"> - susceptibility to erosion and compaction |
| | Farm management | 5.2.1 | Farming standards <ul style="list-style-type: none"> - organic/conventional |
| | | 5.2.2 | Farming Intensity <ul style="list-style-type: none"> - crop yield |
| | | 5.2.3 | Farm management <ul style="list-style-type: none"> - cropping patterns - catch crop use - method of soil cultivation/tillage practice - soil cover - cropping systems |
| | | 5.2.4 | N-fertilisation <ul style="list-style-type: none"> - Livestock density |
| | | | |

| Domain | Subdomain | Chapter | Indicators category |
|------------------|-------------------------|---------|--|
| | | | <ul style="list-style-type: none"> - Livestock excretion - Types of organic fertilisers - plant availability of organic bound N - Manure applied in autumn - Animals out of pasture - Organic fertilisation/ha; organic fertilisation/crop*ha - Mineral fertilisation/ha; mineral fertilisation/crop*ha - Total fertilisation/ha; total fertilisation/crop*ha - Timing of fertiliser application - Splitting/frequency of fertiliser application - Application techniques for fertilisers |
| | | 5.2.5 | Pesticide application <ul style="list-style-type: none"> - Type of Pesticides - Chemical properties - Consumption of pesticides - Application of pesticides/ha (active substances; most frequently used pesticides; most persistent or most toxic pesticides) - Application of pesticides/ha*crop (active substances; most frequently used pesticides; most persistent or most toxic pesticides) - Timing of pesticide application - Splitting/frequency - Application techniques for pesticides |
| | Trends | 5.3.1 | Intensification/Extensification |
| | | 5.3.2 | Specialisation |
| | | | |
| Pressure | Leaching | 5.4.1 | Leaching quantity <ul style="list-style-type: none"> - Depth of water table - Drainage index (DI) - Exchange frequency (EF) |
| | | 5.4.2 | Nitrogen in soil water <ul style="list-style-type: none"> - After harvest soil nitrate - Autumn soil nitrate - Spring soil nitrate - Soil water potential and nitrate content in soil solution |
| | | 5.4.3 | Pesticides in soil water |
| | Surface water pollution | 5.5.1 | Indicators for nitrogen and pesticides in surface water |
| | Point sources | 5.7.1 | Point source of nitrates and pesticides |
| | Aerial immission | 5.7.1 | Pesticide drift |
| | | 5.7.2 | Deposition of nitrogen |
| | N-Efficiency | 5.8 | Nitrogen budgets |
| State/ Impact | Water quality | 6.1 | Concentrations in water |
| | | 6.2 | Concentration trends |
| | Regulatory compliances | 6.3 | Frequency of exceedance of water quality standards |
| Link | Catchment typology | 7.1 | Catchment typology |
| | Lag time | 7.2.1 | Recharging rate |
| | | 7.2.2 | Water age |
| | Source tracer | 7.3.1 | Nitrate Isotope indicators |
| | | 7.3.2 | Point source of pesticide |
| | Vulnerability | 7.4.1 | Nitrate vulnerability |
| | | 7.4.2 | Pesticide vulnerability |
| | Leaching risk | 7.5.1 | Nitrogen loss indicators |
| | | 7.5.2 | Pesticide leaching risk indicators |

*) Indicator not discussed in this report

5. AGRI-DRINKING WATER QUALITY INDICATORS ON FARM LEVEL (=DRIVING FORCE AND PRESSURE INDICATORS)

ADWIs which belong to the domains **Driving forces** and **Pressure** are listed in this chapter, following the order of Table 4.2.

5.1 RESOURCE MANAGEMENT AND PLANNING

5.1.1 Land use (planning)

5.1.1.1 Land use/land cover

Land use refers to the socio economic use that is made of land, land cover to the bio-physical coverage of land (Eurostat, 2018d).

The way agricultural land is covered gives information on possible sources of water pollution: on grassland, there is – except herbicide application in connection with grassland renewal – no intensive pesticide use (DAFM, 2013); on grassland due to intensive fertilisation, nitrate leaching may occur, too (Eriksen et al., 2015; Pervanchon et al., 2005). Conventional fruit- and vegetable growing is usually connected with a high fertilising level and repetitive pesticide use.

EU-wide, the Land Use/Cover Area frame Survey (LUCAS) provides, on the basis of a 2x2 km² grid, harmonised and comparable statistics on land use and land cover. The grid includes 1,090,863 geo-referenced points stratified according to land cover classes (artificial land, cropland, woodland, shrubland, grassland, bare land, water areas, wetlands) and 76 subclasses. From selected sampling points, 270,000 soil samples from the top soil level were drawn and analysed on basic parameters (macro nutrients and soil carbon, pH-level and categorised according to soil type, susceptibility to erosion and compaction). Elementary data linked to the grid points are available as well as aggregated data on NUTS 2 level within the EU-27. LUCAS data are used by DG AGRI as elements of AEI for the evaluation of agricultural impact (Eurostat 2018d). A land cover classification system (LUCAS SU LC) was published in 2015. This system includes the large majority of arable crops and of grassland (Eurostat, 2015).

On the national, regional or local scale, there may even be data-bases available that provide more detailed information. For the assessment of drinking water quality on a smaller scale, these data-bases probably provide a better quality.

A simple indicator connected to land cover is the **percentage of a particular land use**, e. g. “% arable land”, “% grassland” or “% vegetable growing area”.

In case a particular fertilisation practice or pesticide use for a particular crop is in the focus, the indication of land use may refer to a particular crop (-> see 5.2.3.1, cropping patterns).

5.1.1.2 Land use change

An important factor that can influence contamination of water with nitrate or phytosanitary products is primarily land-use change including the shift in land use from grassland to arable crop use. This shift is important, because, when a grassland is tilled, due to the mineralisation of organic matter from aboveground and underground parts of the grassland, it transfers a significant amount of nitrate to the environment.

In areas where arable crops dominate, soils often contain more readily plant available nitrogen (N_{\min}), especially after harvest and when soils are left bare. Conversely, when a crop plot is converted to a grassland plot, a decrease in soil nitrate levels is usually measured.

Indicators for **land use change** can be derived from land use indicators by the introduction of a time sequence.

5.1.2 Water protection planning

Water protection planning refers to all measures which serve to the implications of the Water Framework Directive, the Nitrates Directive and the The Framework Directive on the Sustainable Use of Pesticides. These legal obligations have to be transferred into national or even local level and serve as guidelines for the Water protection planning. Indicators on water protection planning could refer to certain measures, which are part of national legislation, e. g. width of buffer strips, duration of restricted periods for fertilisation, range of active substances admitted or maximum surplus of nitrogen budget (see WP 4 and 6 of FAIRWAY).

5.1.3 Agricultural preconditions

5.1.3.1 Climatic conditions

Climatic conditions form the basic frame for plant growth. Several climatic indicator are commonly used as elements in combined indicators: **precipitation** and **evapotranspiration** are main influencing factors of leaching, runoff and erosion. Data on **temperature (minimum, maximum or average)** are genearily use to estimate pesticide volatilisation and degradation. Data on **wind speed and direction** can be used to estimate pesticide drift and erosion.

Simulation tools therefore take into account climate data, such as monthly avarage temperature and monthly precipitation sums, which can be obtaines from the 'WorldClim' database (<http://www.worldclim.org>) (Hijmans et al., 2005).

5.1.3.2 Soil properties (e. g. soil type, organic carbon concentration)

Soil properties influence water pollution in different ways. The tendency for leaching of nitrates is higher in sandy soils than in heavy soils with a high clay content. Leaching of pesticides due to preferential flow or co-transport of colloidal matter is particularly high in clay-rich soils and in general related to soil properties such as soil structure, organic matter content, clay content, iron oxides, as well as soil hydrological processes and management (e. g. time of application) (Estévez et al., 2008).

With increasing concentration of organic matter in soil and the tendency towards mineralisation, the amount of nitrates being susceptible to leaching increases. On the other side, organic matter can serve as energy source for denitrification and thus, under certain circumstances, can decrease nitrate leaching, e. g. in grasslands and peat soils.

In case local information on soil properties with a high resolution are not accessible or suitable, official databases may be used to asses soil properties. Combining the LUCAS topsoil database with land surface parameters from the NASA-Shuttle Radar Topography Mission (SRTM) and data from CORINE land cover 2000, Ballabio et al. (2015) produced maps on European scale for topsoil clay, silt, sand and coarse fragments content, bulk density and derived from that USDA textural classes and available water capacity at a 500 m grid cell resolution.

The **soil type** may be used as an indicator to estimate nitrogen leaching (most severe in sandy soils) and pesticide leaching (most severe in clay-rich soils due to preferential flow).

For most nonionic compounds, adsorption is correlated with soil organic matter (Bailey, et al., 1970, Wauchope, et al., 2002). **Soil organic carbon** may be used as indicator for pesticide leaching. A

specific parameter is calculated for each pesticide (the K_{oc} , see Chapter 5.1.2.5) which can be derived by the organic carbon content of a soil to estimate the sorption. Besides the concentration of soil organic matter, sorption of pesticides in the soil is determined by its clay content (Schierholz et al., 2000).

Stassemeyer et al. (2017) used data from the European Soil Database (ESDB): dominant slope class, organic carbon concentration in top soil layer (0-30 cm), dominant texture class in top and sub soil, parent material, depth of gley horizon, presence, target and type of water management system (Panagos et al., 2012b). The soil organic carbon concentration in the top 1 m was estimated according to an average ratio as described in Kruijne et al. (2011). Topsoil bulk density and field capacity were derived from Ballabio et al. (2016). The K-factor of the modified universal soil loss equation (MUSCLE) was obtained from Panagos et al. (2012a).

5.1.3.3 Susceptibility to erosion and compaction

Soil erosion may play an important role in particular N and P surface transport to surface waters. Soil erosion can also constitute a major pathway for surface transport of pesticides via soil colloids, especially in subtropical and tropical countries with high intensity precipitation events. It is usually not part of indicators in Europe, where mostly only drift or runoff are considered as pesticide discharge pathways (Holmes, 2014). In a long term soil erosion experiment in Austria, the soil type as well as the cropping system influenced the amount of surface runoff, including pesticide losses, from fields cultivated with maize and winter wheat significantly. While in silty loam textured soils mulch till and no-till led to 14-56 % less surface runoff compared to conventional tilled soils, on fields with loamy soil the low till methods led to an 12-20 % increased surface runoff. This was explained by an increased soil compaction due to the omitted ploughing, leading to a decreased water infiltration into the soil (Klik and Strohmeier, 2011). Also, Vogel et al. (2016) report a 90-100 % reduction of soil erosion due to no till farming and conservation tillage compared to conventional tillage, while other measurements such as buffer strips or permanent grassed waterways had minor effects in reducing surface runoff, especially following severe precipitation events. Open questions remain regarding the influence of no-till systems on preferential flow paths.

However, in a study by Ulrich et al. (2018) in ten small water bodies, it was noted that site characteristics such as soil type, humic content and slope did not explain the differences in accumulation of two herbicides and their transformation products in the water bodies. Rather, the precipitation after pesticide application, interaction with the shallow groundwater or subsurface transport of the products were responsible for higher pesticide transport into the ponds.

Based on their runoff potential, soils are classified by the United States Natural Resources Conservation Service (NRCS) into four hydrological soil groups A to D. Hydrologic soil groups were derived from the texture classes in top and sub soil (Panagos et al, 2012b) and the depth of the gley horizon (Stolbevoy et al., 2007).

For the program SYNOPS-WEB, Stassemeyer et al. (2017) used exposure models for drift, runoff and erosion based on spatially explicit data sets as European Soil Database, temperature and precipitation data (Hijmans et al., 2005) and crop growth scenarios FOCUS (2000).

5.2 FARM MANAGEMENT

5.2.1 Farming type

5.2.1.1 *Organic/conventional*

Pesticide use in organic agriculture is much smaller than in conventional farming. Annex II of Regulation 889/2008 (European Commission, 2008) lists these biopesticides. Most of them are used as insecticides and fungicides, all derive from natural sources and include naturally occurring chemicals, pheromones, bacteria, fungi and insect predators. University of Hertfordshire (2016) points out that these substances may cause environmental risks, too: the BioPesticide DataBase (BPDB) is a comprehensive relational database of data relating to pesticides derived from natural substances.

However, Pelosi et al. (2013) compared field data from conventional versus organic cropping systems with regards to pesticide pressure on three different species of earthworm populations living on the soil surface layer. All fields were plowed conventionally, were cultivated with the same crop (winter wheat) at the sampling times and received either mineral or organic fertilisation. The authors detected decreasing earthworm densities with increasing (conventional) pesticide applications according to the Treatment Frequency Index (TFI), with insecticides having the most negative impact on earthworm populations, followed by herbicides and fungicides.

Lysimeter trials in Hesse and Saxony between 1996 and 2011 revealed that organic farming may bear a risk of nitrogen leaching due to generally intensive legumous nitrogen fixation and organic fertiliser-use as well as plant residues on the field. However, under the premisis of a groundwater-preserving cultivation, the potential for nitrate leaching in organic farming is approximately 10 kg N/ha lower than in conventional farming (40 %). This is due to lower autumn N_{min} -values, to a wider crop rotation and a larger proportion of grassland in organic versus conventional farms (Fink et al., 2013 and 2014). A study in Paris basin indicated, that the amount of excess nitrogen potentially leaching ranges from 14 to 50 kg N/ha below organic farming plots and from 32 to 77 kg N/ha below conventional farming plots (Benoit et al., 2013).

National, regional and local data bases may serve as source of information on the degree of distribution of organic farming. For the reference year 2013, number and size of farms fully converted and under conversion to organic farming are listed by the Eurostat database [ef_lus_main]. **Land in organic farming** can be used as an indicator for the pressure of pesticides and nitrates.

5.2.2 Farming intensity

5.2.2.1 *(Average) crop yield*

Using nitrogen fertilisation as indicator for nitrate contamination seems to be one of the most appropriate solutions for determining risk of nitrate leaching. Anyhow, individual farm data on mineral/organic fertiliser use often are not available (i. e. in the Netherlands and in Germany), and even sales of mineral fertilisers are only registered on the national level in some Member States. Consequently, in quite a few cases, data on nitrogen fertilisation are not accessible, at least not for the time span needed to study a certain groundwater contamination. E. g. in France, very few data are available in databases before 1990.

On the assumption of high nitrogen efficiency (Klages et al., 2018), (average) crop yield may be used instead of data on nitrogen fertilisation. High fertilising efficiency can be found in arable, intensively managed cropping systems. .

There are, however, a range of factors, which may lead to a reduced efficiency of the applied nitrogen (Klages et al. (2018):

- the effect of climate change, with little precipitation in the summer months, which might reduce the transformation of late mineral nitrogen application into yield and especially for wheat into raw protein of the grains,
- a high regional density of animal breeding farms; these farms on one side need to utilise the produced manure as compound fertiliser, on the other side, plant availability of the enclosed nitrogen is not as exact predictable as for mineral N-fertilisers,
- uncertainties on how to account for mineralisation of organic substance in soil biomass, e. g.. after intensive manure application, catch crop cultivation or cultivation of nitrogen-fixing plants,
- the tendency of some farmers to overestimate their predicted harvest and in consequence to overfertilise.

The average crop yield therefore could be an acceptable indicator only for specific farming system. Average crop yields can be obtained on national level from the European statistical database (Eurostat, 2018e).

5.2.3 Farm management

5.2.3.1 Cropping patterns

Most studies show that simplified rotation systems tend to lead to an increase in the use of pesticides and therefore to an increase in the transfer of pesticides to the environment.

For instance, Andert et al. (2016) analysed whether diverse cropping sequences and ploughing would reduce herbicide and fungicide use in arable farming on 60 farms in four regions of Northern Germany using a 2005-2014 dataset. They classified different three-year crop sequences based on literature and expert knowledge into five different categories of crop health riskiness (very high to very low). The highest risk was associated with a high proportion of winter cereals in a crop sequence, increasing the risk for take-all (*Gaeumannomyces graminis var. tritici*), leaf spots (wheat after wheat), stem base and leaf diseases (barley after barley).

Simplified cropping patterns that are susceptible to risks by pests and diseases dominate almost 50 % of the current arable land use in Northern Germany (Steinmann and Dobers, 2013) and in the Paris basin, where wheat can be cultivated three time in five years (Agreste, 2010). Most diversified cropping patterns depend less on herbicide and fungicide use and on ploughing, showing a lower number of treatments. Weeds and diseases were effectively managed with diversified crop sequences even under no-ploughing tillage systems. Simplified rotations were characterized by high pesticide application, especially in non-ploughed cropping systems.

Various mechanisms as reason for low pest densities have been explored in mixed vegetation in comparison to monoculture, such as altered plant odor due to physiological changes in the plant (Finch and Collier, 2000), and alterations of herbivore insect reproduction cycles.

Cropping patterns are reported from the Member States to Eurostat (Eurostat 2018).

National data, maps and statistics (i. e. Thünen Atlas "Landwirtschaftliche Nutzung") on crop cultivation areas, linked to data on pesticide sales and usage in different crops according to Statistics regulation (EC) No 1185/2009 (i. e. Rosberg, 2016) could built the basis for calculations of regional pesticide application. These data should be available in all Member States.

Data on crop cultivation areas could also be linked to fertiliser need of crops (and possibly further data on soil properties and organic fertiliser supply) to verify if there is a link between plant need, N-application and water pollution with nitrates.

Therefore, the **(local) cropping pattern** would be an indicator suitable to combine with other data. As a simplified approach, the percentage of intensively cultivated crops could serve as indicator, e. g. **% winter wheat** in Northern Europe and the **% maize** in Southern France and Northern Italy (see also Chapter 5.1.1).

5.2.3.2 Catch crop use

Catch crops are grown in the period between two main crops, especially in the winter season. The aim of their cultivation is to retain nutrients, especially nitrates, in the root zone, to prevent the nitrates from leaching and so to conserve them for the following crop. It is therefore important to evaluate the amount of nitrogen incorporated into the biomass of the catch crop, its release to the soil during mineralisation and to reduce the applied nitrogen fertiliser for the subsequent crop accordingly (Beisecker et al., 2015, Tendler and Beisecker, 2015).

In France (Brittany), a wheat-(catch crop)-corn and a wheat-corn rotation were compared tested on experimental plots. During several years, nitrogen losses through leaching were measured in autumn/winter by means of porous cups. The losses in the plots with catch crops (7 kg N ha/yr) were ten times less than in the plots without catch crops (85 kg N ha/yr) (Besnard and Kerveillant, 2006). Other studies have shown the importance of catch crops in the reduction of nitrates leaching, too (Martinez, 1990).

In France, sowing catch crops is compulsory in nitrate-vulnerable zones since the last nitrate action programme. In the Netherlands, growing catch crops after maize on sandy soils is compulsory. In Germany, in cooperations of water suppliers and farmers, water suppliers often subsidise catch crops cultivation over the winter season (Chapter 3.5; Oelmann et al., 2017).

As catch crops growth is related to the retention of nitrates in the root zone, the proportion of arable land being covered by catch crops (or reverse, being left as bare soil) could be a simple indicator for nitrates leaching reductions.

Catch crops also are one element of soil cover (see below), and in this function reduce erosion and thus pesticide run-off into surface waters.

The cultivation of catch crops is one element of the Greening part of CAP direct payments. Catch crop areas are part of EFAs (Ecological focus area). In 2015 and 2016, the EFA measure requirements applied to 68 % of arable land in the EU (excluding France) or 59.7 million hectares. Although the requirements are, that 5 % of this arable land must be under one or more of the different EFA elements, in practice, in 2016 8.5 million hectares (14 %) was covered by EFA elements (before weighting factors). In 2015, 27.7 % of the total EFA area was declared by farmers (before weighting factors) as catch crops. In 2016, an increase in catch/cover crops took place in BG, EE, HR, LV, LT, HU, SI (Hart et al., 2017).

Although detailed data on catch crop cultivation are collected for the Greening payments, these are not available publicly at Eurostat. Furthermore, catch crop cultivation may take place under different other regimes, like CAP pillar II-measures or private farmers-waterworks cooperations (Chapter 3.5; Oelmann et al., 2017).

The degree of **catch crop-cultivation** may be used as an indicator (in reverse order) for groundwater pollution due to nitrates.

5.2.3.3 *Method of soil cultivation/tillage practice*

Soil structure influences the hydraulic properties of the soil such as infiltration, runoff, evaporation and redistribution of water in the soil. Soil management practices have an influence on soil structure with consequences on the runoff of pesticides and leaching of both, pesticides and nitrates.

However, predictions of changes in the soil structure remain challenging due to its spatial and temporal variability. Roger-Estrade et al. (2009) propose an indicator of soil structure dynamics based on the proportion of compacted clods in the tilled layer to evaluate the effects of different crop management systems on soil structure and soil water transfer. Fawcett et al. (1994) reviewed the research on the impacts of conservational tillage on pesticide runoff in the USA from the years 1967-1991. According to Freier et al. (2015), glyphosate-containing herbicides were especially used in zero-tillage cropping systems (winter wheat and winter barley). On the contrary, Arondel and Girardin (2000) could show that ploughing was effective in decreasing both herbicide and fungicide use intensity, especially in high risk cropping systems.

There is no consensus regarding the effect of tillage on the transfer of nitrogen, several studies have shown equivalent losses between the two systems (Shipitalo et al., 2000; Oorts, 2006).

Therefore, the percentage of **low/zero-tillage cropping systems** could be used as indicator for herbicide use.

5.2.3.4 *Soil cover*

Bunzel et al. (2014) studied landscape parameters driving aquatic pesticide exposure and effects in four Federal States of Germany using an index to identify regions with high potential negative effects for macroinvertebrates. Both, forested upstream reaches and riparian buffer strips >5 m had reducing effects on the pesticide risk to macroinvertebrates.

Soil loss rates decrease exponentially as vegetation cover increases. Other land use and management factors affect soil loss, e. g. type of crop and tillage practice. The C-factor (cover-management factor) is one parameter out of five to estimate risk of soil erosion within the Universal Soil Loss Equation (USLE) and its revised version, the RUSLE. In comparison to bare fallow land, the C-factor describes how land cover, crops and crop management cause soil loss. Calculated soil loss ratios (SLRs) are computed as a product of five sub-factors: prior land use, canopy cover, surface cover, surface roughness and soil moisture. These sub-factors include variables, such as residue cover, canopy cover, canopy height, below-ground biomass (root mass plus incorporated residue) and time. The SLRs are calculated for several time intervals during a year and multiplied by the corresponding percentage of annual rainfall erosivity to estimate the C-factor. This approach is feasible on plot- to field scale.

For larger spatial scales, simplified methods, like assigning uniform C-factors from literature to a landcover map, or mapping vegetation parameters using image classification, were developed.

LANDUM, a hybrid C-factor land use and management model covers an area of 4,381,376 km² of EU-28 (Panagos et al., 2015). The model is based on a literature review, remote sensing data at high spatial resolution (e. g. CORINE land cover), and statistical data on agricultural and management practices. The model is designed as tool for policy makers to assess the effect of future land use and crop rotation scenarios on soil erosion by water. The impact of land use changes (deforestation, arable land expansion) and the effect of policies can potentially be quantified with LANDUM. The C-factor data and the statistical input data used are available from the European Soil Data Centre (Panagos et al., 2015).

Factors describing the degree of **soil cover** by vegetation therefore could be useful as indicator for erosion and thus for pesticide and nitrogen runoff.

5.2.3.5 Cropping systems

In contrast to cropping patterns, cropping systems include not only the share of crops in time and space but also all related cultivation practices applied to the crops, e. g. soil cultivation, pesticide and fertiliser application. Arondel and Girardin (2000) proposed for a farm network with maize production in the Rhine plains a way of sorting cropping system (CS), in order to assess their impact on groundwater quality, by defining categories of impact and families of criteria. The categories (C1-C4) were as follows:

- C1: CS with a very high environmental risk level (risk caused by an error of practice)
- C2: CS resulting in environmental problems (common agricultural practice)
- C3: CS aimed at preserving environment (use of improved methods)
- C4: CS respecting the environment (important involvement of the farmer for protecting the environment)

Groundwater quality is highly influenced by three agricultural techniques: Nitrogen management, pesticide management and irrigation management. In order to categorise cropping system, evaluation criteria were defined as follows:

| for nitrogen management | for pesticide management | for irrigation management |
|--|---|--|
| <ul style="list-style-type: none">• Amount of N• N-budget• Date of application• Splitting up• Improving techniques | <ul style="list-style-type: none">• Amount of Pesticide• Half life of active ingredients• Mobility• Toxicity• Location of application• Date of application | <ul style="list-style-type: none">• Hydric balance• Amount of first apply |

The evaluation criteria thus can be interpreted as compound indicators to assess the risk of groundwater pollution due to defined cropping systems.

Arondel and Girardin (2000) did not refer to data of (ground- or surface) water quality for the calibration of the categories.

This study shows that the description of a cropping system may be quite complex, as a number of indicators are needed. However, the three categories of indicators are common: one is needed for the description of nitrogen fertilisation, the other for the description of pesticide applications. The last category describes indicators for the water balance which can influence both pesticides and nitrogen transfers. In this specific study, climatic data were not applied to assess the hydric balance.

5.2.4 N-fertilisation

5.2.4.1 Livestock density

Livestock density as indicator describes the density of livestock units (LU) per hectare utilised agricultural area (UAA). Livestock unit is a reference unit to facilitate the aggregation of livestock from various species, using livestock unit coefficients. One LU equals a grasing cow producing 3.000 kg milk per year without feeding additional concentrated foodstuff (Eurostat 2018).

Data are available for the main categories cattle, pigs, sheep, poultry and equidea, on the NUTS 2-level (Eurostat 2018). Data are reported from Member States to eurostat.

On the national or regional level, livestock density can be derived from data on livestock censuses. Estimates in high resolution can be obtained from processing data of different origin, as shown with the Thuenen-Atlas for Germany (Johann Heinrich von Thünen-Institute, 2018).

On a small scale, livestock density can be collected from farm surveys.

5.2.4.2 Livestock feed consumption

One indicator used in nitrogen farm budgets (Chapter 5.9.1) is the nitrogen-import over animal feedstuff, as the internal nutrient circle livestock excretion → fertilisation → harvested product is not considered for this kind of budgeting. Therefore, the amount of **livestock feed consumption** has to be collected in case a farm budget is intended to be calculated.

5.2.4.3 Livestock excretion

Livestock density does not give detailed information on nutrient (especially nitrogen and phosphorus) excretion. Livestock unit (LU) is a derived value, using animal counts from animal censuses. According to Regulation EC 1165/2008 concerning livestock and meat statistics, animal censuses categorise bovine, pigs, sheep and goats far more detailed (Table 5.1; EC, 2008). Information on animal categories and nutrient excretions (= the total amount of N and P excreted by livestock per year as urine and faeces) can be combined to obtain a more substantial estimation of the nutrient concentration in livestock excretion. This approach is suitable on national, regional and farm level.

Velthof et al. (2015) could show in a review on methods to determine N-excretion factors for different animal categories, that methods differ significantly between policy reports and between countries. Part of these differences may be related to different animal production methods, size or weight of the animals and feed composition, but partly also to differences in the aggregation of livestock categories and estimation procedures. Additionally, methodologies and data use often are not well described. Consequently, there is a need for harmonisation.

Hou et al. (2016) propose a method for the estimation of annual feed use and N excretion per animal category for all countries of the EU-27, based on the energy and protein requirements of the animals and statistics of feed use and composition, animal number and productivity (Hou et al., 2016).

Using an input-output-model, in Germany, nutrient excretion for different animal categories and production varieties are calculated (DLG, 2014). These data are also part of the current German Fertilising Ordinance (DüV, 2017). In a simplified approach, the total volume of excretion produced by livestock is calculated by multiplying the number of animals with a rough estimation on the manure production per animal and the nutrient concentration of manure per t. Estimates by this approach on manure production though differ, in France for cattle 8.4 t per year (CA Bretagne, 2014), with a concentration of 5.9 kg of N per t, what equals 50 kg N per year; in Germany for young cattle 8 t per year, but for dairy cows around 20 t per year. N-excretion are calculated from 45 to 57 per year for

Table 5.1: Categories of livestock statistics (EC, 2008)

| |
|--|
| Bovine animals |
| bovine animals aged not over 1 year |
| <ul style="list-style-type: none"> calves and young cattle for slaughter |
| <ul style="list-style-type: none"> other <ul style="list-style-type: none"> male female |
| bovine animals aged over 1 year but under 2 years (except females that have calved) |
| <ul style="list-style-type: none"> male female (heifers; animals that have not yet calved) <ul style="list-style-type: none"> animals for slaughter other |
| bovine animals of 2 years and over |
| <ul style="list-style-type: none"> male female <ul style="list-style-type: none"> heifers <ul style="list-style-type: none"> heifers for slaughter other cows (bovine animals that have calved, including those that are under 2 years old) <ul style="list-style-type: none"> dairy cows other |
| buffaloes |
| <ul style="list-style-type: none"> female breeding buffaloes other buffaloes |
| Pigs |
| piglets with a live weight of less than 20 kg |
| pigs with a live weight of 20 kg or more but less than 50 kg |
| fattening pigs, including cull boars and cull sows with a live weight |
| <ul style="list-style-type: none"> of 50 kg or more but less than 80 kg of 80 kg or more but less than 110 kg of 110 kg or more |
| breeding pigs with a live weight of 50 kg and over |
| <ul style="list-style-type: none"> boars covered sows, of which <ul style="list-style-type: none"> sows covered for the first time other sows, of which gilts not yet covered |
| Sheep |
| ewes and ewe lambs put to the ram |
| <ul style="list-style-type: none"> milk ewes and milk ewe lambs put to the ram other ewes and ewe lambs put to the ram |
| other sheep |
| Goats |
| goats which have already kidded and goats which have been mated |
| goats which have already kidded |
| goats mated for the first time |
| other goats |

a young cattle and from 100 to 153 kg N per year for a dairy cow, depending on breeding intensity and feeding regime (DLG, 2014, DüV, 2017).

Therefore, depending on the calculation method, the livestock excretion is a rather precise indicator, but not easy to calculate. Default values for each type of livestock are available to perform estimations (DLG, 2014), as well as calculation methods (Hou et al., 2016).

5.2.4.4 Type of organic fertilisers used

There are different types of organic fertilisers in use: manure and biogas digestate, both, as liquid and solid type, compost and sewage sludge. Sewage sludge may be in liquid form or dewatered and supplemented with limestone or a synthetic dewatering agent (such as dewatered manure and biogas digestate). Nitrogen in liquid organic fertilisers may be more readily plant available, as a large amount of it is present as $\text{NH}_4\text{-N}$. If applied in access or before planting, part of it may leach beyond the root zone. It is therefore important to apply liquid organic fertiliser in accordance with plant needs. Nitrogen in solid organic fertilisers is bound to the organic matter and plant available only after mineralisation. In practice, only a small part of the nitrogen in the solid organic fertilisers is taken into account as instantly plant available, the rest has to be remembered for future fertilising measures. Quantifying this future available share of organic bound nitrogen is complicated, as a lot of factors are involved (Klages et al., 2018). Anyhow, the more organic bound N is applied, the higher the risk of unwanted release as mineral N. This is particularly important for solid manure which provides less readily available N in the season after application than slurries but releases more N to crops in subsequent years. Using manure N as a sole nitrogen source may therefore limit overall manure N efficiency (Webb et al., 2013). Figure 5.1 shows for different organic fertilisers minimum availabilities of nitrogen as share of total applied nitrogen in the year of application and the succeeding year according to the German fertilising ordinance (DüV, 2017).

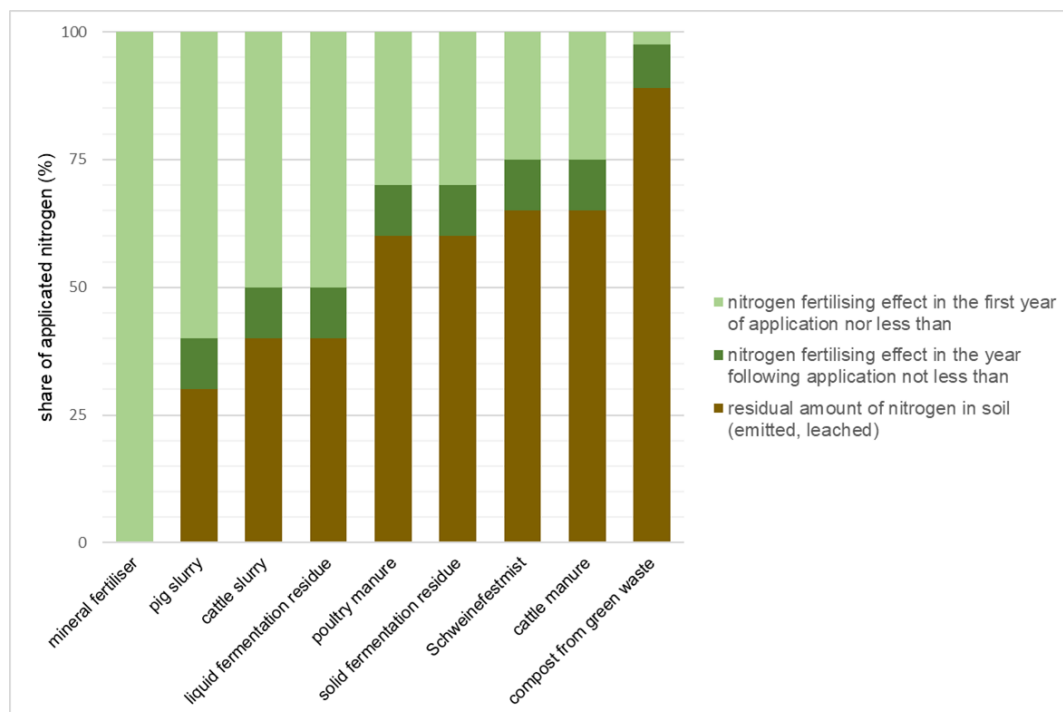


Figure 5.1: Minimum availabilities of nitrogen according to German fertiliser ordinance (DüV, 2017) as share of total applied nitrogen in the year of application and the succeeding year for different organic fertilisers (Klages et al., 2018)

The **type of organic fertiliser** may be helpful to estimate the amount of easily mineralisable organic bound nitrogen, which might be subject to leaching.

5.2.4.5 Manure applied in autumn

In autumn, plant need for nitrogen is usually small, as quite often, a surplus of nitrogen is left in the field from the preceeding crop. Moreover, mineralisation takes place during the autumn months, especially in warm and humid climates (climate change?!). Therefore, in nearly all Member States, manure application/fertilisation in autumn and winter is legally restricted as a national measure of the Nitrates Directive). In case there is no legal reglementation, the degree of manure applied in autumn could reveal the degree of pressure for animal breeders to get rid of some of the organics produced.

With the indicator **quantity of manure applied in autumn** the amount of nitrogen applied with a high risk of N-transfer could be estimated. However, the data to calculate this indicator derive from the farm individual fertilisation plans. They are therefore confidential, and hard to obtain, especially when legal restrictions grasp.

5.2.4.6 Animals out on pasture

The proportion of time, grazing animals are out of pasture varies a lot, according to breeding intensity, region and landscape. With grazing cattle, excretions are not spread evenly on the grassland, but in form of small point sources, which might cause NH₃-emission or NO₃-leaching. The N efficiency of N excreted during grazing is low and therefore usually also mineral fertiliser is applied to grazed grassland. The risk on nitrate leaching from grazed grassland is depending on the grazing intensity (LU per hectare, duration) and period (high leaching in autumn), fertiliser N application rate, site specific factors and weather conditions.

The indicator **animals out on pasture** is a rather imprecise indicator, as there is no mentioning of the timespan, the animals remain on the same plot; also, there is no information on additional mineral fertilisation of the plot that has been grased. Animals out on pasture therefore seems to be a rather weak indicator for the possible leaching of nitrates.

5.2.4.7 Organic fertilisation per hectare or organic fertilisation per crop and hectare

As shown before, there are methods to estimate nutrients (N and P in particular) in organic fertilisers, as well as the availability of N to crops. In a second step, a relation to the UAA available and to specific crops can be established, to get an impression on the fertilising intensity with organic fertilisers.

There are crops which can utilise organic bound nutrients better, e. g. corn/maize (main and strong growth period in the warm season, when there is increased mineralisation) or not as good, e. g. sugar beet, where N-fertilisation should be restricted to avoid negative influence on the harvestable sugar yield. On grassland, especially when used as pasture, due to hygienic reasons, manure fertilisation should only be applied in combination with a waiting period. Therefore, it makes sense to devide the available organic fertiliser according to the actual crop pattern of the area to be examined (Member State, region or farm).

For smaller areas (farm, field), agricultural surveys could be used to learn about farming practices and to estimate the most fertilised crops. In France, grassland and corn silage are the two crops that receive the most organic fertilisation according to surveys (in frequency and quantity).

Organic fertilisation/hectare could therefore be used as indicators for nitrogen leaching, especially in intensive breeding areas. As indicated in Chapter 5.2.4.4, the risk of nitrogen leaching increases with the rate organic fertilisers are applied but also with the percentage of less-avaiable nitrogen.

5.2.4.8 Mineral fertilisation/hectare or mineral fertilisation/crop and hectare

Data on mineral fertiliser sales are generally available on national scale (Chapter 2.1.1), deriving from two sources: reports of the Member States and from the association “Fertiliser Europe”. According to Eurostat (2018), due to the inclusion of intermediary goods and non-agricultural use, these statistics may overestimate the use of mineral fertilisers. Due to differences in reference periods, data sources and methodology, both sources cannot be directly compared.

Estimates on mineral fertilisation at farm level, however, can be obtained by interlinking data on crop production (e. g. agricultural preconditions, crop pattern, qualitative and quantitative yield).

Mineral fertilisation on farm or local level may be obtained by interrogating the farmers. In some Member States, the national transformation of Nitrates Directive obliges farmers to set up a precise, farmwide fertiliser planning, at least for nitrogen (for both, organic and mineral fertilisers). The purchased fertiliser amounts are registered by the farm’s accountancy and the plant nutrient concentration has to be declared according to EU or national rules (EU 2003/2003).

Consequently, as far as mineral fertilisers are concerned, data on fertiliser use may be the most readily usable nitrogen input data (providing the data are available), which may be used as indicator, at least in regions with intensive arable crop production and marginal animal production (e.g. Paris Basin, for instance Case study 4, La Voulzy).

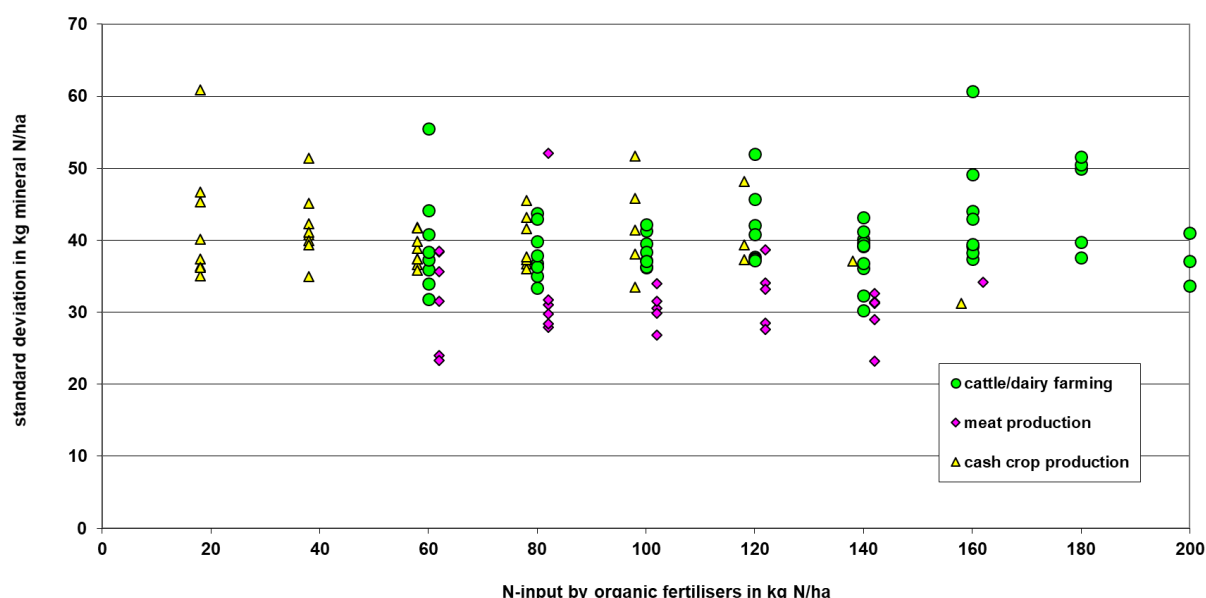


Figure 5.2: Standard deviation of mineral N-fertilisation in kg N/ha in relation to the application of N with organic fertilisers (Osterburg and Tehen, 2012)

In regions with a pronounced animal production and a large amount of manure which has to be utilised on agricultural land as fertiliser, mineral fertiliser usage data do not possess indicator function: Osterburg and Tehen (2012) combined data from a survey carried out between 2008 and 2010 among different types of farms in three German Federal States on mineral and organic fertilisation. They could show that independently from the amount of organic manure applied, the mineral fertiliser use varied considerably within one farm type. In Figure 5.2, farms were classified according to the

nitrogen im- and export on field level. Exported nitrogen mirrors the yield and therefore the fertilising demand. The vertical axis shows a standard deviation of 30-50 kg/ha from the average applied nitrogen. This signifies, that the additional mineral fertiliser dose varies broadly, with no relation to the level of organic fertilisation with manure, ranging from 0 to 200 kg/ha. The variation in the mineral fertiliser dose is so high that it cannot be explained by different frame conditions but rather is due to differences in individual farm management (Osterburg, 2016).

According to this figure, farmers may use approximately the same amount of mineral N, whether they have zero or 200 kg N as organic fertilisers from keeping farm animals at their disposal.

According to Eurostat (2018), more detailed data on mineral fertiliser use in agriculture would be useful for several environmental EU policies. Collecting data in a geo-referenced sample survey would allow the use of these data for modelling environmental impacts at finer spatial scales.

Mineral fertilisation/hectare could be used as indicator to explain nitrogen leaching in arable land areas. However, as explained, in animal breeding areas or mixed farming area it is necessary to use a combination of the two indicators mineral fertilisation by hectare and organic fertilisation by hectare (see below).

5.2.4.9 Total fertilisation/hectare or total fertilisation/crop and hectare

This indicator allows to estimate the amount of mineral and organic nitrogen applied (including directly by animals on pasture) in relation to UAA or UAA of a specific crop.

The determination of available nitrogen requires an estimation of the available nitrogen from mineral and organic sources. N from organic sources might be weighted according to direct and delayed plant availability.

Total fertilisation/hectare can be considered as the addition of two indicators, the indicator measuring organic fertilisation and the indicator measuring mineral fertilisation. This indicator can be used in any type of agricultural sector, livestock or crop sector. The advantage of using the three indicators is to know the impact of one type of fertilisation compared to total fertilisation.

Total fertilisation/hectare is one of the most commonly used indicators, since it easy to understand and to explain. One of its main drawback is that it is not taking into account the output due to the crops and it can not transcribe situations where the fertilisation is stable with increasing yield, e. g. due to increase fertilising efficiency.

5.2.4.10 Timing of fertiliser application, splitting/frequency of fertiliser application

With this indicator, the number and timing of nitrogen applications (organic or mineral) during the period of growth is evaluated. It is based on the recommendations of agronomists to split nitrogen inputs so that fertilisation sticks closer to crop needs. In consequence, less nitrogen may remain in the soil outside the periods of absorption by crops, which may reduce the risk of nitrogen loss (Recous et al., 1997). Generally, nitrogen application splitting allows a better match between applications and needs, a better consumption by crops and opportunities for adjustment of crop fertilisation. The objective is therefore to quantify the number of nitrogen inputs made "at the right time", i. e. during the period of crop needs, on the same plot. The interpretation has to be done in relation to the fertiliser amount and the yield (Klages et al., 2018).

Regularly, there are no European statistical data available on the timing and splitting of fertilisers. Some countries collect theses data at the regional or the national scale. At the catchment scale, information on fertiliser practice could be obtained by on-farm surveys. Another possibility could be an evaluation of farm management programs, which allow access to the farm management data of registered farmers. These data are confidential and not easily to obtain.

Therefore, **timing of fertiliser application** could be an indicator for improved farming practices, but data availability and the confidentiality of individual farm data has to be considered. Timing of fertiliser application and splitting of doses cannot stand alone as indicator but in connection to the application rate.

5.2.4.11 Application technique for fertilisers

The technical equipment used to apply fertilisers possess a substantial influence on the preciseness with which fertilisers are spread.

In order to prevent the pollution of surface waters, boundary and field side spreading devices enable accurate application. This is particularly important for centrifugal mounted spreaders, which are used for mineral fertilisers.

Mineral fertilisers show a large variance in their physical properties. Therefore, an appropriate technical standard of the spreading vanes is one prerequisite to ensure even lateral distribution of mineral fertilisers, the other is to adjust the spreader technique to the actual mineral fertiliser which shall be spread. Uneven lateral distribution of mineral fertilisers may lead to a local oversupply with nitrogen, which might induce increased partial leaching. Fields in question show a characteristic light and dark green striped pattern (Klages et al., 2018). Especially spreaders for mineral fertilisers (centrifugal broadcasters) need regular calibration for every new mineral fertiliser used. This is due to extremely variations in physical properties of the fertilisers, e. g. grain size and grain size distribution, hardness of grain, degree of moisture or dust content (Klages et al., 2017).

Using the nitrogen in organic fertilisers more effectively reduces losses to the environment. For biodiversity protection reasons, technique for organic fertilisation is supposed to minimise gaseous losses. A large amount of nitrogen is lost as ammonia, especially under unfavourable weather conditions and in case the organic fertilisers are not immediately after spreading incorporated into soil (using chisel or plough) or directly applied near (using drip hose booms) or into soil (using trailing shoe or slit technique).

Manure N efficiency may be increased by up to 15 % through a requirement to take allowance of the N conserved by reduced ammonia (NH₃)-emission techniques. In comparison to application methods, which mix the liquid manure with soil, the injection of slurry reduces N immobilisation and thus increases manure-N efficiency by 10-15 %. In growing cereals, NH₃ emissions can be reduced by band spreading within the canopy. Compared with undigested slurry, anaerobic digestion of slurry may also increase manure-N availability within the season of application by 10-20 %, slurry acidification may increase manure-N efficiency by 35-65% by reducing total NH₃ losses by 70 % compared with unacidified slurry stored without cover and not incorporated after spreading (Webb et al., 2013).

In cases the amount of nitrogen applied with techniques reducing NH₃ emissions is not adjusted to a reduced loss of N, there is an increase possibility of groundwater pollution by nitrates (Klages et al., 2018).

Precision farming connects highly resolved information on nutrient plant need and other site factors (often obtained from remote sensing) to advanced fertiliser application techniques. Precision fertilisation varies in a plot according to plant need. A N surplus due to partial weak development of a crop or existing N-reserves in the soil can be avoided. Precision fertiliser techniques are available both for mineral and organic fertilisers. For organic fertilisers, near-infrared spectroscopy (NIRS) is sometimes used to determine the nitrogen in the liquid manure or digestate during the loading procedure or even while spreading (Böhrens, 2007).

The indicator **technical standard of fertiliser application** could give a good picture on the feasibility of precise fertilisation according to plant needs. Anyhow, data are collected only sporadically.

Furthermore, a good technical standard is not linked to the absolute amount of N applied, therefore this indicator cannot be used on its own for the risk of nitrate leaching.

5.2.5 Pesticide application

5.2.5.1 Type of Pesticides

According to (EC) No 1185/2009, the nationally sold annual weight (kg) of all active substances has to be collected under certain major groups and product categories and forwarded to the EU Commission (Eurostat 2018, 2018b), (see also Table 2.1). Aggregated data of this kind are not suitable to serve as indicator.

5.2.5.2 Chemical properties of Pesticides

The chemical properties of pesticides are listed in the Pesticide Property Database – PPDB (University of Hertfordshire, 2017). There is a separate database available for Bio-Pesticides – BPDB. University of Hertfordshire (2016).

The two **chemical properties** the most commonly used are the **DT 50-value** and the **K_{oc}**.

The kinetics of dissipation in soil in the field results in different results depending on the type of reactions observed (abiotic or biotic). A consensus has emerged for the use of a first-order equation for the description of these phenomena (Beulke et al., 2001a, Calvet et al., 2005). In general, only the (bio) degradation data are taken into account, in particular because they are the simplest data to obtain. This first-order equation can use the half-life (DT50) which represents the time to halve the initial amount of product. The DT50 is an indicator of the persistence of the pesticide in the soil. The DT 50-value is thereby often used as a parameter to measure pesticide accumulation.

The partition coefficient K_{oc} is defined as the ratio of pesticide concentration in a state of sorption (i. e. adhered to soil particles) and the solution phase (i. e. dissolved in the soil water) (see also Chapter 3.4.2). Thus, for a given amount of pesticide, the smaller the K_{oc} value, the greater the concentration of the pesticide in solution. Pesticides with a small K_{oc} value are more likely to leach into groundwater than those with a large K_{oc} value. Sorption for a given pesticide is greater in soils with a higher organic matter content. Thus, pesticide leaching is thought to be slower in soils rich in organic matter than in soils low in organic matter. The K_{oc} is part of several (national) indicators and models (Kookana et al., 2005), sometimes supported by lysimeter studies (Nolting and Schinkel, 1998).

The DT 50-value and K_{oc}-value can be used individually for specific questions such as the environmental test of a certain pesticide in a certain environment or soil type (Kookana et al., 2005, Kucharski and Sadowski, 2009).

Other physical properties, such as water solubility, octanol/water partition coefficient, and volatility from soil, have often been invoked as indicators of leachability, thus affecting the estimated risk of pesticide leaching into groundwater or surface water aquifers.

5.2.5.3 Application of pesticides/hectare

The way the usage data which have to be collected according to (EC) No 1185/2009 are obtained by the Member States may differ considerably: while in Germany usage data are deduced from a network of survey farms (panel) (Rossberg, 2016) and in Ireland, annual surveys on different crops/permanent cultures are conducted (Pesticides Registration and Control Division, 2018), in Denmark, farmers are required to upload their pesticide use data (Kudsk et al., 2018). Therefore, the Danish data may be more detailed and realistic, while others have the character of estimates.

5.2.5.4 Application of pesticides/hectare and crop

For pesticides, the amount applied and the frequency of applications strongly depend on the cropping systems and the agricultural crops cultivated (Roßberg, 2015). According to (EC) No 1185/2009, Member States have to report which pesticides (active substances) are used for which crop. National statistics on cropping patterns are usually available. These two information sources can be combined to obtain a realistic **estimate on the active substances usually applied** for a certain crop. These statistical data have also been used for the prioritisation of pesticides. For instance, the German environmental agency (UBA), the German Technical and Scientific Association for Gas and Water (DVGW) and a Bavarian State Environmental Lab developed out of these data a guideline for the water works concerning pesticides/metabolites to be included in the screening of the groundwater (Banning et al., 2018).

Additionally, statistics on sales data of pesticides can be used to crosscheck estimates on pesticide use/ha and crop.

5.2.5.5 Timing of pesticide application, splitting/frequency of pesticide application

Changes in cropping systems can have an impact on the use of pesticides. The lengthening of the rotation of cultures makes it possible to alternate the spring crops and the winter crops in order to break the cycles of the pests. Pests being fewer, the use of pesticides is less necessary. Thus, in order to reduce the pesticide use, longer and more diversified rotations are necessary.

In the case of very short rotations, pests specialise in one type of crop (for their feeding) and get a specific reproduction cycle that fit with the crop rotation. The impact can be important when the climatic context is favorable.

Unlike fertilisation, the division of doses of pesticides is rarely recommended because it is assumed that it increases the resistance of pests. In fact, in order to reduce the doses, it is often recommended to use two different active ingredients at lower doses.

The pesticide spraying is recommended when temperatures are low and relative humidity is high. In general, it is better not to spray when relative humidity is less than 40 per cent and air temperature is above 25°C. This reduces the chance of drift due to temperature inversions or evaporation. Then, optimum spraying conditions are generally early mornings.

The **splitting/frequency of pesticide application** is, in form of the Treatment frequency index (TFI, see Chapter 5.6.2.6) well established as indicator. **Timing of pesticide application** may have a strong influence on pesticide losses to the environment, but to establish the data record may be difficult.

5.2.5.6 Application techniques for pesticides

Pesticide drift is the airborne movement of pesticides from an area of application to any unintended site. Drift can happen during pesticide application, when droplets or dust travel away from the target site. To limit pesticide drift, drift reduction nozzles can be used. Many of these nozzles control the flow rate. The exit orifice controls the pattern formation. The result is larger spray droplets which are less susceptible to drift. Also, some of these nozzles can be used over a wider pressure range, which produces large droplets at low pressure and small droplets at high pressures. (Mueller et al, 1997, Nuytents et al, 2007, Kalsing et al, 2018)

Pesticide application techniques employs drift reduction and low loss equipment may be used as indicator for a reduced pesticide drift risk. This information may be used in relation to the total number of pesticide sprayers in a certain area.

5.3 TRENDS

Within the DPSIR-framework, timetrends can be analysed. For AEIs, the trend indicators mintensification – extensification and specialisation were established.

5.3.1 Intensification/Extensification

Intensification/Extensification of crop production may go along with a change in pesticide use. The transformation of large proportion of grassland in in arable cropping area and vice versa has a marked influence on nitrate leaching: due to mineralisation, the ploughed grassland releases a significant amount of nitrates into the soil (Laurent et al., 2004). The newly introduced rules on Greening within the current framework of CAP (2014-2020) therefore have limited the proportion of grassland which may be turned over (see also Chapter 5.1.1.2, land use change).

On EU-level, the main indicator is the trend in the shares of UAA managed by low, medium and high intensity farms, the supporting indicator is the average input expenditure per hectare in constant input prices (Eurostat, 2018). Data are collected by the Farm Accountancy Data Network (FADN, 2018). On regional level, data may be collected from local farmers.

5.3.2 Specialisation (driving force)

Farm specialisation describes the trend towards a single dominant activity in farm income. A farm is specialised in case a particular activity provides at least two thirds of the production or the business of an agricultural holding (Eurostat, 2018).

Specialisation of agricultural production may go along with a change or an increase in fertilisation and pesticide use. Specialisation may be detected as change of pattern in land use, i. e. a narrowing of cropping patterns towards a smaller number of crops (see also Chapter 5.2.3.1, cropping patterns and Chapter 5.2.3.5, cropping systems).

The main indicator is the share of the utilised agricultural area (UAA) managed by specialised farming, i. e., a farm where a single type of production or service dominates farm income. The supporting indicator is the number and share of specialised holdings, i. e. the farms where a single type of production or service dominates farm income (Eurostat, 2018).

5.4 LEACHING

5.4.1 Leaching travel time

5.4.1.1 *Depth of water table*

The depth to the water table is defined as the perpendicular distance between the upper edge of the surface and the upper edge of the groundwater surface (DIN 4049-3). The deeper the water table, the longer it will take until nitrates or water soluble pesticides/metabolites will reach (the highest) ground water level.

5.4.2 Leaching quantity

In order to determine the quantity of substances translocated down the soil profile or washed out into ground water, it is necessary to quantify or at least estimate the quantity of water being released into the ground water body. Various indices may be used:

5.4.2.1 Drainage index (DI)

The DI is derived from the soil's taxonomic subgroup classification in the US system of Soil Taxonomy and its soil map slope class and reflects the soil's natural wetness condition. The DI ranges from 0 to 99; the higher the index, the more water the soil can supply to plants. The main factors affecting the DI is the depth to the water table and the soil volume available for rooting, soil texture is of minor relevance (Schaetzl et al., 2009).

As the drainage index is based on classification system not used in Europe, it is not applicable under the set frame conditions.

5.4.2.2 Exchange frequency of the soil solution (EF)

One indicator for leaching is the Exchange frequency of the soil solution (EF), calculated as ratio of a transport and a storage term (Müller, 2004).

$$EF (\% y^{-1}) = (SeepRate * 100) / WHC(rz)$$

SeepRate = groundwater recharge in mm y⁻¹

WHC = water holding capacity

A low EF is equivalent to a long residence time of water in the root zone and therefore to a low risk of leaching. According to Buczko et al. (2010), it is often used in Germany.

5.4.3 Nitrogen in soil water

Sampling and analysis of mineral nitrogen in soil can be done separately for the layers 0-30, 30-60 and 60 to 90 cm. The result of the analysis can be indicated separately as nitrate-N and ammonia-N in kg N per hectare. Apart from the correct timing, sampling and analysing, a correct conversation from concentration to quantity of the nitrogen analysed is relevant (NLWKN, 2007).

5.4.3.1 After harvest soil nitrate

After harvest soil nitrate determination gives indication on how much of the fertilised nitrogen is not incorporated in plant biomass (Appel and Fritsch, 2015).

5.4.3.2 Autumn soil nitrate

The autumn soil nitrate content reflects the amount of mineral nitrogen in soil before the leaching period during the winter season has begun. Sampling should be done after mineralisation of plant residues has been accomplished and before the leaching has started (NLWKN, 2007).

Autumn N_{min} is the less expensive analytical control method for ground water protection measures. In Flanders, this indicator is used as indicator for nitrate leaching. It is part of the Action Plan of Flanders for the national transformation of the Nitrates Directive. In water protection areas in Germany, autumn N_{min} is used for monitoring the catchment area (Osterburg and Runge, 2007).

The **autumn N_{min}** refers to a single plot or field. The determined nitrogen amount may be subject of immediate leaching, and therefore functions as a good indicator for the concentration of nitrates in the leachate and for the amount of nitrates washed out. A disadvantage is the strong relation to site and year, so results may not be directly compared (Osterburg and Runge, 2007).

5.4.3.3 Spring soil nitrate

In combination with nitrate measurements in autumn (and after harvest) spring soil nitrate measurements give information on the N-dynamics in soil, especially how much of the plant available nitrogen has been lost over the winter months (Appel and Fritsch, 2015).

5.4.3.4 Soil water potential and nitrate content in soil solution

With the aim to analyse the risk of nitrate leaching under different management practices and cropping systems, soil water potential and nitrate concentration in soil solution can be measured simultaneously, using Tensionic tensiometers. The indicator for the amount of nitrate lost between two depths below rooting zone is calculated from a variable calculated from the hydraulic gradient and the nitrate concentration of the soil solution. The indicator reveals down- and upwards movement of the soil water, e.g. during the vegetation period or in arid conditions (Cuny et al., 1998).

5.4.4 Soil water content and pesticide transfer

Soil moisture affects leaching behaviour of pesticides. For the example of Betazon, Guimont et al. (2005) could show for water percolated columns with soil aggregates, that soil moisture induces the physical entrapment in the soil structure.

Giuliano et al. (2016) monitored for different maize cropping systems water drainage and pesticide leaching, using tension plate lysimeters, installed at 1 m depth. Two indicators were used to compare the drainage and pesticide leaching of the cropping systems: the cumulative drainage per year (expressed in mm) and the number of pesticide leaching events with at least one compound (mother compound or metabolite) quantified at a concentration $\geq 0.1 \mu\text{g/l}$ (corresponding to the limit for drinking water).

Herbicides may leach under the influence of artificial irrigation or rainfall events, an effect that was more pronounced in medium soils with low organic matter content (Monquero et al., 2008). Fait et al. (2010) studied the effect of the three different irrigation methods sprinkler, basin or border systems on the leaching of the herbicide Terbutylazine (TBA) and its metabolite Desethylterbutylazine (DEB) in ground water on ten farms in Italy cropped with maize. The results showed that basin irrigation led to the highest concentrations in the ground water, indicating that this irrigation system can influence the leaching of both TBA and DEB. Irrigation can also lead to pesticide leaching by preferential flow, especially during the first days after application (Schierholz et al., 2000). From these studies, it can be concluded that pesticide transfers are increasing when the water content is increasing.

5.5 INDICATORS TO ESTIMATE SURFACE WATER POLLUTION

5.5.1 Indicators for nitrates in surface waters

In contrast to nitrogen in groundwater (where a unified threshold is defined for all groundwater bodies in Europe), for surface water the Water Framework Directive requires the establishment of type-specific reference conditions for surface water body types. The Water Framework Directive thus proposes to define type-specific conditions for these reference values which may be either spatially based or based on modelling, or may be derived using a combination of these methods. Where it is not possible to use these methods, Member States may use expert judgement to establish such conditions. Good surface water status means the status achieved by a surface water body when both its ecological status and its chemical status are at least good (EU/WFD 2000).

A driving force indicating nitrates in surface waters is the susceptibility to erosion and compaction (see under Chapter 5.1.3.3)

5.5.2 Indicators for pesticides in surface waters

Generally, a monitoring of pesticide concentrations in rivers with a catchment > 10 km², in lakes with a surface area > 50 ha and groundwater has been obligatory in the European Member States since the year 2000. Surface water bodies below these sizes are not considered within the EU-Water Framework Directive. This may pose risks to small water bodies, which are often located in rural areas with intensive agricultural use. To address this issue, several EU Member States have integrated the consideration of small water bodies in their National Action Plans. Differently treated in the national indicators. Include either run-off and/or drift.

5.5.2.1 Number of active ingredients and metabolites in water samples

Hossard et al. (2017) used the indicators surface water concentration of pesticides with the threshold of >0,5 µg pesticide per liter and the number of active ingredients and metabolites found in the water samples to evaluate the effectivity of the environmental plan (Chambres d'agriculture France, 2018) in France.

5.5.2.2 Insecticide Runoff Potential (RP)

Kattwinkel et al. (2011) calculated the RP under current conditions (1990) and under a model future climate and land use scenario (2090), using a spatially explicit model on a continental scale, with a focus on Europe. To assess the indirect effects of climate change, RP and landscape characteristics that are relevant for the recovery of affected populations were combined to estimate the ecological risk (ER) of insecticides for freshwater communities.

5.6 POINT SOURCES

Point sources origin from single, identifiable spots. They are distinguished from nonpoint sources in that they discharge directly into waters at a discrete point (Puckett, 1994; Nemčić-Jurec et al, 2013). A cadastre of possible direct dischargers into surface water could be helpful in tracing point sources for water pollution.

5.6.1 Nitrate: grazing animals near surface waters, farmyard, manure/silage/fertiliser storage facilities

Point sources for nitrates on livestock farms may be slurry lagoons, manure depots with an inappropriate building or location or farmyards, including situations as tank-filling respectively cleaning, accidental spills or fruit washing facilities (Carter, 2000). Point sources are mainly due to misuse or inadequate management. Also small, privately owned wastewater-treatment units may have the effect of point sources.

If grazing animals have access to a small stream or lake, nitrogen and other plant nutrients may enter surface water due to animal excrements or runoff (Bohner et al., 2007).

Dense populations and discharges from point sources like septic systems or broken sewer systems contribute significantly to water pollution by nitrate in urban and suburban areas (Nemčić-Jurec et al, 2013).

5.6.2 Pesticides: farmyard, pesticide storage facilities

Point sources for pesticide pollution includes the accidental/unintentional emptying or cleaning of sprayer tanks. They can also occur during unwanted applications on farmyards or on impervious surfaces during the preparation of the spayer tanks. They can also happen due to pesticide storage facilities leakage in a farm or in a plant.

An important debate concerns the assessment of the respective shares of water contamination with pesticides due to diffuse pollution and point source pollution. According to the studies, punctual pollution could represent more than 20 % of the total contamination (Müller et al., 2002; Leu et al., 2004), but that share greatly varies with the catchment (20 % to 70 %). Emissions of this type of pollution are generally much more polluting than those produced by diffuse pollution, due to the high concentrations reached in a short time span.

5.7 AERIAL IMMISSION

5.7.1 Pesticide drift

Estimates of pesticide contributions to surface water by spray drift can be made by using the Rautmann-Ganzelmeier curves (Rautmann et al., 2001), which describe the deposition of pesticides on a water course depending on the distance between the boundary of the treated surface and the water course.

The functions of Ganzelmeier-Rautmann are a model of deposition on a body of water and not the outputs from the field (it is difficult to calculate all the outputs by drift of the plot). So a receptacle, here a stream is always needed to do drift calculations.

The Ganzelmeier-Rautmann curves are functions adjusted to experimental data points and give the deposits on the surface (in the form of a relative surface concentration, that is, in percent of the application rate on the plot) depending on the distance of the treated surface.

It should be noted that the curves reflect an application without technique reducing drift, but which observes good agricultural professional practice (wind speed ≤ 5 m/s, tractor speed ≤ 8 km/h, spray bar in position not too high etc.). If good professional practices are not observed (which is illegal in Germany, where the experiments were done), the resulting drift may be higher.

5.7.2 Deposition of nitrogen

The nitrogen in atmospheric deposition is to a large extent also related to agricultural emissions. In the last decade, the NO_x and NH_3 emissions in Europe declined mainly due to policies that enforced measures in transport, industries and the Nitrate directive (EEA, 2014). N deposition could be modelled (e. g. Banzhaf et al, 2015), the deposition can reach 10 kg(N) or 20 kg(N)/ha and more in Northwestern Europe. The N deposition is not an indicator by itself but it can be used in other indicators since in some region, the N from atmospheric source is not negligible and can be taken into consideration when defining N fertiliser need or calculating N budgets.

The United Nations Economic Commission for Europe (UNECE) defined a network called Convention on Long-range Transboundary Air Pollution (CLRTAP) to reduce and monitor air quality and pollution in the region. A scientifically based and policy driven program under CLRTAP is the European Monitoring and Evaluation Program (EMEP), an international co-operation to solve transboundary air pollution problems by providing e. g. modelling results for monitoring and policy making. Results provided by EMEP show that in a majority of the EMEP sites a decreasing trend N deposition since 1990 is visible. Results can also be used as data input for composite indicators (EMEP, 2018).

5.8 NITROGEN BUDGETS

Nutrient budgets for agriculture are distinguished according to the boundary (farm, soil or land) they refer to (Eurostat, 2013).

5.8.1 Nitrogen farm budget

The farm budget refers to the farm boundaries and records the nutrients in all products that enter and leave the farmgate. The budget can also be calculated at a larger, e. g. a country level in that case the whole farming sector in a country is considered as a single farm (Eurostat, 2013).

5.8.2 Nitrogen soil (surface) budget (=net nitrogen budget)

The soil budget takes the soil as boundary. Only nutrient inputs to the soil and nutrient outputs from the soil are taken into account. The soil budget therefore requires data on manure and fertiliser applications to the soil. The term "net" refers to the fact that the result of the soil surface budget approach results in N surpluses excluding N emissions occurring before the application of manure and fertilisers to the soil (Eurostat, 2013).

5.8.3 Nitrogen land budget (=gross nitrogen budget, GNB)

The land budget approach aims to estimate the total nutrient at risk of pollution (air, soil and water). The land budget therefore requires data on excretion. The term "gross" refers to the fact that the result of the land budget, the Gross Nitrogen Surplus (GNB), includes all N emissions to the air (Eurostat, 2013).

The GNB as AEI is on national/EU-level calculated as follows (Eurostat, 2018a).

Table 5.2: Elements of the Gross Nitrogen Budget as AEI (Eurostat, 2018a)

| Inputs | Outputs |
|---|--|
| Fertilisers <ul style="list-style-type: none">• inorganic fertilisers,• organic fertilisers (excluding manure) Gross manure input , which is calculated from <ul style="list-style-type: none">• manure production (nitrogen excretion; according to the current methodology no reductions are made for nitrogen losses due to volatilisation in stables, storages and with the application to the land)• manure withdrawals (manure export, manure processed as industrial waste, non-agricultural use of manure, other withdrawals)• change in manure stocks• manure import Other nitrogen inputs , which consist of <ul style="list-style-type: none">• seeds and planting material• biological nitrogen fixation by leguminous crops and grass-legume mixtures• atmospheric deposition | <ul style="list-style-type: none">• Total removal of nitrogen with the harvest of crops (cereals, dried pulses, root crops, industrial crops, vegetables, fruit, ornamental plants, other harvested crops)• Total removal of nitrogen with the harvest and grazing of fodder (permanent grassland and fodder from arable land including temporary grassland)• Crop residues removed from the field |

- Eurostat (2018a) points out, that the current national budgets quoted are not comparable between different countries due to differences in definitions, methodologies and data sources used by countries.
- OECD suggests the GNB as an appropriate indicator to calculate comparable indicators on regional and national scale (1993; 2007).
- In Austria, Wick et al. (2012) used the nitrogen land budget to compare agricultural budgets with the concentration of nitrates in corresponding catchments. They found a good statistical correlation.
- In the Netherlands, Nitrate leaching is estimated from the N surplus and leaching fractions that are depending on land use and soil type. Through calculations based on experimental data from various sources, the limits on the use of cattle slurry and mineral fertiliser in grass and silage maize production on sandy soils were calculated (Schröder et al, 2007).
- In France, the CORPEN budget (2006) was developed to measure nitrogen surplus on farm level. This indicator allows to identify farms with a risk of environmental enrichment in nitrogen. This indicator could measure
 - 1) cumulative phenomena (enrichment in nitrogen by temporary storage in a nonleachable form) for which the nitrogen budget can be an acceptable indicator (with the limits related to gaseous losses) but cannot measured,
 - 2) instant phenomena (a stock of nitrogen in mineral form leached by rain).

Both phenomena lead to water pollution. The CORPEN budget indicator is a relevant long term indicator which cannot bring out short term risks of pollution.

- In Germany, both, the nitrogen farm budget (StofBiIV, 2017) and the nitrogen soil (surface) budget (DüV, 2017) are legally binding implemented in national legislation. The fertilising ordinance (DüV, 2017) functions as national implementation of the Nitrates Directive.

Wick et al. (2012) report, that a couple of authors doubt the applicability of the soil surface budget for the reflection of the actual nitrate leaching. The budget is a theoretical concept which describes only a potential for a contamination of groundwater (de Ruijter et al., 2007; Lord and Antony, 2002, Sieling and Kage, 2006). Wick et al. (2012) further explain, that some authors find only poor statistical relationship between the soil surface budget result and nitrate leaching, using correlation analysis (Buczko et al., 2010), analysis of covariance (Lord and Antony, 2002; Rankinen et al., 2007) and regression analysis (Buczko et al., 2010; Rankinen et al., 2007; Sieling and Kage, 2007). According to Wick et al, these statistical evaluations possess the weakness of being limited geographical and temporary.

6. AGRI-DRINKING WATER QUALITY INDICATORS ON DRINKING WATER LEVEL (=STATE INDICATORS)

6.1 WATER QUALITY MONITORING PROGRAM

Water quality monitoring programs provide the fundamental data to evaluate the ADWIs. Therefore, the robustness and representativeness of state/impact indicators strongly depend on the water quality monitoring data.

Table 6.1: Overview of the monitoring programs in the Nitrates Directive in EU Member States participating in FAIRWAY (modification of Table 6 of Fraters et al. 2009)

| Country | Groundwater | | | Surface Water | | |
|------------------------|--|--|--|---------------|--|---|
| | Starting year | Monitoring point | Sampling frequency | Starting year | Monitoring point | Sampling frequency |
| Denmark | 1988(G ¹) 1989 (D ²) | 2000 wells (G); 6400 wells (D) | 1 time per year – 1 time per 6 year (G); 1 time per 3-5 year (D) | 1989 | 231 sites (F ³); 89 sites (L ⁴); 96 sites (MC ⁵) | 12-26 times per year (F); 1-20 times per year (L); 3-26 times per year (MC) |
| France | 1992 | 2625 sites | 1 time per 4 years | 1992 | 1719 sites | 1 time per 4 years |
| Germany ⁶) | 1992 | 172 sites | At least 1 time per year | 1984 | 152 sites (F); 10 sites (MC) | |
| | 2016 | 700 sites with data available since 2008 | | | 256 sites (F) 68 sites (L) 14 (MC) | average: 4 times in winter |
| The Netherlands | 1984 | 360 sites (G); 220 sites (D) | 1 time per year - 1 time per 4 year(G); 4 time per year (D) | | 30 sites (F); 39 sites (MC) | 12-24 time per year |
| UK-England | 1990 | 3700 sites | 4 time per year | | 7000 sites | 12 time per year |
| UK-Northern Ireland | 2000 | 85 sites | 4 time per year | 1970s | 683 sites | 12 time per year |

¹Groundwater monitoring wells; ²Drinking water supply wells; ³Freshwater; ⁴Lakes; ⁵Marine and Coastal water;

⁶Osterburg and Wolter (2017); BMUB, BMEL (2017)

All the Member States of EU operate water quality monitoring programs to fulfil the national regulations and EU-level obligations. At the EU-level, there are four directives that define the

monitoring and reporting requirements regarding drinking water quality and the impact of agriculture on it: Nitrate Directive (91/676/EEC), Water Framework Directive (WFD, 2000/60/EC), Groundwater Directive (2006/118/EC), and Drinking Water Directive (98/83/EC). These directives provide the overall guidelines of monitoring protocols such as minimum sampling frequencies, monitoring parameters. All monitoring networks deliver data to European Environmental Agency (EEA), where the data are available on their website both as maps and in aggregated forms of numerous reports.

Each Member State uses its own monitoring program to comply with these directives (Table 6.1). Therefore, the monitoring programs of the EU Member States have very different structures and designs, depending on various factors such as their history, financial situations, national monitoring obligations and other societal needs. A comprehensive overview of different national monitoring strategies in connection with the Nitrates Directive can be found in Fraters et al. (2009). Table 6.1 shows a summary of the monitoring programs of the Member States participating in FAIRWAY.

In France, in the monitoring network, the frequency of analysis varies, depending on the parameters. For instance, in the Loire-Bretagne bassin, 52 parameters are analysed on a regular basis (2 times/year), 171 parameters are analysed only during “Photographic” analysis (1 time/cycle) and 63 parameters on a selection of points are analysed on intermediate analysis (once in the middle of the cycle). For a certain drinking water plant, the number of parameters could reach almost 700 parameters since there is no limit of pesticide that can be analysed.

In Germany, the monitoring framework for ground- and surface water had been adjusted in 2016 (Osterburg and Wolter (2017); BMUB, BMEL (2017)).

In WP 3, we will compile all types of monitoring data for each case study site. The data availability and quality are expected to vary greatly; therefore, they may become one of the most important criteria in the prioritisation process.

6.2 INDICATORS FOR WATER QUALITY

6.2.1 Annual average concentration

The annual average concentration is the simplest and most widely used state indicator for both nitrates and pesticides. The threshold values for the drinking water and groundwater are 50 mg NO₃/L for nitrate, 0.1 µg/L for a single pesticide, and 0.5 µg/L for the total pesticides (Table 6.2). The Drinking water Directive and Groundwater Directive set these limits.

Validity and robustness of the annual average concentration strongly depend on the quality and quantity of the monitoring data. Furthermore, this indicator does not reflect the temporal and spatial variability of the nitrate and pesticide in the water.

6.2.2 Statistical trend analysis

Trend is another state indicator to show the temporal changes in water quality at a long-term scale (e.g. decades). Significant upward or downward trends can be determined either with statistical, linear methods (e.g. linear regression) or with non-parametric methods (e.g. based on Mann-Kendall) (Visser et al., 2007; Aguilar et al., 2007; Hansen et al., 2011).

A trend in groundwater quality is defined as a change over a specific period in time within a given region that is related to land use or water quality management (Schlosser et al, 1988; Loftis, 1996). Both temporal variations due to climatic and meteorological factors and spatial variability may complicate trend detection. Important is the period of time under consideration. Periods of 8 to 30

years have been recommended, depending on the sampling frequency for water analysis (Grath et al., 2001).

Table 6.2: Summary of state indicators and their threshold values and limits for water quality and regulatory compliances

| Main domain | Indicators | contaminants | Threshold/limit | Unit |
|-----------------------|--|-----------------------|-----------------|----------------------------------|
| Water quality | Annual average concentrations | NO ₃ | 50 | mg/L |
| | | Individual pesticide | 0.1 | µg/L |
| | | Sum of all pesticides | 0.5 | µg/L |
| | Trend | NO ₃ | - | upward, downward, no significant |
| Regulatory compliance | Frequency of exceedance quality standard | NO ₃ | - | % |
| | | Individual pesticide | - | % |
| | Frequency of findings quality standard | Individual pesticide | Detection limit | % |
| | Maximal concentrations | NO ₃ | 50 | mg/L |
| | Maximal concentrations | Individual pesticide | - | µg/L |
| | | Sum of all pesticides | - | µg/L |
| | | All pesticides | - | - |
| | Number of substances | | - | - |

6.3 INDICATORS FOR REGULATORY COMPLIANCE

To better characterise the drinking water quality, particularly the regulatory compliance, the water monitoring data is statistically analysed for various indicators. These indicators may reveal how stable the water quality is over a monitoring period, usually a year (the monitoring periode is in DK not a year as sampels are takes every 3 to 5th year in wells and for samler waterworks also quite seldom in the drinkingwater. They are sometimes applied to monitor raw water quality, but the primary focus is to ensure the stability of treated drinking water quality at the waterworks system.

7. AGRI-DRINKING WATER INDICATORS FOR LINKING FARM AND DRINKING WATER LEVEL (=LINK INDICATORS)

7.1 INDICATORS FOR CATCHMENT TYPOLOGY

Catchment typology is a link indicator to help identifying the dominant water pathways of contaminants in each system.

Catchment typology is a catchment classification framework aiming to group catchments according to their hydrogeological functions. Catchments, therefore, can be classified in many different ways depending on interests and applications (Wagner et al., 2007 and references therein). Here we focus on the catchment typology, which has been developed to evaluate agriculture impacts on water quality.

Rittenburg et al. (2015) propose a conceptual framework of catchment typologies to evaluate the effectiveness of best management practice in agricultural catchments. They define three catchment typologies (A, B1 and B2) by: 1) the budget between precipitation intensity and soil infiltration capacity and 2) the thickness of the soil – i. e. permeable layer (Table 7.1).

In type A catchments, precipitation intensity is greater than soil infiltration capacity; therefore, water cannot infiltrate in the subsurface. Then, water and contaminants will run over the ground surface (i. e. overland flow).

In type B1 catchments, soil infiltration capacity is greater than precipitation intensity while the thickness of permeable layer is thin. In this case, the unsaturated zone may become saturated quickly; consequently, overland flow, interflow, and tile drainage may be the dominant pathways.

In type B2 catchments, soil infiltration capacity is greater than precipitation intensity and the thickness of permeable layer is large. In this case, water may infiltrate into the deeper subsurface. Groundwater and tile drainage may be the dominant pathways.

Table 7.1: Catchment typology and dominant flow paths (modified from Figure 1 of Rittenburg et al., 2015)

| | | Type A | Type B1 | Type B2 |
|---------------------------|---------------------|--|---|---|
| Hydro-geological criteria | Hydrological factor | Precipitation intensity > soil infiltration capacity | Precipitation intensity < infiltration capacity | Precipitation intensity < infiltration capacity |
| | Geological factor | Regardless of soil* thickness | Thin soil | Deep soil |
| Dominant pathways | | Overland flow | Overland flow, interflow, tile drainage | Groundwater, tile drainage |

* Soil refers to a permeable layer.

7.2 INDICATORS FOR LAG TIME

How fast water moves through the hydrogeochemical system is a crucial information to decide on mitigation measures, groundwater protection strategy and to design a monitoring program (Meals et al., 2010). The catchment typology may provide qualitative estimates of the lag time. For instance,

in an overland flow dominated-system, lag time may be “very short” e. g. hours to one day; thus, the effects of mitigation measure can be seen shortly. The lag time can be qualitatively estimated by recharging rate and water age.

7.2.1 Recharging rate

Recharging rate is an indicator of the transit time of water from the ground surface to the saturated zone (Scanlon et al., 2002). In general, recharging rates are exchangeable with transfer time in the unsaturated zone, infiltration rate, percolation rate, and drainage rate.

7.2.2 Groundwater age

Several studies have demonstrated that the age of groundwater can be included as an essential component of evaluation of the impact of agricultural N mitigation measures on groundwater nitrate concentrations (e. g. Hansen et al, 2017). Its inclusion may help to link changes in land use and agricultural management practices to changes in groundwater quality. Groundwater age determination allows concentrations in groundwater to be related to the time of recharge instead of the time of sampling, which, in turn, makes comparison between groundwater quality and pollutant losses from agriculture possible.

Various measurement techniques and hydrological models are available to estimate the groundwater recharging rates and water ages. The recharging rates can be estimated by direct measurements of water infiltration rates, estimations from various tracers, calculation of water mass balance, and analysis of a hydrograph (Table 7.2). The recharging rates also can be calculated using various types of hydrological models.

The water age can also be modelled but is determined mainly by age tracers such as radionuclides (e.g. ^{37}Ar , ^{35}S , ^{14}C) and stable and transient tracers (e. g. CFCs, SF_6 , ^{18}O , ^3H , ^{40}Ar ; Bethke and Johnson, 2008; Busenberg and Plummer, 1992; Laier, 2005).

Time and spatial scales of these methods vary widely and different uncertainties are associated with each method. Therefore, it is recommended to use multiple methods to estimate the recharging rates and water ages (e. g., Bethke and Johnson, 2008; Scanlon et al., 2002).

Table 7.2: Indicators and methods for lag time estimation

| Indicator | Similar indicators | Methods |
|-----------------|---|--|
| Recharging rate | <ul style="list-style-type: none"> Transit time Transfer time in the unsaturated zone Infiltration rate Percolation rate Drainage rate | <ul style="list-style-type: none"> Direct measurements (e. g. seepage meters, infiltration experiment) Tracers (e. g. conservative tracers, age tracers, heat, dye) Water mass balance Hydrograph analysis (e. g. water-table fluctuation, rainfall-runoff response, baseflow discharge) Hydrological modelling |
| Water age | <ul style="list-style-type: none"> Water residence time | <ul style="list-style-type: none"> Age tracers (e.g., radionuclides, noble gases) Hydrological modelling |

7.3 INDICATORS FOR SOURCE IDENTIFICATION

7.3.1 Nitrogen stable isotopes

Nitrogen stable isotopes are indicators used to identify the source types of nitrates in water from mineral fertiliser or organic fertiliser (Xue et al., 2009). Nitrogen has three isotopes (^{13}N , ^{14}N , and ^{15}N). ^{13}N is a radioisotope of which half-life is around 10 minutes. ^{14}N is the most abundant stable isotope (99.6%). The N stable isotopes can be used as an indicator because the ratios of ^{15}N to ^{14}N slightly differ depending on the sources of N. Stable isotope ratios are expressed as the deviation ($\delta^{15}\text{N}$; unit ‰) from the international standard ratio.

Xue et al. (2009) compiled previously reported $\delta^{15}\text{N}\text{-NO}_3$ values and evaluated the potential of N stable isotopes as a N source indicator. They reported that different N sources show different $\delta^{15}\text{N}\text{-NO}_3$ values. For example, $\delta^{15}\text{N}\text{-NO}_3$ of mineral fertilisers such as ammonium fertiliser, nitrate fertiliser, and urea varied between -6 ‰ to +6 ‰. Manure and sewage showed high $\delta^{15}\text{N}\text{-NO}_3$ values: typical $\delta^{15}\text{N}\text{-NO}_3$ values of manure were between +5 ‰ to +25 ‰ and those of sewage were between +4 ‰ to +19 ‰.

When a single N source dominates, $\delta^{15}\text{N}\text{-NO}_3$ can be a useful tool (Xue et al., 2009). However, when multiple sources are present, the $\delta^{15}\text{N}\text{-NO}_3$ interpretation can be highly uncertain because isotope fractionation occurs during the N cycles through various soil and microbial reactions. To overcome the uncertainty, combining with other isotopes such as $\delta^{18}\text{O}\text{-NO}_3$ or boron isotopes ($\delta^{11}\text{B}$) are recommended.

7.3.2 Sources of pesticides

Pesticides from point sources are released and transported in a different manner compared to those of diffusion sources. For example, accidental spills during tank filling may result in extremely high but localised concentrations of pesticides in water. Consequently, the point source may show a sharp concentration breakthrough curve. In addition, the point sources may be active randomly; therefore, the pesticide concentration can differ greatly over time.

Thorling et al. (2015) had identified such patterns by analysing long-term monitoring data of pesticides in groundwater in Denmark. They, then, proposed a set of indicators and threshold values to identify influx of point sources (Table 7.3). Several regions in Denmark has implemented this protocol since 2018.

This set of pesticides indicators and threshold-values may be applicable only for Denmark and for systems that are similar to Denmark (i. e. matrix-flow dominating the groundwater system). For the surface water system, different indicators and thresholds will be required. For instance, the most obvious signal of point source input to the surface water is high pesticide concentrations at low discharge (Holvoet et al., 2007).

Table 7.3: Indicators and threshold values for pesticide point source (Thorling et al. 2015)

| Indicators | Threshold |
|--|--|
| Numbers of pesticide | >4 over the detection limit or >2 over the water quality limit |
| Maximum concentration | >1 µg/L for individual pesticide |
| Temporal variation in concentrations | >1 order of magnitude |
| Spatial variations in concentrations | Any difference in 100 m distance |
| Decay rate of pesticide concentration in water | >0.01 µg/L/yr |

7.4 INDICATORS FOR VULNERABILITY OF THE HYDROGEOLOGIC SYSTEM

7.4.1 Nitrate Vulnerability Assessment (NVS)

Groundwater nitrate vulnerability is defined as the sensitivity of an aquifer to be contaminated by nitrate. Groundwater vulnerability assessments are means to synthesize complex hydrogeological information into a form usable by planners, decision and policy makers, geoscientists and the public.

7.4.1.1 Depth to nitrate reduction interface

The depth to the nitrate reduction interface in the groundwater can be used as a single and simple indicator for nitrate vulnerability. Indeed, nitrate vulnerability assessment is a highly comprehensive analysis. Therefore, depth to nitrate reduction interface from the land surface, if direct observations are available, can potentially be used as a secondary indicator to give a simple estimate of the nitrate vulnerability.

7.4.1.2 Assessment methods for nitrate vulnerability

In general, four types of assessment methods for vulnerability are employed:

- Index methods such as DRASTIC (Foster et al., 2013)
- Statistical methods (e. g. logistic regression)
- Process-based groundwater models (e. g. MODFLOW; Sonnenborg et al. 2015)
- Cognitive Site-specific Concept for Assessment of Nitrate Vulnerability of Aquifers (SCANVA; Hansen et al. 2016)

7.4.2 Pesticide vulnerability assessment

Pesticide vulnerability assessment considers both pesticides properties and the environmental conditions. As mentioned earlier, pesticide properties govern its persistence and mobility in the environment and consequently the pesticide vulnerability of the environment. Therefore, pesticide vulnerability assessment should consider both aspects.

An extensive review of pesticide risk indicators is available in Chapter 7.5.2. The predictive power of these risk indicators may vary greatly depending on their structure. For instance, Pierlot et al. (2017) evaluated the predictive quality of 26 pesticide risk indicators. They compared results among the indicators and with measured data from three sites in France as well. They reported that the more complicated risk indicators were, the better predictive their quality was. For instance, MACRO, which is a process-based model of 1-D flow of water and pesticides, showed the best predictive power. While the indicators that only based on the pesticides dose (e. g. TFI) showed the lowest predictive quality.

A pesticide vulnerability map at the European level is available (Tiktak et al., 2006).

7.5 ENVIRONMENTAL RISK INDICATORS

A large number of environmental risk indicators have been developed to assess the risk of nitrogen losses from agriculture and the water pollution risk of pesticides. These indicators may refer to all kind of indicators presented in this paper, from driving forces over pressure, state/impact and link indicators.

7.5.1.1 Nitrogen loss indicators

N loss indicators (NLIs) are defined according to Buczko and Kuchenbuch (2010a) as environmental management tools for assessing the risk of diffuse N losses from agricultural fields.

They range in complexity from simple proxy variables to elaborate systems of algebraic equations. Table 7.4 shows an overview of nitrogen loss indicators being developed for the quantification of N losses from the agricultural managed areas. With reference to the DPSLIR-model, Nitrogen loss indicators may be composed of driving forces, pressure and link indicators.

Table A-4 in the annex gives an overview of the approaches of the different indicators listed in Table 7.4 to assess N-losses (Buczko and Kuchenbuch 2010a). Buczko and Kuchenbuch (2010a) divide the N loss indicators into three main- and 5 sub-groups.

- **NLIs based on the N source**

The amount of nitrogen which is possibly available to nitrogen leaching and other diffuse N losses can be estimated by two different types of approaches: either by calculating a nitrogen budget (=N input/output budget, see Chapter 5.9) or by measuring directly the mineral N content in the soil profile, usually immediately before the start of the main leaching period (N_{min}-concentration, see Chapter 5.5.3).

- **NLIs based on transport terms**

Other indicators only (or primarily) refer to the transport properties of the soil, the vadose zone and/or the aquifer.

- **Groundwater vulnerability indices:** The widely used groundwater vulnerability indices are based on the concept of the “intrinsic vulnerability” of the groundwater and are used independently from the type of contaminant. They are often utilized with respect to vulnerability for diffuse nitrate pollution from agricultural areas.
- **Approaches based on the hydrology of the soil zone:** The Exchange frequency of the soil solution within the effective root zone’ (EF) and similar NLIs are based on the hydrology of the soil zone (see Chapter 5.4.2).

- **Composite NLI approaches**

- **Score-based NLIs:** An example for a score based NLI is an aquifer vulnerability map, based on the evaluation and scoring of various environmental frame conditions such as presence or absence of a primary aquifer, depth of the groundwater, soil drainage class, recharge available and land use (Cepilecha et al., 2004)

DRASTIC is the most widely used method to evaluate the intrinsic vulnerability not assigned to a specific chemical pollutant as e. g. nitrate. It evaluates the vulnerability based on the hydrogeological structures of the site and considers seven factors (Aller et al., 1987):

1. Depth to groundwater
2. Recharge (Net)
3. Aquifer media
4. Soil media
5. Topography (slope)
6. Impact of unsaturated zone media
7. Conductivity (hydraulic) of aquifer

Pollution potential is rated for each factor: for example, groundwater deeper than 100 m, the rate value is 1 while the depth between 0-5 m rated as 10. The factors are also weighted for their importance. Then, the vulnerability can be assessed by summing up these seven factors.

- **Model-type NLIs: simple equation:** Simple equations to estimate nitrate leaching were used by De Jong et al. (2007) in Canada: the authors combines the amount of residual soil nitrogen, estimated from the annual nitrogen budget with an estimation of nitrate leaching using a simplified water balance.
- **Model-type NLIs, complex approaches:** Table 5.2 lists a range of NLI-models which combine the above approaches. Further information on the single models can be found in the comprehensive review of Buczko and Kuchenbuch (2010a).

Buczko and Kuchenbuch (2010a) summarised their review as follows:

- NLIs developed from the “agricultural viewpoint” are usually restricted to the soil zone (what corresponds to the driving force and pressure ADWIs within the DPSLIR-framework in the FAIRWAY project) and estimate the N losses that leave the root zone. The fate of diffuse nitrogen losses – and their impact on the environment, are very much influenced by the properties of the unsaturated (vadose) zone beneath the root zone (thickness, hydraulic conductivity, texture, organic matter content) and the aquifer). The authors conclude, that it is not sufficient to estimate the amount of N that leaves the root zone alone (this is the reason why we introduce the Link indicator for the DPSLIR-framework).
- The authors criticise a lack of calibration and validation of the NLIs against field data.
- As each NLI is using another scaling, a comparison between them is hampered.
- Especially composite NLIs show – related to the number of single components and their weighting – a low relative sensitivity for changing conditions.

Cannova et al. (2008) compiled a review on the modelling of N dynamics in order to assess environmental impact of cropped soils. The spacial scale of most of the models discussed (51 of 62 models studied) was the field scale, followed by the watershed scale (6 models) and the farm scale (4 models). Most of the models operating at farm and watershed scale are indicators.

Table 7.4: Overview Nitrogen Loss Indicators and related approaches to assess the risk of N loss from agricultural fields (Buczko and Kuchenbuch, 2010a, complemented)

| Main group | Sub-group | N loss indicator (acronym) | Reference | Loss processes |
|---------------------|--------------------------------------|---|----------------------------------|----------------|
| Source-based (S) | | (S1) N budget (NBal) | Oenema et al. (2003) | NL |
| | | Cassis N | Poisvert et al , (2016) | NL |
| | | Nopolu | Doublet et al, (2013) | NL |
| | | Nitrogen soil surface budget („Nährstoffvergleich nach DüV“) | DüV (2017) | NL |
| | | Nitrogen farm budget („Stoffstrombilanz“) | StoffBiV (2017) | NL |
| | | (S2) “EQUilibre de Fertilisation” (EQUIF) | Aveline et al. (2009) | NL |
| | | (S3) Residual soil mineral nitrogen (RSN) | Schweigert and Zimmermann (2003) | NL |
| | | (S4) N application rate (NFertApp) | Bockstaller et al. (2009) | NL |
| | | (S5) N use efficiency (NUE) | Shaffer and Delgado (2002) | NL |
| | | (S6) N concentrations of maize plants at silage maturity (Ncm) | Herrmann et al. (2005) | NL |
| Transport-based (T) | Groundwater vulnerability (TG) | (TG1) DRASTIC | Aller et al. (1987) | NL, VZ, GW |
| | | (TG2) Protection function of the vadose zone (“Schutzfunktion der Grundwasserüberdeckung”-SG) | Hölting et al. (1995) | NL, VZ |
| | | (TG3) Aquifer Vulnerability Index (AVI) | van Stempvoort et al. (1993) | VZ |
| | | (TG4) Multivariate Logistic Regression for nitrate contamination of groundwater (MLR) | Nolan (2001) | NL, VZ, GW |
| | Based on hydrology of soil zone (TS) | (TS1) Exchange frequency of the soil solution (EF) | Müller (2004) | NL |

| Main group | Sub-group | N loss indicator (acronym) | Reference | Loss processes |
|-------------------|------------------------|---|----------------------------|--------------------------|
| | | (TS2) Drainage index (“Indice de drainage”) (P/RU) | CORPEN (2006) | NL |
| | | (TS3) Leaching Index (LI) | Williams and Kissel (1991) | NL |
| Composite NLI (C) | Based on scores (CS) | (CS1) Colorado vulnerability map (CO-VM) and matrix (COVMX) | Cepilecha et al. (2004) | NL, VZ |
| | | (CS2) “Environmental Sustainability” (EnSus) | Woods et al. (2006) | NL, SR |
| | | (CS3) modified Nitrogen ranking scheme (mNRS) | Magette et al. (2007) | NL, SR |
| | | (CS4) Nitrate Leaching Hazard Index for Irrigated Agriculture (NLHI-IRR) | Wu et al. (2005) | NL |
| | | (CS5) Nonpoint-Source Agricultural Hazard Index (NPSAH) | Trevisan et al. (2000) | NL |
| | | (CS6) N Index of the Ministry of Agriculture, Food and Rural Affairs in Ontario (OMAFRA-NI) | OMAFRA (2003) | NL |
| | | (CS7) Pennsylvania N Index (PA-NI) | Heathwaite et al. (2000) | NL |
| | Model-equation (CE) | (CE1) Indicator risk of water contamination by nitrate-nitrogen (IROWC-N) | De Jong et al. (2007) | NL, (DN) |
| | | (CE2) Potential nitrate concentration in leachate (PNCL) | Bach (1987) | NL, (DN) |
| | Model-complex NLI (CC) | (CC1) Annual Leaching Risk Potential (ALRP) | Pierce et al. (1991) | NL, (AV, DN,) VZ |
| | | (CC2) “IN losses” indicator (IN) | Pervanchon et al. (2005) | NL, AV, DN, NO |
| | | (CC3) Methodology for the evaluation of the risk of nitrate leaching (Méthode d’Evaluation des Risques de Lixiviation des Nitrates)(MERLIN) | Aveline et al. (2009) | |
| | | (CC4) N-Index Tier-1 (NIT-1) | Delgado et al. (2008) | NL, AV, DN, ER, SR, (VZ) |
| | | (CC5) Norway N index (NO-NI) | Bechmann et al. (2009) | NL, DN, ER, SR |
| | | Netherlands: combination of N budget and leaching fractions | Schröder et al. (2007) | NL |

NL=leaching, VZ=flow through vadose zone, AV=ammonia volatilization, DN=denitrification, ER=erosion, SR=surface runoff, GW=groundwater flow, NO=NO (nitric oxide) emission

In Table 7.5, different N-indicators are evaluated (Lebacqz et al, 2013).

Table 7.5: Description and comparison of four indicators related to nitrogen management, on the basis of selection criteria concerning relevance, practicability, and end user value of these indicators (Lebacqz et al., 2013)

| | | | Mineral nitrogen fertilisation | Livestock stocking rate | Nitrogen surplus | Nitrogen indicator (IN), Bockstaller et al., 2008) | Groundwater nitrate concentration |
|-------------|----------------|---------------------------|--|---|---|--|---|
| Description | | Definition | N mineral fertilisers inputs | Density of livestock on the forage area | Difference between N inputs entering and N outputs leaving the farming system (= farmgate budget) | Output of a model simulating NO ₃ -leaching, NH ₃ and N ₂ O emissions | Direct measurement |
| | | Unit | kg N/ha | Livestock units(LU)/ha | kg N/ha or kg N/kg product | Scores | mg NO ₃ /liter |
| | | Type | Means-based | Means-based | Emissions (budget) | Emissions (model-based) | Effect-based |
| | Relevance | Temporal scale | Annual | Annual | Annual–monitoring | Annual, rotation | Monitoring |
| | | Spatial scale | P/F | F | F | P/F | Watershed/R |
| | Practicability | Validity | Weak link with the environmental impact, not to be used alone and for a single year (CORPEN, 2006) | Literature (Vilain, 2008) | Literature (Thomassen and de Boer 2005; Vilain, 2008) | Literature (Bockstaller et al., 2008) | Direct link with the environmental impact |
| | | Data availability | ++ | ++ | + | – | -- |
| | | Quantitative/ qualitative | Quantitative | Quantitative | Quantitative | Quantitative → qualitative | Quantitative |
| | End user value | Ability to summarise | – | – | + | ++ | ++ |
| | | Reference values | Regional, sectoral reference | Regional, sectoral reference | Regional, sectoral reference | Scores 0–10 (10=no losses, acceptable value from 7) | 50 mg NO ₃ /liter |
| | | Farmer's leeway | ++ | + | + | +/- | – |

P=parcel level; F=farm level; R=regional level; ++, +, +/-, -, -- relative degree of availability, ability to summarise, and possibility for the farmer to influence the output value

7.5.2 Pesticide risk indicators

7.5.2.1 General characteristics of Pesticide risk indicators

Pesticide risk indicators, as specified in the National Action Plans of the EU Member States, are all associated with a goal expressed in terms of volume, frequency of use or risk and impact. Some indicators have adopted quantified and time-bound targets, while some have not. The general trend has been to move away from volume reduction goals towards reduction in use, environmental impact and risk. A major constraint of volume reduction targets is that they do not take into account the replacement of lower-dose pesticides with newer and more potent ingredients (Barzman and Dachbrodt-Saaydeh, 2011).

Pesticide risk indicators are mathematical equations that consider data inputs such as application rates, toxicity levels of a pesticide's active ingredient, meteorological data, the soil characteristics of farm fields, and other information to generate potential risk scores for pesticide applications. These risk scores represent the best estimate of a pesticide's impact on the surrounding environment and can be used to evaluate and quantify mitigation measures.

Pesticide risk indicators are generally based on models that predict the environmental impact of certain pesticides. Studies to evaluate and validate the indicators in the field are rare. The lack of validation studies of indicators also hampers the evaluation of mitigation measures (Greitens and Day, 2007).

There are three principal areas at issue for pesticide environmental indices, namely: the criteria and standards chosen to assess the environmental impact of pesticides; the methods used to estimate their environmental impact (including the aggregation of diverse data); and the data used (e.g. their accessibility and reliability). The choice of parameters and methods by which to assess the types and range of impacts is the starting point for indicator development (Falconer, 2002).

Work on pesticide indices and ranking models has been driven by a wish to compare different chemicals as a step towards more sustainable crop protection strategies. There is currently a significant information gap, for farmers and policy-makers, with regard to the relative merit or dis-merit of different pesticides from an environmental perspective.

7.5.2.2 Shortcomings and challenges of risk indicators for pesticides

There are many conceptual and practical challenges to indicator development and application, especially with regard to assessment of indirect environmental effects, given the multi-dimensionality of pesticide usage, properties and impacts. A significant problem lies in obtaining sufficient and accurate input data, coupled with the lack of knowledge and understanding of the links between pesticide use, emissions, environmental concentrations and any adverse effects.

Furthermore, data on eco-toxicological effects have to be collected using standardised testing protocols if they are to be comparable across different circumstances. New products are emerging onto the market constantly, but there are only limited data on the effects of these, and the problems of data-set incompleteness need acknowledgement in indicator development if they are to be used as real decision-making bases.

Pesticide indicators are inevitably partial, given that they are based on selected components of interest, and on a particular configuration of preferences where parameters relating to disparate impacts are aggregated. In this sense, indicators are unavoidably biased (Falconer, 2002).

Spatial scale issues need consideration, and the potential biases of aggregation must be at least acknowledged, if not overcome. Risks and impacts are likely to vary spatially, implying that

assessment models should be differentiated between regions, in terms of their structure or the data on which they are calibrated.

Finally, an important issue for indicators of all types is the timescale over which a pesticide's environmental burden is assessed. Adverse environmental effects may be separated from pesticide application by long time lags, especially in the case of chronic health effects. A major disadvantage of indicators based on current usage is that they exclude consideration of impacts arising from past usage of persistent compounds.

7.5.2.3 Characterisation of the most frequently used/most important pesticide risk indicators

Table A-5 in the annex gives a compilation of pesticide risk indicators used in Europe, including specific targets of Member States and level of spatial applicability. The large number and diversity of pesticide risk indicators can be explained by

- Role of indicators in EFSA admission process for active substances,
- Diversity of active substances,
- Diversity in products/formulations/combination,
- Diversity of target organisms/environmental compartments,
- Problems in direct detection in environment.

As shown in Table A-5, European countries use very diverse and different indicators for their pesticide monitoring and reduction aims according to regulation (EC) No 1185/2009.

Below, the most frequently used/important indicators for pesticide risks are further explained. These indicators refer not only to leaching risks, but in many cases focus on other environmental and health risks.

7.5.2.3.1 Groundwater Ubiquity Score (GUS) Index

One of the indicators that take into account only leaching is the Groundwater Ubiquity Score or GUS (Gustafson, 1989). The GUS is an experimentally calculated value that relates pesticide half-life and K_{oc} (from laboratory data). The GUS may be used to rank pesticides for their potential to move toward groundwater. It can be calculated as

$$GUS = \log_{10} (\text{half-life}) \times [4 - \log_{10} (K_{oc})].$$

Although the GUS index is interesting in terms of its simplicity to use – only few data are required and these data are widely available in environmental fate databases, it has a low validation status and ignores the contribution of the weather, soils and the subsoil to the risk of leaching.

7.5.2.3.2 Environmental Impact Quotient (EIQ)

The EIQ consists of three components, a farm worker component aggregating human toxicity information, a consumer component aggregating human chronic toxicity, pesticide fate in soil and food and leaching to groundwater and an ecological component adding up effects on aquatic and terrestrial organisms (Kovach et al., 1992). For each parameter evaluated EIQ uses a rating system from 1 (least harmful) to 5 (most harmful). The overall EIQ is expressed as the average value of the three components. The EIQ has been applied in studies assessing trends in impact of pesticides in orchard fruit in the UK over years (Cross, 2012), the environmental impact of glyphosate resistant weeds in Canada (Beckie et al., 2014) and in studies comparing cropping systems based on conventionally bred crops with genetically-modified herbicide resistant crops (Stewart et al., 2011).

7.5.2.3.3 Pesticide Environmental Risk Indicator (PERI)

The PERI (Nilsson, 1999) (Pesticide Environmental Risk Indicator) aims at evaluating pesticide use by farmers over a range of years as part of a certification process. It was developed as a part of the International Organization for Standardization (ISO)-14001 certification process for use by farmers to record and evaluate possible environmental risks over time. PERI combines variables from groundwater, surface water, and air compartments in one equation to obtain an environmental risk score (ERS). The potential emission to groundwater and air is represented by a score between 1 and 5, using data on soil degradation, mobility and Henry's constant. The final score is determined by combining the score for emissions with a score for toxicity (in different compartment).

7.5.2.3.4 Toxicity – Human Health Persistency (THP) approach

The THP hazard rating approach was developed by the Organization for Economic Co-operation and Development (OECD, Paris, France) in 1982. Individual relative risk levels and the overall THP value constitute the two components of this approach. (OECD, 1982) The THP rating approach consists of three variables: Toxicity to the aquatic environment (T), hazard to human health by oral intake (H) and the persistence rating value (P), which is related to the probable half-life expressed in days.

The THP rating approach can be used to compare and rate the hazards that pesticides pose to humans, wildlife, and the overall ecosystems through exposure to water and land. To better understand and refine contaminant fate and transport, risk indicators could be integrated with forensic methods (e. g., chemical and/or isotopic fingerprinting, contaminant transport models, geographic information system (GIS) representation and statistical methods) to reduce limitations of risk indicators and improve the risk assessment evaluation (Muhammetoglu et al., 2010).

7.5.2.3.5 Environmental Yardstick for Pesticides (EYP)

The EYP has been developed as a tool for farmers to select pesticides with the least environmental impact and to quantify the impact of their use. For each pesticide the yardstick assigns environmental impact points for the risk to water organisms, the risk of groundwater contamination and the risk to soil.

There are three output values: acute risk to water organisms (most sensitive organism); risk of groundwater contamination; acute and chronic risk to soil organisms. The potential risk is expressed in environmental impact points (EIPs). The more EIPs a pesticide gets, the higher its impact on the environment. The EIPs are based on the predicted environmental concentration (PEC) in a certain compartment and the maximum permissible concentration (MPC) set by the Dutch government. The EIP are initially assigned for a standard application of 1 kg active ingredient per hectare. For different rates of application, the number of EIP is multiplied by the actual dose.

The score on the yardstick depends on chemical properties (persistence and mobility in soil, toxicity) of both active ingredient and principal metabolites, dose rate, organic matter content of the soil (influences transportation in soil), time of application (influences degradation and transportation in soil), method of application (influences the amount of emission to surface water) and distance to surface water (influences the amount of emission to surface water).

The data on degradation rates, adsorption coefficients, toxicity to aquatic organisms and toxicity to soil organisms are drawn from data sheets compiled by the Dutch Regulatory Committee for agrochemicals.

As the name indicates the EYP only considers environmental effects of pesticides. EYP is not as widely used, as for example EIQ, but has been applied to assess the impact of pesticide use in integrated and conventional potato production in the Netherlands (De Jong and De Snoo, 2002).

EYP calculates PEC values but rather than comparing these values to LC/LD/EC/ED50 and NOEC values they are multiplied by pesticide toxicity data to produce Environmental Impact Points (Reus and Leendertse, 2000).

7.5.2.3.6 *Treatment Frequency Indices (TFI)*

The TFI was developed in Denmark 2008 and replaced the simple measurements of the applied pesticide volume as indicator. It has been in use since in several countries worldwide as national or regional indicator or as part of projects. The TFI is calculated by the theoretical number of pesticide treatments per hectare, based on standard dose rates of active ingredients, and the amount of pesticides sold yearly. An advantage of the TFI is that the indicator can be aggregated into a single value, e.g. a TFI of 1 is equivalent to one full dose applied on a certain agricultural area (Gravesen, 2003).

The TFI was e.g. used to calculate differences in the efficiency of a range of cropping systems concerning fungicide or herbicide use reduction (Andert et al., 2016; Bürger and Gerowitt, 2009), to compare organic and conventional cropping systems in terms of earthworm abundance in the topsoil (Pelosi et al., 2013) or to estimate the intensity of pesticide and fertiliser application on tomato plants in Benin (Perrin et al., 2015). Some working groups have used the TFI specifically to track herbicide usage in different cropping systems (Herbicide treatment frequency index). In general, the TFI can be used for any type of pesticide (fungicide, insecticide, herbicide etc.).

The TFI is also applied to fulfil the targets layed down in the German national action plan (NAP) to meet the requirements of Regulation (EC) No 1185/2009 concerning statistics on plant protection products (Freier et al., 2015).

One constraint of the TFI is that progress towards products with lower toxicity cannot be covered by the indicator: the TFI does not account for the chemical or toxic properties of some specific substances of the pesticide. Additionally, ecological effects or damages cannot directly be assigned to pesticide applications, since interactions and intermediate steps often have a major influence on pesticide environmental behaviour (Ongley, 1996). Consequently, a reduction in treatment frequency is not sufficient to reach conclusions regarding trends in environmental and health risks, even though a correlation is commonly assumed (Barzman and Dachbrodt-Saaydeh, 2011).

As the TFI is not related to the active substances used, no relation can be established to elevated concentrations of single substances in raw water.

7.5.2.3.7 *Pesticide Load Index, Load Index (PLI)*

The PLI is defined as the amount of the applied product multiplied by the toxicity to non-target-organisms. The indicator has the unit “number of applications (toxicity doses) per ha and year”. As special feature, the toxicity of the pesticide (LD₅₀, LC₅₀, determinable for different organisms) is considered in the assessment. The LD₅₀ value is often used to analyse the influence of a certain pesticide on non-target organisms such as the beneficial organism *Trichogramma brassicae* (Ghorbani et al., 2016). The Load Index thus describes the calculated number of toxic doses in the sold amount of pesticides.

The PLI was developed and is used in Denmark as advancement to the TFI. The PLI was the basis of a new pesticide taxation system with the aim to tax pesticides according to their toxicity. Additionally, for the implementation and effectivity of the indicator, farmers in Denmark are required to upload their pesticide use data, i. e. the annual pesticide statistics. Thus, the PL can be calculated on the basis of pesticide use data rather than on basis of sales data that may not reflect the actual use by farmers. The data can also be used to create maps with detailed information on pesticide use in different regions and to identify hot spots of pesticide use for designing monitoring programmes and launch initiatives to reduce the pesticide load (Kudsk et al., 2018).

The PLI as used in Denmark constitutes of three sub-indicators: the PL for human health, the PL for ecotoxicology PL_{ECO} and the PL_{FATE} for the environmental fate. PL_{ECO} is calculated on the basis of LC/LD/ EC_{50} values of the active ingredients for acute toxicity to fish, daphnia and earthworms. PL fate is calculated on the basis of the half-life in soil (DT_{50}), the bioaccumulation factor (accumulation of toxic substances in aquatic organisms) and the SCI-GROW index (a model developed by the US-EPA to estimate pesticide concentrations in vulnerable ground water) (Kudsk et al., 2018).

One constraint of the PLI, as with the TFI, is that ecological effects or damages cannot directly be assigned to pesticide applications, since interactions and intermediate steps often have a major influence on pesticide environmental behaviour (Ongley, 1996). Also, the PLI/LI does not include information on exposure risks or buffer zones required for risk mitigation.

The PLI consists of three sub-indicators for human health, ecotoxicology and environmental fate, respectively. For each of the three sub-indicators a pesticide load (PL) is calculated and expressed as the PL per unit commercial product (kg, L or tablet). PL for human health (PL_{HH}) is based on the risk phrases on the product label, while PL for ecotoxicology (PL_{ECO}) is calculated on basis of the LC/LD/ EC_{50} values of the active ingredients for acute toxicity to mammals, birds, fish, daphnia, algae, aquatic plants, earthworms and bees and NOEC values for chronic toxicity to fish, daphnia and earthworms. PL for environmental fate (PL_{FATE}) is calculated on basis of the half-life in soil (DT_{50}), the bioaccumulation factor (BCF) and the SCI-GROW index. PL does not consider the actual exposure, i. e. it reflects the relative risks associated with the use of pesticides (Kudsk et al., 2018).

7.5.2.3.8 Norwegian Pesticide Risk Indicator (NERI)

The Norwegian pesticide risk indicator (NERI) was developed with a dual purpose, as a tool to assess the risk of pesticide use and as a method for taxation of pesticides (Stenrød et al., 2008). Like EIQ, NERI is a rating system. For human health, NERI classifies products into 4 risk classes (low, medium, high and very high risk) according to the risk phrases on the label. NERI also considers the risk of operator exposure when preparing the spray mixture and when applying the pesticide by multiplying the scores for human health with scores for formulation type and application method.

Environmental risk is assessed by adding up scores for effects on earthworms, bees, birds, aquatic organisms, mobility and leaching potential, persistence, bioaccumulation and a score for formulation type. Based on the accumulated score, NERI classifies products into three environmental risk classes. By combining the information on human health and environmental risk, classifications products are grouped into 7 pesticide tax classes.

A total environmental risk index is calculated for each active ingredient in each individual product. The total environmental risk index, for each individual active ingredient in each product is multiplied by the area on which the product is used a particular year, to give the relative environmental load from a specific pesticide. These indices are summed for the area and time period investigated to obtain a cumulative risk index.

7.5.2.3.9 Environmental Information System (EIS Pesticides)

The environmental information system (EIS Pesticide) for pesticide issues was created using spatial data warehouse technology. This system allowed qualifying agricultural activities along with river basin characteristics. Specific spatial objects were designed to characterise practices at the relevant scales. The axes of analysis allowed providing results at different levels of integration, for different dimensions e. g. time, sprayed surface area, or pesticide type. The system was tested using datasets collected in the Charente watershed and its sub-basins and calculated pesticide pressure indicators on demand for each aggregation level defined (Vernier et al., 2013).

7.5.2.3.10 SYNOPSIS

SYNOPSIS is a risk indicator developed in Germany (Gutsche and Strassemer, 2007) to assess environmental risks.

Besides pesticide use data, SYNOPSIS also requires information on crop stage, application technique, soil type, location, topography of the field, etc.. Based on this information, SYNOPSIS calculates the Predicted Environmental Concentrations (PEC) for different compartments and compare the PEC values to the LC₅₀ and NOEC values for the various target organisms and Exposure Toxicity Ratios (ETR) are calculated for each target organism. In contrast to PLI or EIQ, SYNOPSIS considers the effect of mitigation measures such as buffer zones or low drift spraying equipment because the concept is based on the calculation of PEC values. Originally, SYNOPSIS was developed to assess the environmental risks at farm or regional level but not at national level (Hernández-Hernández et al., 2007; Strassemer et al., 2018). SYNOPSIS-GIS is used to assess the field specific risk indices for all agricultural fields within a certain region. These field specific risk indices are then aggregated on regional level to identify so called hot spots (Gutsche and Strassemer, 2010) or evaluated to analyse pesticide use strategies under regional environmental conditions (Strassemer and Golla, 2018). In a separate approach, SYNOPSIS-TREND calculates relative risk scores on national level, based on sales data and environmental scenarios. This approach is used as indicator to evaluate national risk trends within the NAP.

7.5.2.3.11 SYNOPSIS-WEB

SYNOPSIS-WEB is a free-to-use online tool to assess acute and chronic pesticide risks to soil, surface water and pollinators, as well as via leaching to groundwater. It can be used to compare and assess pesticide risk under realistic application patterns and environmental conditions (Strassemer et al., 2017). SYNOPSIS-WEB can reliably model the aquatic exposure of pesticides detected during monitoring and additionally revealed risks from pesticides that could not be detected in surface water due to their high toxicity at concentrations close to the limit of quantification. The program has the potential to provide relevant information to European farmers, authorities and agronomists for developing and optimizing integrated pest management (IPM) strategies with particular focus on minimizing environmental risks. The structure of the model allows for future adaption and integration of novel approaches to risk assessment for a wider range of reference organisms and a larger set of mitigation measures. Anyhow, Strassemer et al. (2017) point out that further evaluation of the tool is needed to assess model outputs concerning exposure assessment for soil, groundwater and field margin biotopes.

7.5.2.3.12 I-Phy

I-Phy (former name Ipest) was developed by van der Werf and Zimmer (1998) and is a so-called fuzzy expert system (Van Der Werf and Zimmer, 1998). It relates to the potential environmental impact of the application of a pesticide in a field crop and is defined by four modules. One reflects the presence (rate of application) of the pesticide, the other three reflect the risk for three major environmental compartments (groundwater, surface water, air).

The input variables for these modules are pesticide properties, site-specific conditions and characteristics of the pesticide application. I-Phy calculates the risk of surface water contamination, risk of groundwater contamination and risk of air contamination based on information on pesticide properties, site specific conditions and application conditions. I-Phy has been used to assess the sustainability of cropping systems in France (Bockstaller et al., 2008; Chikowo et al., 2009) and recently an improved groundwater module was published (Lindahl and Bockstaller, 2012).

7.5.2.3.13 System for Predicting the Environmental Impact of Pesticides (SyPEP)

SyPEP model was developed help farmers, extension services and regulating agencies by providing information on the environmental impact of pesticides. The indicator calculates a long-term PEC for groundwater, a short-term PEC for groundwater, and a PEC for surface water. It then divides toxicity information by the PEC in each environmental compartment. The resulting value in each of the three compartments is then ranked on a 0–5 scale to arrive at a SyPEP score (Pussemier, 1999; Pussemier and Steurbaut, 2004).

7.5.2.3.14 Environmental Potential Risk Indicator for Pesticides (EPRIP)

EPRIP calculates and compares PECs across the environmental compartments of air, soil, groundwater and surface water (Oliver et al., 2016; Padovani et al., 2004; Trevisan et al., 2009). It is based upon the ratio of PEC, which represents the estimated exposure at a local scale (field and surroundings) with short-term toxicity data. ETR values are transformed into risk points (RP) using a scale from 1 to 5 where the PEC value and corresponding RP are: <0.01 is RP 1, <0.1 is RP 2, <1.0 is RP 3, <10 is RP 4 and >10 is RP 5. The final EPRIP score is obtained by multiplying the RP values calculated for each compartment: surface water, groundwater, soil and air (Oliver et al., 2016; Trevisan et al., 2009).

To arrive at a PEC, the indicator uses a variety of equations that consider a pesticide's exposure potential and sitespecific application data. Then, EPRIP divides the PEC by the pesticide's toxicity data in order to generate an EPRIP potential risk score for beneficial organisms and humans. EPRIP could be a useful tool for farmers, technical advisors and regulating authorities to provide information on the environmental effects for different pesticide treatment strategies and to facilitate the selection of the best option to reduce the risk associated with pesticide use.

7.5.2.3.15 Multi-attribute Toxicity Factor Model (MATF)

It is used to calculate the toxicity of pesticides for the 'Healthy Grown' Wisconsin Potato IPM Labeling Project. The MATF indicator ranks toxicity data in order to generate toxicity factor scores for beneficial organisms and humans. It then multiplies these scores by the pesticide's application rate in order to produce toxicity units for each application, with more toxicity units indicating more potential risk (Benbrook et al., 2002).

7.5.2.3.16 HAIR

Hair calculates risk indicators related to the agricultural use of pesticides in EU Member States. HAIR combines databases and models for calculating potential environmental effects expressed by the exposure toxicity ratio (Kruijne et al., 2011). The set of risk indicators currently built in HAIR includes aquatic indicators for algae, daphnia and fish, a groundwater indicator, terrestrial indicators for birds, mammals, earthworms and honey bees, and occupational risk indicators for operators, re-entry workers, bystanders and residents (Kruijne et al., 2011). The intended use of HAIR is to calculate trends in aggregated risk at national scale in support of the evaluation of EU policies, based on compound properties from EFSA and pesticide sales and usage from EUROSTAT databases. HAIR can also be used with more refined usage input data.

7.5.2.3.17 Pesticide Emission Assessment at Regional and Local Scales (PEARL)

PEARL is a one-dimensional numerical model of pesticide behaviour in the soil-plant system. It simulates water flow in soil and considers changes in groundwater levels due to rainfall. Soil evaporation and plant transpiration are calculated. For the FOCUS scenarios, crop growth is simulated with a simple growth model that assumes a fixed length of the growing season. In this growth model, both the leaf area index and the rooting depth are a function of the development stage of the crop. Heat flow in soil is described, too. The thermal properties are a function of porosity and

water content and are therefore a function of time and soil depth. PEARL is based on: (i) the convection/dispersion equation including diffusion in the gas phase with a temperature dependent Henry coefficient, (ii) a two-site Freundlich sorption model (one equilibrium site and one kinetic site), (iii) a transformation rate that depends on water content, temperature and depth in soil, (iv) a passive plant uptake rate. The model includes formation and behaviour of transformation products and describes also lateral pesticide discharge to drains (but drainage is switched off for the FOCUS scenarios). PEARL does not simulate preferential flow. Volatilisation from the soil surface is calculated assuming a laminar air layer at the soil surface. PEARL uses an explicit finite difference scheme that excludes numerical dispersion (the dispersion length was set to 5 cm) (Leistra and Boesten, 2010; Leistra and Van Den Berg, 2007; Tiktak et al., 2013).

7.5.2.3.18 *GeoPEARL*

This program combines the one-dimensional pesticide leaching model PEARL with a geographical information system to calculate the leaching potential of pesticides into local surface waters and the regional groundwater. To describe seepage and drainage fluxes, the model was loosely coupled with a regional groundwater model. Simulations carried out for four different pesticides showed that the average fluxes of pesticide into local surface waters were higher than the average fluxes of pesticide into the regional groundwater. The behaviour of the different substances differed substantially (Tiktak et al., 2002).

7.5.2.3.19 *TOXic substances in Surface Waters (TOXSWA)*

TOXSWA is a quasi-two-dimensional numerical model of pesticide behaviour in a small surface water system, including its sediment. It describes the behaviour of pesticides in a water body at a small scale, i. e. a ditch, pond or stream adjacent to a single field. It calculates pesticide concentrations in the water layer in horizontal direction only and in the sediment layer in both horizontal and vertical directions. TOXSWA considers four processes: (i) transport, (ii) transformation, (iii) sorption and (iv) volatilisation. The transformation rate covers the combined effects of hydrolysis, photolysis and biodegradation and is a function of temperature. It does not simulate formation of metabolites. Sorption to suspended solids and to sediment is described by the Freundlich equation. Sorption to macrophytes is described by a linear sorption isotherm but this feature is not used for the FOCUS scenarios. Pesticides are transported across the water-sediment interface by diffusion and by advection (upward or downward seepage, zero for FOCUS scenarios) (Aadriaanse, 1996, 1997, Aadriaanse and Beltmann, 2009).

7.5.2.3.20 *Integrated Model for Pesticide Transport (IMPT)*

A tool for predicting diffuse-source pesticide concentrations in surface waters used for drinking water supply (Pullan et al., 2016).

7.5.2.3.21 *Surface WAter Scenarios Help (SWASH)*

SWASH (te Roller et al, 2015) is a management and communication tool for the data transfer between three models involved in Step 3 calculations for the FOCUS Surface Water Scenarios. These scenarios have been developed as part of the EU evaluation process under 91/414/EEC (see FOCUS Website). Spray drift, drainage and run-off are the routes of pesticide entry into surface waters. Using spray-drift deposition tables and the MACRO, PRZM and TOXSWA models the exposure concentrations in surface waters can be assessed.

8. PRIORITISATION OF AGRI-DRINKING WATER INDICATORS

In this chapter, an overview on principles and aims of a prioritisation process is given (Chapter 8.1), followed by a summary on the outcome of a survey among FAIRWAY case studies on indicators used (Chapter 8.2) and an explanation of the stepwise prioritisation process chosen in FAIRWAY for WP 3 (Chapter 8.3).

8.1 THE PROCESS OF PRIORITISATION OF INDICATORS

The absence of a properly documented indicator selection process is not a minor issue: Niemeijer and de Groot (2008) explain, that the choice of indicators highly influences conclusions as to whether environmental problems are serious or not, whether conditions are improving or degrading, and in which direction causes and solutions need to be sought. The authors propose to use the enhanced DPSIR-framework to frame the indicator-selection: causal chains are linked to form a causal network, similar to a flowchart. These are according to Niemeijer and de Groot (2008) the steps to steps to build a casual network:

1. Broadly define the domain of interest.
2. Determine boundary conditions that can help determine which aspects to cover and which to omit.
3. Determine the boundaries of the system.
4. Identify (abstract) indicators covering the factors and processes involved.
5. Iteratively map the involved indicators in a directional graph.

Figure 8.1. shows the ideal process for indicator selection. The following elements and criteria are of relevance for the process:

- **Contextualization**

Contextualisation describes the preliminary choices and assumptions (Bockstaller et al., 2008) and includes a definition of the purpose of the analysis, the desired level of operation (farm, region, member state...), the temporal analysis scales and also the involvement of stakeholders (Lebacqz et al., 2013).

- **Agricultural relevance**

According to CORPEN (2006), indicators for nitrate pollution that describe or estimate the condition of a plot (e. g. soil cover, nitrogen budgets and model-derived indicators) are more relevant than the indicators that only describe fertilisation practices (e. g. phased fertilisation). Indicators of high relevance should be preferred. Indicators of low relevance should be used only as part of a set. These sets are, however, difficult to interpret: the larger the number of indicators, the more likely they give divergent assessments. To avoid this, single indicators can be combined within a chart or an index. Table A-6 in the annex shows estimates on plot level of the relevance of a range of indicators evaluating the potential of nitrates pollution of ground- and surface waters.

- **Data availability within case studies/official statistics**

Often, limitation of data availability compelled data driven approaches to focus on agricultural practices and hence on means-based indicators. Model-based and effect-based data indicators require context-specific data, e. g. climate and soil characteristics or specific on-site measurements, that are for some reason not available. A solution may be the use average data as default values, for a region or a sector (Lebacqz et al., 2013).

- **Feasibility**

With increasing scale, direct methods are getting too expensive and are replaced by indirect methods. Table A-7 in the annex shows for plot, farm and regional level how the feasibility of indicators for the potential of nitrate pollution of ground- and surface waters was evaluated for France by CORPEN (2006).

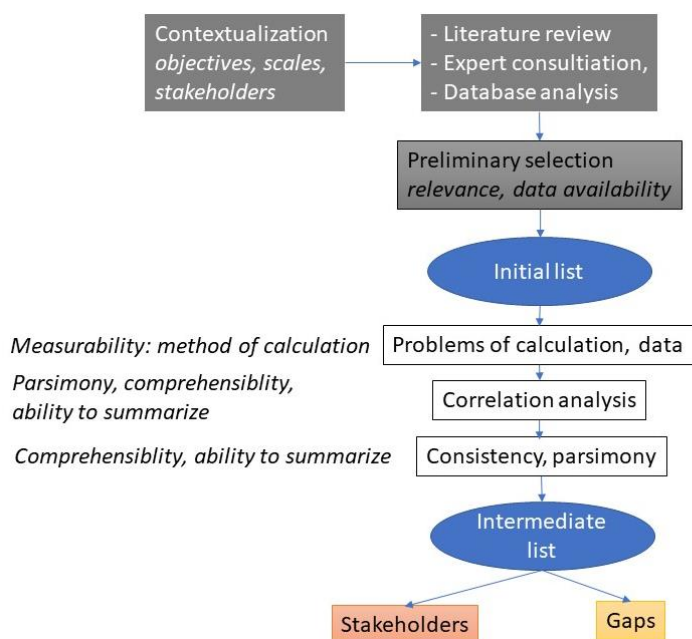


Figure 8.1: Selection of indicators to analyse the sustainability of a farming system with a data-driven approach based on farm accounting databases. The selection process uses several criteria in order to select a set of indicators from the initial list (Lebacqz et al., 2013, adapted)

According to Lebacqz et al. (2013), criteria for a prioritisation of indicators can be summarised under the main categories

- **relevance,**
- **practicability and**
- **end user value.**

In data-driven approaches, most means-based indicators and some intermediate indicators, such as nutrient surplus, can be used to assess environmental themes, because they are based on farmers' practices. As means-based indicators often possess a low quality of prediction of environmental impacts, in order to increase accuracy, Bockstaller et al. (2008) propose to use a combination of indicators for the same theme. This procedure may be complicated in practice and requires an aggregation process but allows to focus on significant variables to develop simplified indicators.

In order to be able to compare indicators, functional units are applied (Thomassen et al. 2008):

- the expression of impacts per amount of product (i.e. liter of milk, kilogram of meat) is related to the function of market goods production,
- the expression per hectare of agricultural land refers to the function of non-market goods production, such as environmental services (Basset-Mens and van der Werf 2005).

Indicators concerning global impacts, e. g., greenhouse gas emissions, should be expressed per unit of product, while indicators related to local impacts, e. g., eutrophication potential, should be expressed per hectare (Halberg et al. 2005a).

Indicators differ with respect to the compartments considered (i.e. soil, surface water, groundwater and air) and effects taken into account. Therefore, the results obtained can strongly depend on these factors (Oliver et al., 2016). The evaluation of indicators should consider multiple applications and wide range of applicability. They should also take into account the synergistic effects of applying different pollutants (e. g. pesticides) and they should consider the application method and the level of application (regional, field scale).

8.2 SURVEY ON ADWIs ALREADY USED IN THE FAIRWAY CASE STUDIES

Aim of WP 3 of FAIRWAY is to prioritise and evaluate data-driven indicators for the monitoring of the impact of agriculture activities on nitrates and pesticides in drinking water.

A questionnaire on ADWIs already in use was compiled and sent to all FAIRWAY case studies. Case study leaders were asked to choose out of a set list those indicators for drinking water pollution by nitrates and pesticides used in their case study. They were also asked to indicate the level (plot, farm, regional or higher) on which data for the calculation of these indicators are available. Case study leaders were also asked for further suggestions on ADWIs. The results of this survey are enclosed in this report as Table A-2 in the Annex and also available as Milestone 9 (MS9) from the FAIRWAY website.

Main results of this survey are as follows:

- The aim, size and structure of the different case studies are different, and so are the ADWIs in use.
- Those case studies with focus on nitrate pollution do not dispose pesticide indicators and vice versa.
- ADWIs and the data to calculate them may be available on plot, farm or regional level.
- There are far more indicators and data in use which are related to nitrogen than to pesticides.
- Indicators in use for pesticide pollution are combined/compound indicators.

Questions on confidentiality of farm data aroused in conjunction with the survey. This is due to uncertainties related to the new regulation on data protection (EU 2016/679), but also due to a tightening of fertiliser legislation in some Member States.

8.3 FIRST STEP OF PRIORITISATION OF INDICATORS IN FAIRWAY

From the preceeding chapters of this review report, the following aspects for a further prioritisation of ADWI can be deduced:

- ADWI are useful on all levels: at farm level as an aid in farmer's consultation, at local or even national level as an evaluation and monitoring tool for administration work and for policy-makers.
- Regarding the two kinds of pollutants – nitrate and pesticides – frame conditions are quite different:
 - Nitrate is one single substance, being mobilised and immobilised, leached, transported by runoff and emitted. It is essential for plant growth and omnipresent, even under "natural" conditions.
 - On the contrary, around 250 so called "active substances" of pesticides are authorised by EFSA. Placement on the market of pesticide product needs national approval. They may only consist of the registered active substances registered on EU-level, pure

or in mixture, and of additives, for a better handling of the pesticide. Pesticides are supposed to be – to the greatest possible extent - harmless. They are supposed to degrade or at least to be absorbed by the soil matrix, but not to leach into groundwaters. Improper handling may however lead to runoff or drift and therefore to pollution of surface waters.

In the Chapters 5 to 7 of this review report, possible ADWIs are listed and explained. The ADWI in Chapter 5 include those being subject of the survey among the case studies (see Chapter 8.2), including those indicators the case study leaders were proposing to be included in a further evaluation. Additionally, indicators used for pesticide monitoring/risk assessment were included, the range of pesticide indicators used in case studies was limited (see Table A-2).

From the number of indicators listed in Chapter 5 can be deduced, that indicators, which act in the agricultural sector as driving forces and as pressure indicators, are far more numerous than state respectively impact indicators. In this sense, the relation being visualised in Figure 2.2 for AEI related to water quality on European level is mirrored for the frame conditions of the FAIRWAY project. The large number of driving forces and pressure indicators which stand for agricultural activity also explains, that from this part of the DPSLIR-model, many factors may influence water pollution. State indicators which are used for the evaluation of the water quality are on the contrary far more standardised, like the water quality standards they are supposed to monitor.

We have introduced the new concept of Link indicators within the DPSLIR-model (Chapter 7), in order to explain the time lag between agricultural activity and water pollution and to elicit, which farm management practices would at all lead to water pollution.

A prioritisation of ADWI is therefore above all necessary for the driving forces and pressure indicators in the agricultural sector, in order to focus on the most

- **significant,**
- **prevalent**
- **effective and**
- **easy to use indicators.**

The survey on ADWIs already used in case studies and the most promising indicators discussed in Chapter 5 lead to a first weighting of indicators. The result is listed in Table 8.1. On the right part of the table, three columns were added, which show the evaluation of a survey among FAIRWAY case studies about data availability in order to calculate ADWIs (Milestone 3.1). Answers would also indicate the resolution in space, in which data can be delivered from the case studies (at plot, farm or regional/larger scale).

In Table 8.1, ADWI, for which data can be supplied by the case studies are marked in orange. ADWI for which data can (possibly) not be supplied by case studies are marked in blue. This may be the case because these data are not used in certain or all case studies, or because in the data survey carried out in the beginning of FAIRWAYS (MS 3.1), we did not ask for the specific information. This applies to background information (e. g. climate, topography, rock types) about the case study sites, which may be critical for leaching risk assessment and catchment typology; therefore, in the data compilation stage, we will collect such data as well. It also refers to specific information particularly on pesticide use. Case studies do not seem to collect specific data on the use of single active substances. But from sum parameters and general indices, no link can be drawn to the parameter at sink level (e. g. pesticide analyses of raw water).

Table 8.1: Ranking of ADWI according to significance and prevalence based on a survey carried in WP 3 of FAIRWAY

| Subindicator of ADWIs | Prevalance: evaluation of data availability in case studies (number of times mentioned) | | |
|--|---|------------|----------------|
| | Plot scale | Farm scale | Regional scale |
| Land use/land cover | 6 | 2 | 5 |
| Land use change | | | |
| Legislation | | | |
| Precipitation/evapotranspiration | 2 | 2 | 12 |
| Temperature | | | |
| Wind | | | |
| Soil type | 5 | 1 | 4 |
| Organic carbon | | | |
| Organic/conventional | 1 | 7 | 1 |
| (Average) crop yield | 1 | 7 | 1 |
| Cropping patterns | | | |
| Method of soil cultivation/tillage practice | | | |
| Soil cover | | | |
| Livestock density (LU/ha /yr on an area of reference) | 3 | 7 | 4 |
| Livestock excretion (kg N/ha/yr on an area of reference) | 1 | 5 | 1 |
| Organic fertilisation/ha; organic fertilisation/crop*ha | 2 | 6 | 0 |
| Mineral fertilisation/ha; mineral fertilisation/crop*ha | 4 | 4 | 6 |
| Total fertilisation/ha; total fertilisation/crop*ha | 2 | 7 | 2 |
| Type of Pesticides | | | |
| Chemical properties | | | |
| Consumption of pesticides | | | |
| Application of pesticides/ha (active substances; frequently used; most persistent or toxic) | 2 | 6 | 0 |
| Application of pesticides/ha*crop (active substances; frequently used; most persistent or toxic) | | | |
| Timing of pesticide application | | | |
| Splitting/frequency of pesticide application | | | |
| Nitrates in soil water | 4 | 1 | 2 |
| Pesticides in soil water | | | |
| Nitrogen leaching risk indicators | | | |
| Pesticide leaching risk indicators | | | |
| Surface transport of nitrogen and pesticides (with soil/fertiliser particles) | | | |
| Pesticide Drift | | | |
| Volatile N-compounds | | | |
| Nitrate: grazing animals near surface waters, farmyard, storage facilities | | | |

| Subindicator of ADWIs | Prevalance: evaluation of data availability in case studies (number of times mentioned) | | |
|--|---|------------|----------------|
| | Plot scale | Farm scale | Regional scale |
| Pesticides: farmyard, pesticide storage facilities | | | |
| Annual average nitrate concentration (mg NO ₃ /l) | 4 | 1 | 8 |
| Concentration trend analysis | | | |
| Frequency of exceedance quality standards (%) | 2 | 0 | 8 |
| Nitrogen maximal concentration in drinking water collection points | 3 | 0 | 8 |
| Catchment typology and dominant flowpath | | | |
| N stable isotopes | | | |
| Number of substances that exceed water quality standards at least once the year | 4 | 0 | 7 |
| Maximum concentration by substance (if >0.1 µg/l) in drinking water collection points | 4 | 0 | 7 |
| Frequency of exceedance quality standards in the drinking water (percentage of the number of samples where the 'drinking water' standard is exceeded) by substance | 4 | 0 | 6 |
| Vulnerability assessment maps of aquifer and surface water | 2 | 0 | 7 |

Indicators, for which data are not readily available in the case studies may be calculated if these data are free available from other data sources. Table A-3 in the annex lists data sources for free available data in order to calculate ADWIs. One example is the use of pesticides, which may be deduced from local cropping patterns and from usage data reported from the Member States according to Regulation (EC) No 1185/2009.

The next step towards prioritisation will be done in FAIRWAY using data of cathments in the case studies (see Chapter 9). For this reason, data are requested from the case studies.

9. FURTHER PRIORITISATION AND EVALUATION OF AGRICULTURAL DRINKING WATER INDICATORS

In order to further drive forward the prioritisation of the selected ADWIs, we intend to connect ADWIs from the agricultural and the water work side, using statistical methods.

We also intend to further investigate on the Link indicator, especially how this ADWI fits in between the other indicators. We intend to examine

- the feasibility of indicators calculation,
- the link between indicators and
- the relevance of some indicators, as statistical calculations give the mathematical expression for the link that exists between them.

For this purpose, a database of ADWI-data on catchment level will be collected from the FAIRWAY-case studies. Preparatory work has been carried out, in order to specify the data request to the case studies. In the following chapter, trial calculations being conducted with a small database are further explained.

9.1 A STEP FURTHER THE ADWI, CALCULATING LINKS BETWEEN PRESSURE AND STATE

The implemented database – here called ‘draft database’ – contains French data, provided by ‘Eau de Paris’ (for more information, see WP2 case study information).

9.1.1 ADWI pressure indicators in the French case study

French Ministry of Agriculture (RGA: General agricultural survey) provides, for each municipality, the Utilized Agricultural Area (UAA) and the distribution of this area between crops (ex: wheat, maize, rapeseed). These data come from farm surveys achieved in 1970, 1979, 1988, 2000 and 2010. A time step transformation (interpolation) has been carried out to obtain yearly data, for each major crop (fallow, meadow, sunflower, peas, maize, oilseed rape, sugarbeet, spring barley, winter wheat). These data were integrated in the draft database and now graphs can be plotted to illustrate evolutions over time.

It should be highlighted that over the studied period, cereals are most important in terms of proportion of land use.

Nitrogen fluxes were calculated using a soil surface budget method (Oenema et al. 2003) implemented in an online tool (Cassis-N, Poisvert et al, 2017).

In this method, data of different scales are used (and combined/homogenised in the tool itself):

- Regional (SAA: annual agricultural statistics, and UNIFA: Union of Industries of fertilisation),
- Departmental (SAA and UNIFA),
- Municipal (RGA: general agricultural survey).

Providing the spatial delimitation of the studied catchment (shapefile format), calculations are performed and expressed in relation to this catchment leading to the following outputs:

- Mineral fertilisation,
- Organic fertilisation,

- Atmospheric deposition,
- Fixation,
- Output (plant N consumption),
- Surplus (i. e. budget calculation).

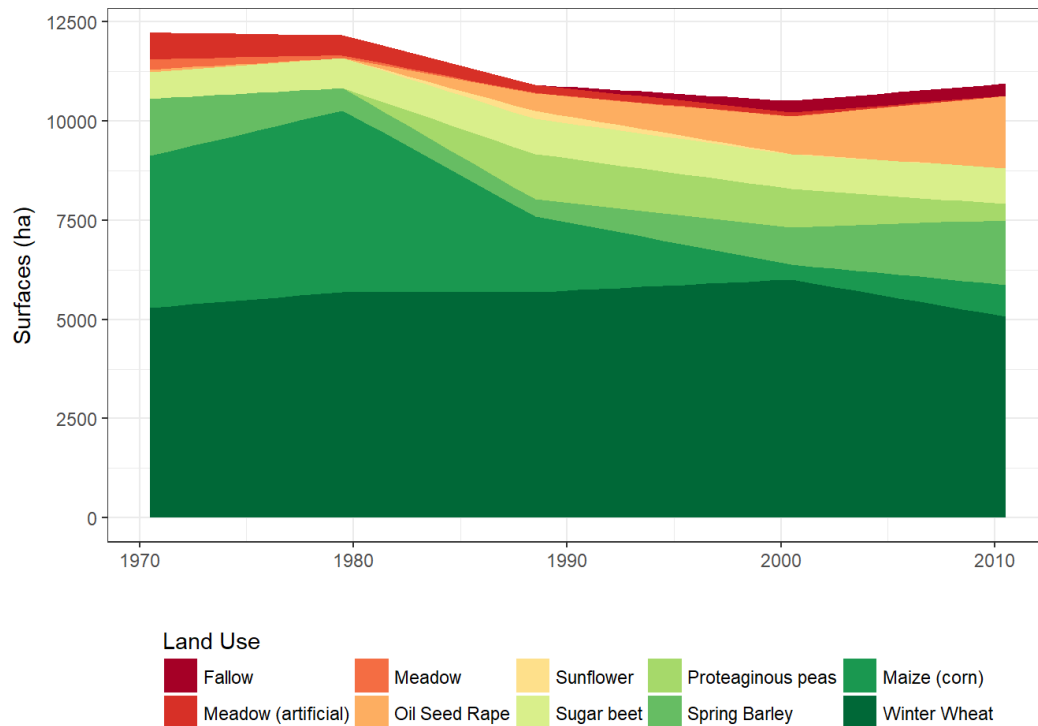


Figure 9.1: Evolution of land use on the French Case Study catchment (La Voulzie) based on ministry of agriculture statistics

In addition, a N soil surface budget calculation is performed using a N budget = [mineral fertilisation + organic fertilisation + fixation + atmospheric deposition]- [Output (plant N consumption)]. Plant N consumption included grazing (grass N consumption) but there very little animal production in this catchment. All these data were then released at annual time steps and integrated to the draft database. This budget is referred as a surplus in Cassis-N method.

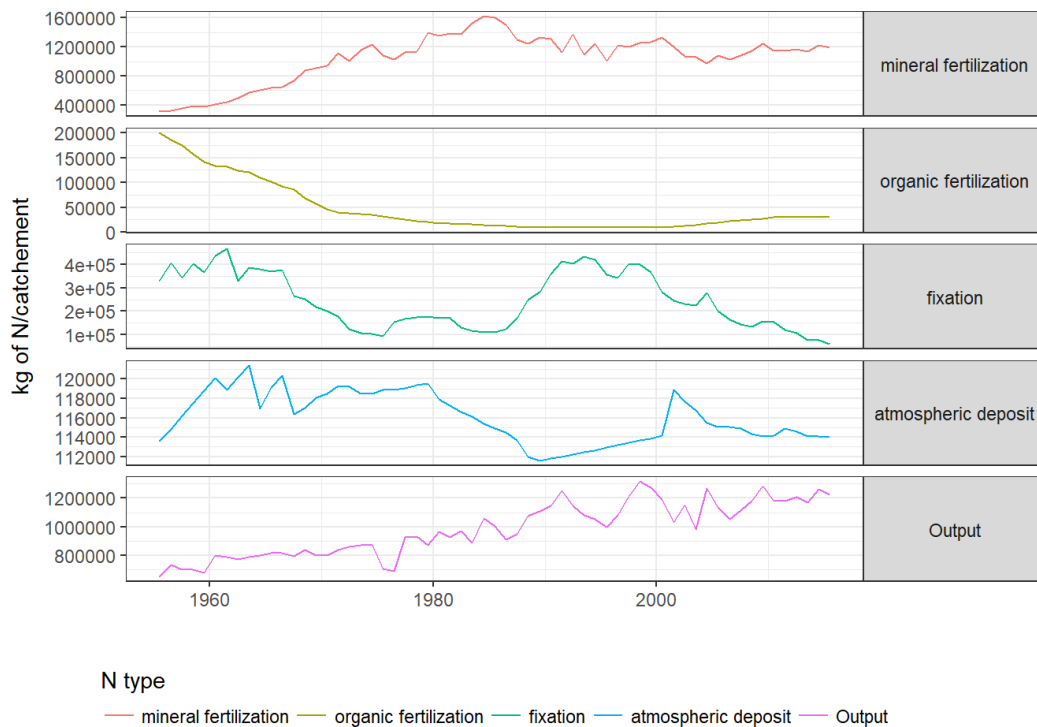


Figure 9.2: Pressure indicator time series coming for Cassis-N calculation. It depicts the several sources of nitrogen inputs (in kg N/catchement) at the soil scale and outputs due to plant N consumption

Most of the hydrologic data were collected by Eau de Paris at the “La Voulzie” spring and are transmitted to the BRGM. The hydraulic head is measured at the BRGM piezometer located in the city of Bauchery Saint-Martin (6 km, north-east). All these data are available at irregular time steps varying from daily to monthly. Bulk data were integrated to the draft database and a homogenisation of the time steps was performed.

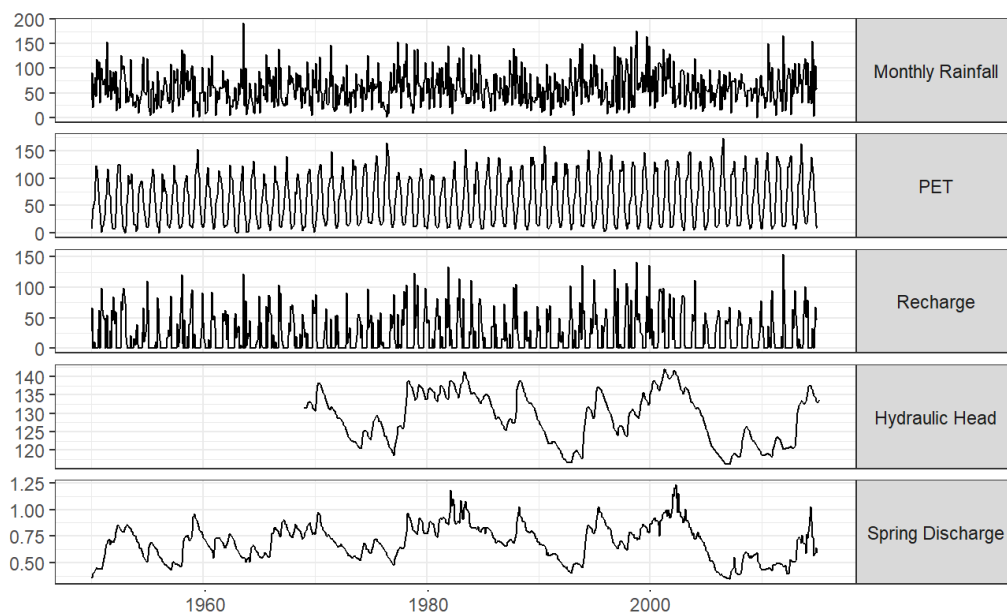


Figure 9.3: Pressure indicator chronicle - Main hydrological time series

9.1.2 ADWI state indicators in the French case study

The concentrations of nitrate were collected by Eau de Paris at the “La Voulzie” spring and were transmitted to the BRGM. All major chemical compounds are analysed, but nitrate only will be used in the present project. Nitrate time series starts in the 50's with a concentration close to 20 mg/L and exhibit a nearly continuous rise up to the year 2000. After that date nitrate concentrations seems to be more stable. Reasons of stabilisation could be found in climatic driving forces (more humid period for example), but part of the stabilisation could also be due to the implementation of action plans at the national (nitrates directives) and local (Fertimieux) level.

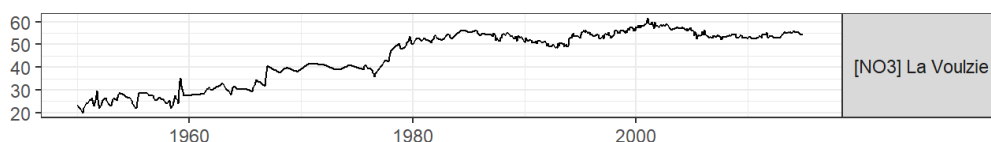


Figure 9.4: States indicator time series- NO₃ concentration in water at spring “La Voulzie”

9.1.3 Linkages between ADWI

9.1.3.1 ADWI calculation and linkage

In order to find a link between pressure and state indicators it is intended to investigate relations that exist between nitrogen input on a study site and the observed effect on water quality. When needed, information on the hydrogeological/hydrological functioning is shown.

For that reason, statistical links between indicators that were integrated in the draft database were computed and tested.

Pre-processing of the available data had been carried out, mainly in order to homogenise time steps for all data. In a general manner, main processing consists in scaling down data to annual values by averaging or summing data. Annual data are attributed to the first July of the running year.

9.1.3.2 Impact of recharge on spring discharge

At a yearly scale, linkage between recharge and spring discharge can be evaluated using a cross correlation function (ccf). The intensity of the correlation returned by $ccf(x, y)$ varies between 0 and 1, and being 1 at best. For a range of lag (k) the correlation is calculated between $x[t+k]$ and $y[t]$ and then plotted on a bar chart. Each bar on the chart is then separated from another by 12 months (i. e. one year).

From this analysis, it can be seen that the best correlation is found for a lag $k = -12$ months, which means, that the spring discharge time series can be rather well explained by the evolution of the recharge of the year before. This analysis is of importance, since nitrate is measured in water from a spring, whereas nitrogen inputs are measured at the soil/root zone. Transfers from the soil/root zone to water should then be described in simple terms.

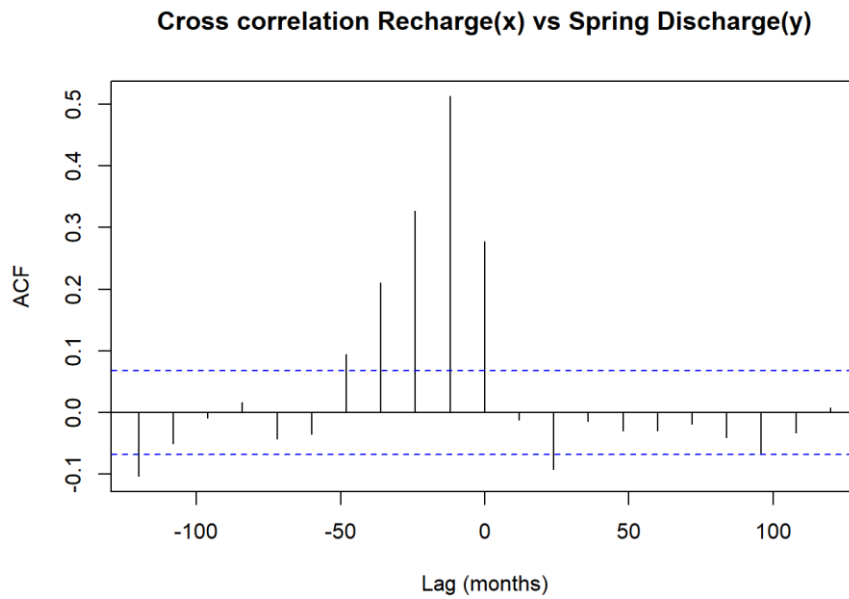


Figure 9.5.: Cross correlation graphic – Recharge (x) vs Discharge (y) of “La Voulzie” spring. ACF expresses the correlation between $x[t+k]$ and $y[t]$, k being the lag. Each vertical bars are separated by 12 months (1 year)

Using information coming from the cross correlation analysis, recharge shifted by 12 months and discharge are plotted on the same graph. It highlights the similarity of the time evolution. One should remark that main evolutions are similar, but small variations (peaks mainly) diverge in some cases.

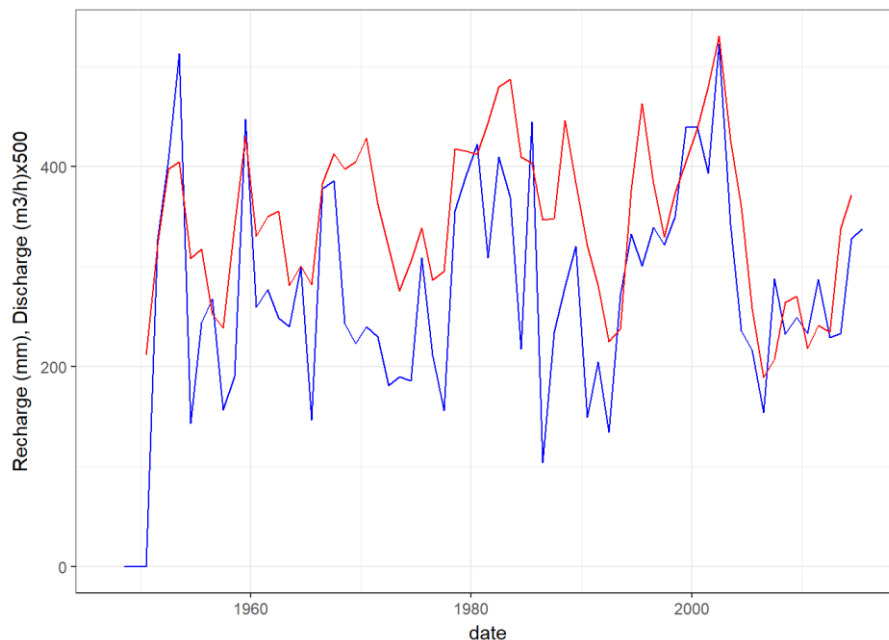


Figure 9.6: Recharge and discharge of the “La Voulzy” spring between 1955 and 2016, recharge time series is shifted by 12 months to the passed, in relation to information provided by the cross correlation analysis

9.1.3.3 Exploring the link between recharge and NO_3^-

Annual variation in nitrate concentration could be due to variations of the flow regime. As discharge flow rate is mainly governed by recharge rate (see Chapter 9.1.2.2), the relation between recharge

and nitrate concentration could be directly investigated. Using the same cross correlation method as before, best correlation between annual recharge and nitrate concentration is found at lag $k = -36$ months (correlation is the highest when evaluated between $y[t]$ and $x[t-36]$), which correspond to 3 years. In that case, the relation is weak ($CCF=0.20$ at best) in comparison of the previous case. The trends in the nitrate time series is one of the more evident explanation.

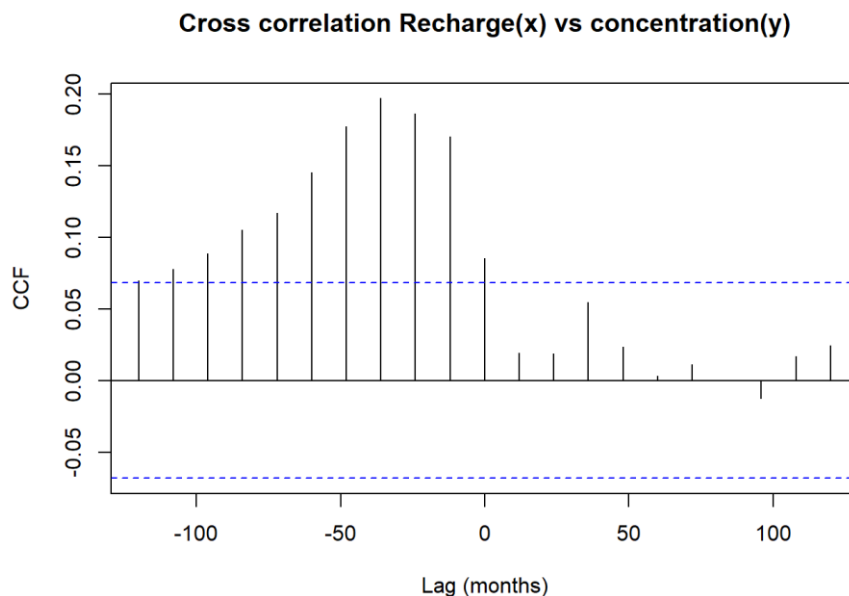


Figure 9.7: Cross correlation graphic – Recharge (x) vs NO_3^- concentration (y) in “La Voulzie” spring. ACF expresses the correlation between $x[t+k]$ and $y[t]$, k being the lag. Each vertical bars are separated by 12 months (1 year)

Further tests showed, that the two time series do not have the same cyclicalities. Discharge has an annual cyclicity (12 months), while the time series of concentrations has a cyclicity of 8 years. Recharge (blue dashed line) shifted by 3 years and annual mean nitrate concentration. Due to the increasing trend in nitrates, similarity between the curves is not as good as for the recharge/discharge approach.

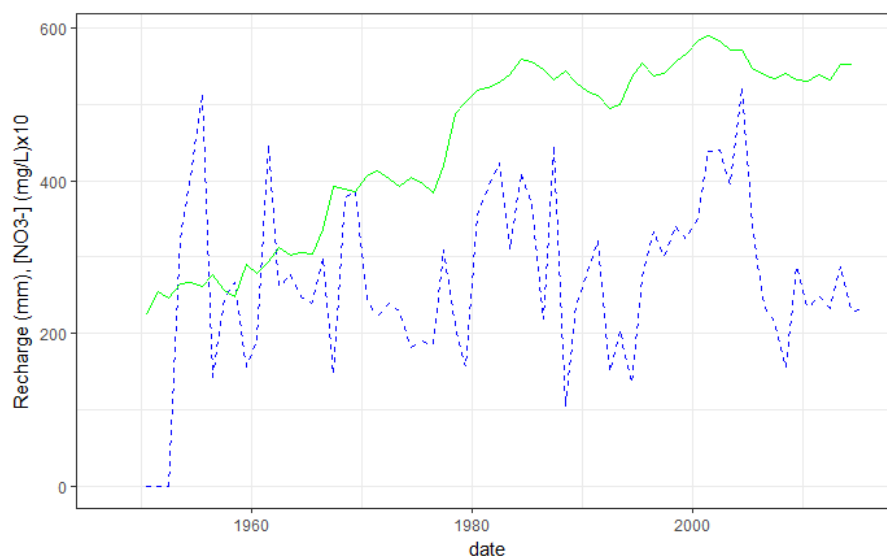


Figure 9.8: Recharge shifted by -3 years (blue dotted line) and nitrate concentration of the “La Voulzy” spring between 1955 and 2016

9.1.3.4 Linkage between Cassis-N surplus and NO_3^- concentration

Cassis-N calculates the nitrogen surplus and therefore is similar to the GNB, but does not follow exactly the calculations intended by OECD rules (OECD 2007) as, for instance, volatile N-losses from manure are not considered. This indicator could be considered as representative for the amount of nitrates actually inflowing in the aquifer. So, a relationship between the nitrogen budget and the nitrate concentration is expected. Using a similar approach, the best correlation between nitrogen budget and nitrate concentration was searched for.

The best correlation was found at lag $k = -12$ months, which means, that the strongest correlation between x (GNB) and y (NO_3) is found for $x[t-12]$ and $y[t]$. This signifies, that nitrogen surplus data of the year before (12 months before) are the most appropriate to explain a linkage between nitrogen surplus and NO_3^- -concentration. Nevertheless, the correlation is relatively weak (but significant).

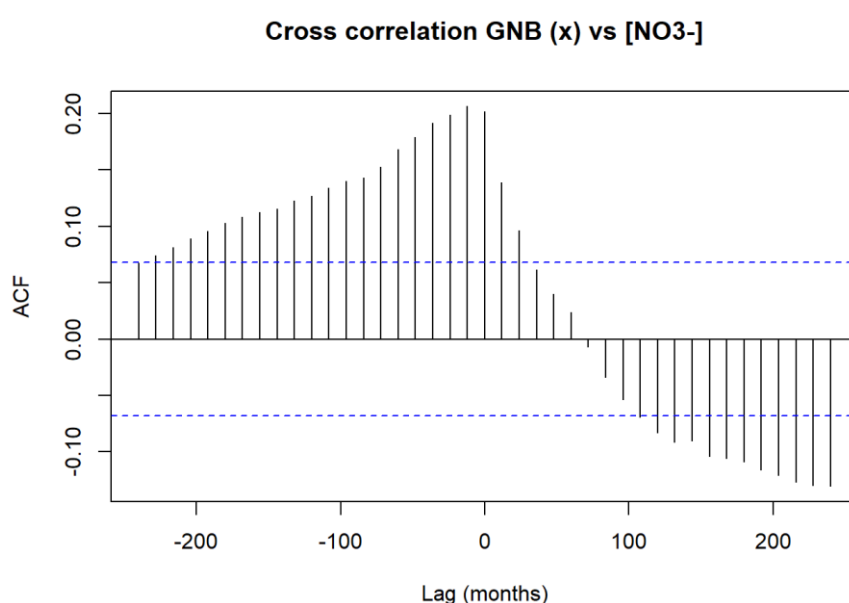


Figure 9.9: Cross correlation graphic – Surplus (x) vs NO_3^- concentration in “La Voulzie” spring (y)

Plotting the two time series on the same graph highlights the rather poor correlation between this two time series. The increasing trend of the NO_3^- , whereas the Cassis-N surplus is decreasing starting from 1990, can explain this lack of strong relationship. On the following plot, NO_3^- -concentrations are in green (shifted by 12 months) and the Cassis-N surplus is plotted in purple (dashed lines).

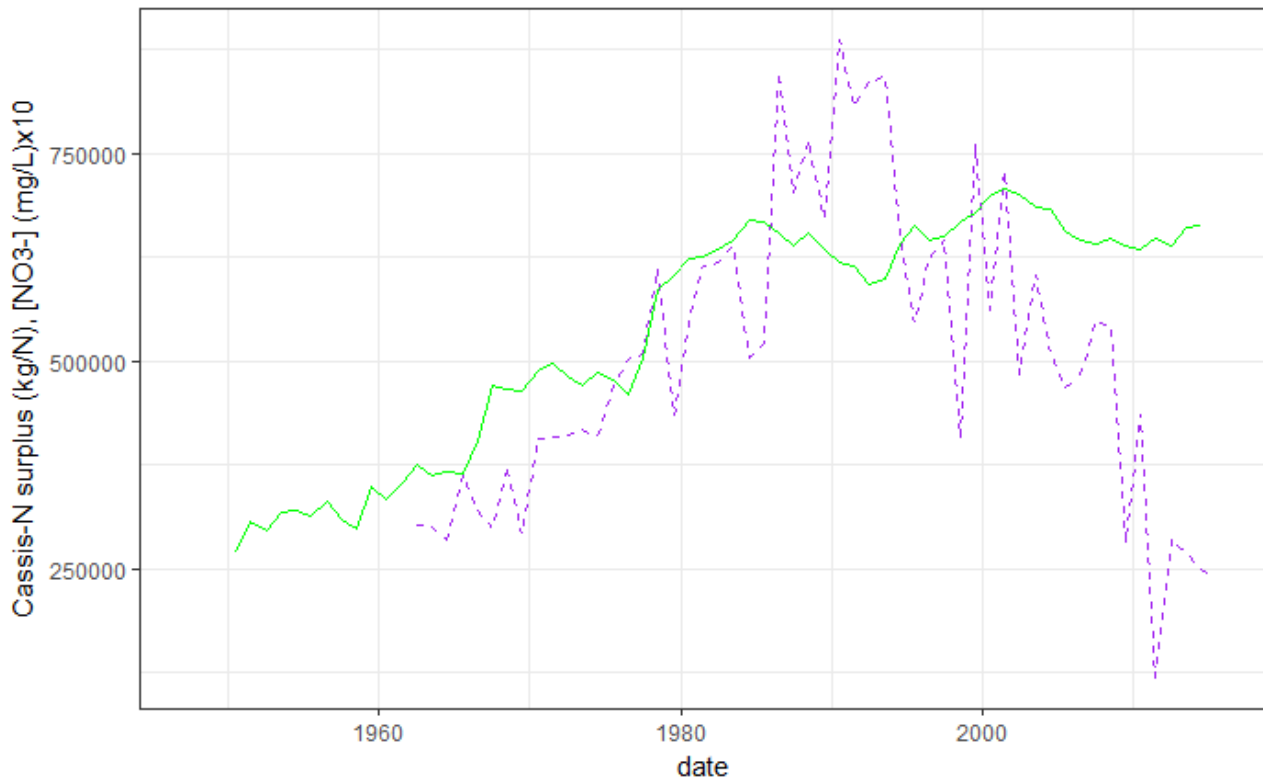


Figure 9.10: Nitrate surplus (purple dashed line) and nitrate concentration (green solid line) of the “La Voulzy” spring between 1955 and 2016

9.1.3.5 Linkage between Mineral fertilisation and NO_3^- concentration

Cassis-N also provides the mineral fertilisation. Since there is very little organic fertilisation on the catchment (Figure 9.2), this indicator could represent by itself the load of nitrogen entering the system. A relationship between the mineral fertilisation and the nitrate concentration in the water of the well is expected even though processes of nitrogen consumption by crop would regulate the inflow in the aquifer.

Since mineral fertilisation is a much more direct indicator than the surplus, it represents a much simpler opportunity to test the input/output link into the system.

In that case, the correlation is much better (0.8) and represents a rather good explanation of the variation of nitrate concentration. A disturbing result is the absence of lag for the peak of correlation. Nevertheless, giving the objectives of this first approach, one can invoke several processes that can affect the statistical analysis and explain the results. Investigating these processes remains out of the scope of this study.

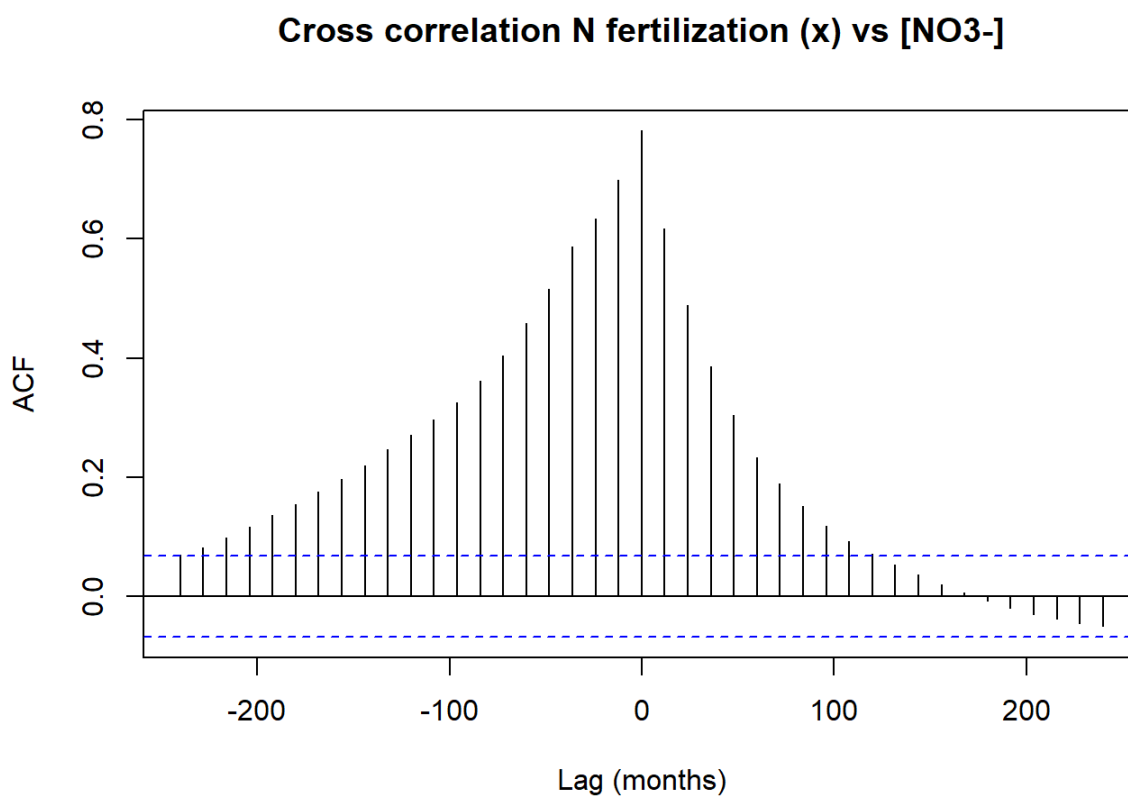


Figure 9.11: Cross correlation graphic – Mineral fertilisation (x) versus NO₃⁻-concentration in “La Voulzie” spring (y)

Plotting the two time series on the same graph highlights the rather good correlation between this two time series. The correlation (0.8) is better than with surplus (0.2).

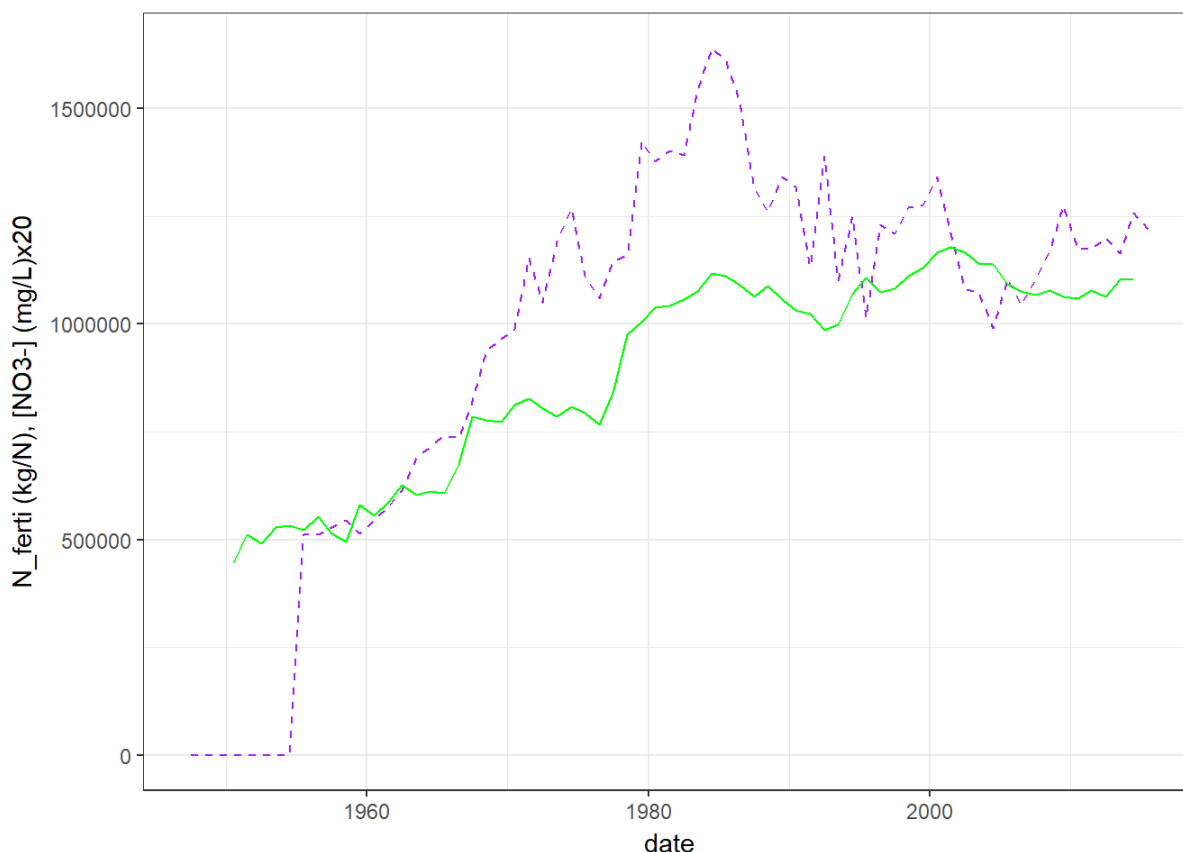


Figure 9.12: Mineral fertilisation and nitrate concentration of the “La Voulzy” spring between 1955 and 2016

9.1.4 Future on indicators and database

9.1.4.1 Main ideas for databases

The first attempt to build this database enabled the first calculations of indicators as well as the first links between pressure indicators and state indicators. These links have shown that the most integrated and aggregated indicators (GNB or Cassis-N surplus) are not the ones that yield the best results. Thus, the study of the cross-correlation between N-surplus and concentration of nitrates in the spring water does not show the best results. Additional data could be integrated to better account for water and solute transfers in the unsaturated zone, but there is a risk of obtaining a too complex indicator or a too complex model to explain links between indicators. The integration of many explanatory factors in order to obtain a model has been realised by the BRGM on the source of the Voulzy, this type of work deviates from the will to simplify the FAIRWAY project.

9.1.4.2 First test in order to implement the data base at the project scale

The first tests were carried out with the French case study data. It shows that diversity of time steps are important to take into account. An appropriate approach could be developed. Integration of other case studies data is a work to achieve in order to deliver a final and definitive database by the end of the project.

Again, the topic “data availability respectively accessibility” will be of relevance. Linking data and developing algorithms will bring us to questions on :

- data resolution in the time and space and

- data quality and uncertainty.

The most effective data according to the simulations on catchment level should be further tested in the case studies on relevant target groups, in order to identify the most feasible indicators.

In the meantime, other indicators will be calculated and compared with each other in order to eventually link the pressure indicators and the state indicators.

9.1.5 Main insight of the approach

First attempts to integrate case studies data in a rather simple database and to explore link between this indicators shows that:

- the data base modelling (i. e. the establishment of the database) is of importance to have an internal platform for the discussion of what data/indicators may represent and who they can be linked,
- the issue of time steps has to be taken into account,
- the issue of spatial definition of data also has to be taken into account,
- the search of links between pressure and state indicators can be time consuming and could be strongly dependent of the data available for each case study. A major risk of invoking rather complex relations between indicators is identified, which lead to consider probably more conceptual (i.e. flowcharts) than statistical links between indicators.

Evaluation of the indicators

After meaningful indicators have been identified, they need to be further evaluated. Evaluation of indicators can be effectuated by different methods (Bockstaller et al., 2008).

- **Sensitivity analysis**

Aim of a sensitivity analysis is to test how the indicator outputs react to input variables: the information can be used to select the most effective indicators.

- **Evaluation of the quality of the indicator**

Bockstaller et al. (2008) report, that the classical approach for evaluating the accuracy of a model prediction is to compare calculated and measured data. However, this approach may be difficult to apply to simplified indicators (Rigby et al., 2001, Reus et al., 2002) and propose a three-step methodological framework for the evaluation of environmental indicators.

- **Evaluation of the indicator design**

This evaluation could be effectuated by an expert panel, alternatively, a peer-reviewed article is suitable. Aim is to identify need of improvement.

- **Evaluation of the indicator output**

This step is based on the comparison of the indicator output with measured data. While indicators based on a simulation model can be directly evaluated using the measured data, simplified indicators need a modified approach for their evaluation.

- **Evaluation by end-users**

A consistent and comprehensive set of indicators is useful for the correct interpretation of complex systems. Taking into account the interactions of indicators enables the investigator to map appropriately the main structure and processes of the system (Binder et al., 2010).

With a selection process based on the concept of a causal network, interactions between environmental themes and indicators can be taken into account. To assess the environmental impact of nitrogen fertilisation on surface water ecosystems, selection is made by considering a network composed of causal chains related to crop production, socioeconomic issues, air, soil, and water (Niemeijer and de Groot 2008)

The identification of correlations between indicators is recommended in the process of selecting a minimal, consistent, and sufficient set of indicators. By way of illustration, Thomassen and de Boer (2005) showed for dairy farms in the Netherlands, that there was a correlation between nitrogen surplus and eutrophication potential on farm. This means, that the nitrogen surplus is relevant "to a moderate extent" to assess the environmental impact of eutrophication with more easily available data.

- **Evaluation by end-users**

The purpose of this last step is to evaluate the acceptance of the end-users for the new indicator. The developer can at this stage collect feed back, especially suggestions for improvements.

10. IT-/SENSOR- AND AUTOMATIC SAMPLER TECHNIQUES FOR PESTICIDE AND NITRATE SAMPLING

10.1 SENSORS FOR PESTICIDE MEASUREMENT IN WATER

10.1.1 Optical Sensors

Optical sensors provides a facile, rapid and low-cost approach for sensitive detection of pesticide based on FL, UVEvis, Raman, SPR or chemiluminescence signal variations. Generally, an optical sensor contains recognition unit that can interact specially with desired target pesticide and transducer component that is employed for signaling the binding event. Recognition elements including enzyme, antibody, molecularly-imprinted polymers, aptamer, and host-guest recognizer, draw increasing attention of scientific researcher to improve analytical performance of sensor. By combining the recognition units-assisted target response, the current well-established optical probes can be divided into four broad categories based on signal output formats:

- fluorescence (FL),
- colorimetric (CL),
- surface-enhanced Raman scattering (SERS),
- surface plasmon resonance (SPR),
- chemiluminescence.

The optical sensors for pesticide detection based on various optical detection modes are fully described in a recent review (Yan et al., 2018) and are outlined below.

10.1.1.1 Fluorescence sensing strategy

With high sensitivity and simplification, fluorescence-based sensors as one of the most commonly used sensing candidate, have been widely applied in broad fields, including environmental monitoring ((Li et al., 2016, Guo et al., 2015, Wu et al., 2014), as the signal change can be collected vis spectrofluorophotometer and observed by naked eye on-site (Paterson and de la Rica, 2015, Wu et al., 2016, Zhang et al., 2011). As the development of advancing technologies, various kinds of materials have been widely employed for the fabrication of FL sensing platform, including fluorescent dyes (Strobl et al., 2017), semiconductors nanomaterials (Wu et al., 2013), metal nanomaterials (Chen et al., 2015, Wang et al., 2017), carbon materials (Yuan et al., 2016), and rare earth materials (Li et al., 2015). Meanwhile, it is very critical to choose and design a proper recognition unit that combined with FL probe for responding the fluorescent “turn off”, “turn on”, or “ratiometric” signal. Nsibande and Forbes reviewed the development of quantum dots-based FL probe for pesticide detection in terms of enzyme, molecularly-imprinted polymers (MIPs) and host-guest recognizer (Nsibande and Forbes, 2016). On the basis of the application of recognition elements, FL sensing strategies can be typically classified into several types: enzyme-mediated methods, antibody-assisted methods, MIPsbased methods, aptamer-based methods, host-guest complexes probe and other approach (see Yan et al., 2018 for details).

10.1.1.2 Colorimetric sensing strategy

Owing to its convenience and simplicity, colorimetric (CL) sensing strategy has proven to be a powerful analytical approach for the analysis of variety of analyte, including ions (Wang et al., 2014), chemical warfare agents (Yue et al., 2016), small organic molecules (Liu et al., 2011) and biomarkers (Sun et al., 2014). A prominent merit of CL sensing is that their direct visualization output makes them promising candidates for point-of-care assays. Therefore, the key challenge for fabricating CL platform is transforming response behavior into visual color change. Reviewed the remarkable

achievements of nanomaterials, AuNPs as fascinate signal transducer have been widely utilized to design CL sensors for pesticide detection. Xu et al. developed AuNPs-based probe for the directly monitoring of acetamiprid based on the strong affinity between cyano group and gold (Sun et al., 2011). The sensing mechanism was based on the state change of AuNPs from dispersion to aggregation. The concentration of acetamiprid can be qualitatively estimated from the color change (red to blue). The color change during nanoparticle aggregation is highly dependent on their distance and concentration. Chen et al. (2018) used citrate-stabilized AuNPs for the rapid detection of terbutylazine and dimethoate by visualizing the color change. This AuNPs-based CL sensor showed high selectivity and good sensitivity for pesticide detection in real environment samples. Recently, a CL sensor array was constructed for identifying five OPs based on the dispersion-aggregation behavior of AuNPs by Fahimi-Kashani and Hormozi-Nezhad (Fahimi-Kashani and Hormozi-Nezhad, 2016). Apart from unmodified AuNPs, functionalised AuNPs have been utilized to improve selectivity for CL detection of pesticide as well. Sun et al. displayed p-amino benzenesulfonic acid functionalised AuNPs as signal reporter for detecting carbaryl (Sun et al., 2013). Based on the similar protocol, Kim et al. (2015) introduced imidazole into AuNPs-based probe to improve the sensitivity and shorten the detection time for quantitative analysis of diazinon. In addition, melamine (Liu et al., 2015), p-nitroaniline dithiocarbamate (Rohit et al., 2016) and guanidine acetic acid (Bhamore et al., 2016) were also served as ligand to decorate AuNPs for selective CL detection of pesticide. Despite many advantages of those aggregate sensors including easy-to-use and cost-effective, more endeavors are still needed to improve the sensitivity and selectivity. The combination of recognition elements is preferred as they address the above limitations. Thus, numerous efforts have been devoted to integrating the specific affinity of recognition units with the optical properties of metal nanoparticles for realizing pesticide analysis in a sensitive, selective and accurate manner. From perspective of recognition elements, CL sensing strategies can be typically summarised as four types: enzyme strategies, antibody assays, aptamer-based methods and other approaches (see Yan et al., 2018 for details).

10.1.1.3 Surface enhanced Raman scattering strategies

Raman spectroscopy can identify the chemical content of different molecular species via the collection of molecular vibrations, that is, Raman spectroscopy possess the capability of molecular “fingerprint” recognition for distinct molecule/analyte. Surface enhanced Raman scattering strategy (SERS) essentially integrated the molecular specificity of Raman spectroscopy with optical properties of plasmonic nanostructures (Gruenke et al., 2016). Owing to optical resonance properties of coinage-metal nanostructures, the local electromagnetic field can be significantly enhanced, accompanying the improvement of the SERS signal. Taking advantages of ultrafast analysis capabilities, label-free, high stability and nondestructive characterization, the application of SERS received numerous concern in the field from biomedical diagnosis to environmental monitoring (Cialla-May et al., 2017, Henry et al., 2016, Ali et al., 2016). By means of coinage-metal nanostructures, SERS can even achieve an ultra-sensitivity down to the single-molecule level, which offered new opportunities toward obtaining single molecule recognition (Ding et al., 2016, Zrimsek et al., 2017). Recently, the development of SERS technique for pesticide detection in the aspect of sensitivity, reproducibility, selectivity and portability was recently reviewed (Pang et al., 2016). The following are recent achievements in pesticide SERS strategy as a powerful analytical tool that have focused on the development of metal nanostructures-enhanced amplification. In this section, according to the coinage metal nanoparticles-based solid substrates, SERS nanoprobe are typically designed as gold substrate, silver substrate and Au@Ag bimetallic substrate (see Yan et al. 2018 for details).

10.1.1.4 Other detection strategies

Other detection techniques, such as surface plasmon resonance (SPR) strategy and chemiluminescence strategy, have also gained strong driving forces in the detection of pesticide due to their convenient manipulation and high efficiency. By taking advantage of the outstanding distinguish ability provided by recognition unit, SPR and chemiluminescence strategy possessed excellent sensitivity and selectivity for real-time monitoring (see Yan et al. 2018 for details on some of the attractive research on SPR and chemiluminescence strategy).

10.1.1.5 Outcome and perspectives

Continuous concerns over pesticide residues have provided a long-driven force to develop novel techniques. In the past decade years, thousands of research literatures have been published for the routine and convenient monitoring of pesticide to meet increasing market and social requirements. Yan et al. (2018) have recently reviewed various kinds of optical strategy that were ingeniously designed and successfully applied for the detection of pesticide, with a specific focus on the fluorescence, colorimetric and surface-enhanced Raman scattering sensing strategies. With the emergence of high affinity of recognition elements, as well as various novel signal transduction approaches, optical assay reveal good performance to quantify pesticide residues in complex environment and food matrices, especially in the simplification and visualization design, making them ideally suitable for on-site application.

On the basis of the discussed research, the stability, accuracy, sensitivity and selectivity of optical sensor can be improved as follows: (1) the development of recognition units with excellent distinguish capacity to offer selectivity and sensitivity toward targeted analytes. For example, bi-enzyme cascade catalytic format has the merit of multi-signal amplification, greatly improving the sensitivity. (2) the utilization of novel nanomaterials that employ as signal reporters, substrates and catalysts. Ratiometric probe with dual-emission can provide built-in correction to eliminate environmental effects, exhibiting advantage in terms of enhanced sensitivity and accuracy. Nanozymes possess lower cost, higher stability, and excellent recyclability in comparison with natural enzymes, which improved the stability of sensor. Furthermore, the integration of optical strategy into paper-based analytical devices can be constructed in simplicity and miniaturization, further promoting the commercialization of devices.

Even though optical sensor has a promising future in pesticide determination, there are sustainable challenges to be addressed in the field. Particularly, most optical sensors still retain at laboratory level of testing and verifying proof-of-concept, which have not been exploited in practical applications. In the aspect of recognition events, the stability of recognition units (such as enzymes, antibody and aptamer) can be easily influenced by environmental conditions, such as temperature and pH. Furthermore, the integration of recognition event into the analytical system is a vital step in the fabrication of a successful sensor. The conjugation between recognition elements and functionalised nanomaterials will inevitably increase the complexity, cost and time of optical sensor, especially suppress the distinguish ability of recognition elements. From the perspective of nanomaterials, nanomaterials-based analytical platforms are in the starting stage of development. The specificity and catalytic activity of current nanozymes are lower than that of natural enzymes, in turn impeding the use of nanozymes. The synthesis of functional materials/nanomaterials with relatively narrow size distribution will seriously influence the performance of sensors, because inhomogeneous distribution of nanoprobe can reduce analysis accuracy. Thus, future endeavors should directly focus on addressing above obstacles.

While remarkable progress has been made toward the design of optical sensor for pesticide detection, tremendous opportunities and new trends are emerging. Coupling newly developed recognition elements (nanobodies, peptide aptamers and so on) with functional

materials/nanomaterials will afford exciting opportunities for the monitoring of pesticide, which can improve the performance of sensors. On the other hands, the integration of field-deployable devices with optical sensor perform promising on-site applications, with the aid of 3D printing technologies, improving the reproducibility and stability of sensors. By taking advantage of miniaturized device and wire-less networking, the recognition event of pesticide can be transformed into a measurable digital signal by hand-held devices, such as smartphone, then the detection results can deliver to the servers. Thus, the portable detecting platforms can be carried out outside of laboratory setting with minimal user involvement, paving the way for a new generation of analytical devices in real-time detection. Yan et al. (2018) envision that, therefore, optical sensors will assuredly act significant roles in future on-site monitoring of pesticide.

10.1.2 Electrochemical sensors

10.1.2.1 Electrochemical sensors based on carbon nanotubes

In Table 10.1, the most relevant works related to pesticide electrochemical monitoring using carbon nanotubes-based electrochemical sensors reported in recent years are summarised. From that, Wong et al. (2017) have made a general overview of the current scenario related to this research topic, and, as can be seen, a number of works have been reported using different electrode architectures for the detection of various target analytes. Electrochemical sensors designed with pristine carbon nanotubes or combinations of carbon nanotubes with other modifiers can be found amongst these. There are modified electrodes consisting of CNTs and ionic liquids (ILs), porphyrin, phthalocyanines, metallic nanoparticles, and others. Thus, Wong et al. (2017) discussed the technical issues and the main analytical features, as well as the future challenges of these reports in specific subsections, which were classified according to the type of electrode modifier.

The review after Wong et al. (2017) demonstrated that carbon nanotubes provided electrochemical sensors with relatively good analytical performance in pesticide determination. Pesticides from different classes were electrochemically quantified using carbon nanotubes-based electrochemical sensors. The main electrode modification strategies consisted of the incorporation of carbon nanotubes within the composition of carbon paste electrodes and the modification of the surface of glassy carbon electrodes using the classical dropping cast method. Carbon nanotubes were used alone or in combination with different types of modifiers, including conductive polymers, phthalocyanines, porphyrins, metallic nanoparticles, ionic liquids, and graphene, among others. In general, a typical result achieved from the modification of carbon paste or glassy carbon electrodes is the very high increment of the analytical signal and the displacement of the working potential closer to zero. Both of these effects are desired to ensure high sensitivity and good analytical selectivity. The revised works demonstrated the construction of analytical curves with good linear concentration ranges (typically two concentration decades or more) and low detection limits (at least at the micromolar level). Moreover, in most cases, a good stability of response, precision of measurement, and accuracy in the recovery of spiked environmental samples are proved. Therefore, the positive effects of the use of carbon nanotubes as electrode modifiers for the preparation of electrochemical sensors dedicated to pesticide monitoring is very well illustrated and demonstrated. From the well-established electrochemical sensing performance of carbon nanotubes-based sensors toward pesticides, a set of challenges should be investigated and overcome for the advance of this important research topic.

Table 10.1: Electrochemical sensors based on carbon nanotubes for the detection of pesticides (after Wong et al., 2017)

| Analyte | Electrode | Linear Range (mol·L ⁻¹) | Limit of Detection (mol·L ⁻¹) | Reference |
|----------------------------------|--------------------------------|--|---|--------------------------|
| Amitrole | FeTAPc-MWCNT/BPPGE | – | 5.0×10^{-10} | Siswana et al. 2008 [77] |
| Amitrole and diuron | FeTAPc-SWCNT/GCE | 5.0×10^{-5} – 1.0×10^{-4} | 2.1×10^{-7} and 2.6×10^{-7} | Mugadza et al. 2010 [78] |
| Bentazone | PANI-β-CD/fMWCNT/GCE | 1.0×10^{-5} – 8.0×10^{-5} | 1.6×10^{-6} | Rahemi et al. 2013 [79] |
| 6-benzylaminopurine | MIP-MWNT@SnS ₂ /GCE | 1.0×10^{-10} – 1.0×10^{-2} | 5.0×10^{-11} | Gan et al. 2016 |
| Carbaryl | MWCNT/CoPc/GC | 3.3×10^{-7} – 6.6×10^{-6} | 5.5×10^{-9} | Moraes et al. 2009 [80] |
| Carbendazim | FMWCNTs/GCE | 5.2×10^{-11} – 2.6×10^{-4} | 5.2×10^{-11} | Sundari et al. 2010 [81] |
| Carbendazim | fullerene/MWCNT/Nafion/GCE | 2.0×10^{-8} – 3.5×10^{-7} | 1.7×10^{-8} | Teadoum et al. 2016 [82] |
| Carbendazim | GO-MWNTs/GC | 1.0×10^{-8} – 4.0×10^{-6} | 5.0×10^{-9} | Luo et al. 2013 [83] |
| Carbendazim | MWCNT/GCE | 2.6×10^{-5} – 3.1×10^{-6} | 5.5×10^{-8} | Ribeiro et al. 2011 [84] |
| Carbendazim | MWNT-PMRE | 2.0×10^{-7} – 1.0×10^{-5} | 9.0×10^{-9} | Li et al. 2009 [85] |
| Cyromazine | MWCNTPE | 2.5×10^{-6} – 5.0×10^{-4} | 7.2×10^{-7} | Mercan et al. 2011 [76] |
| Cypermethrin | P3MT/MWCNT/GCE | 3.6×10^{-8} – 6.0×10^{-7} | 3.6×10^{-12} | Sundari et al. 2011 [86] |
| Deltamethrin | P3MT/MWCNT/GCE | 3.8×10^{-8} – 4.9×10^{-7} | 3.8×10^{-12} | Sundari et al. 2011 [86] |
| Dicofol | P3MT/MWCNT/GCE | 1.4×10^{-7} – 6.7×10^{-7} | 1.4×10^{-11} | Sundari et al. 2011 [86] |
| Diuron and fenuron | GO-MWCNTs/GCE | 9.0×10^{-6} – 3.8×10^{-4} and 9.0×10^{-7} – 4.7×10^{-5} | 1.5×10^{-6} and 3.5×10^{-7} | Mani et al. 2015 [87] |
| 2,4-dichlorophenoxyacetic acid | FePy-MWCNT/CPE | 9.9×10^{-6} – 1.4×10^{-4} | 2.1×10^{-6} | Wong et al. 2013 |
| Fenvalerate | P3MT/MWCNT/GCE | 1.4×10^{-7} – 5.9×10^{-7} | 1.4×10^{-11} | Sundari et al. 2011 [86] |
| Isoproturon | P3MT/MWCNT/GCE | 3.4×10^{-7} – 1.2×10^{-6} | 3.4×10^{-11} | Sundari et al. 2011 [86] |
| Lindane | MIP-MWCNT/Cu | 1.0×10^{-10} – 1.0×10^{-3} | 1.0×10^{-10} | Anirudhan et al. 2015 |
| MCPA and 4-chloro-2-methylphenol | PANI-β-CD/fMWCNT/GCE | 1.0×10^{-5} – 5.0×10^{-5} | 1.1×10^{-6} and 1.9×10^{-6} | Rahemi et al. 2015 [88] |
| MCPA | PANI-β-CD/fMWCNT/GCE | 1.0×10^{-5} – 1.0×10^{-4} | 9.9×10^{-7} | Rahemi et al. 2012 [89] |
| Methiocarb | CNT/PE | 6.7×10^{-6} – 2.6×10^{-4} | 2.0×10^{-6} | Inam et al. 2013 [75] |
| Methyl-parathion | BMIMPF ₆ -SWNT/GCE | 2.0×10^{-9} – 4.0×10^{-6} | 1.0×10^{-9} | Fan et al. 2008 [90] |
| Methyl-parathion | Au/CNTs/GCE | 3.8×10^{-7} – 5.3×10^{-5} | 1.9×10^{-7} | Zhang et al. 2009 [42] |
| Methyl-parathion | Pd/MWCNTs/GC | 3.4×10^{-7} – 4.8×10^{-5} | 1.7×10^{-7} | Huang et al. 2010 [91] |
| Pentachlorophenol | QDs-MWCNT/GCE | 8.0×10^{-8} – 4.0×10^{-6} | 2.0×10^{-9} | Feng et al. 2015 [92] |
| Pyrimethanil | IL-MWCNT/GCE | 1.0×10^{-7} – 1.0×10^{-4} | 1.6×10^{-8} | Yang et al. 2015 [93] |
| Triclosan | MWCNT/GCE | 1.7×10^{-7} – 6.0×10^{-6} | 5.7×10^{-8} | Yang et al. 2009 [94] |
| Vinclozolin | C ₆₀ -MWCNTs/GCE | 2.5×10^{-6} – 8.8×10^{-6} | 9.1×10^{-8} | Rather et al. 2012 [95] |
| Voltage | P3MT/MWCNT/GCE | 3.4×10^{-7} – 1.2×10^{-6} | 3.4×10^{-11} | Sundari et al. 2011 [86] |

Au: gold; β-CD: β-cyclodextrin; BMIMPF₆: 1-butyl-3-methylimidazolium hexafluorophosphate; BPPGCE: basal plane pyrolytic graphite electrode; CNT: carbon nanotube; CoPc: cobalt phthalocyanine; C₆₀: fullerene; FePy: 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III); FeTAPc: iron(II) tetraaminophthalocyanine; FMWCNTs: functionalized multi-walled carbon nanotubes; GO: graphene oxide; IL: ionic liquid; MIP: molecular imprinted polymer; MWCNT and MWNTs: multi-walled carbon nanotubes; MWCNTPE: multi-walled carbon nanotubes paste electrode; PANI: polyaniline; Pd: palladium; PMRE: polymeric methyl red film; P3MT: poly(3-methyl thiophene); QDs: quantum dots; SWCNT: single-walled carbon nanotube.

An interesting approach for future investigations is the possibility of designing multiplexed arrays using microfluidic devices, with which different analytes could be simultaneously determined in different sensing points. This challenge is linked with a current and relevant trend in (electro)analytical chemistry, which is the miniaturization of the analytical devices, with minimization of the consumption of chemical reagents and waste generation, as well as the proposition of portable instrumentation for analysis in the field (outside of the lab doors). From an analytical point-of-view, the amperometric and voltammetric methods dedicated to the sensing of pesticides should to be subjected to more rigorous analytical tests in order to verify the selectivity and reproducibility (and improve them if necessary), long-term stability, and applicability in diversified matrix samples, once most of the electroanalytical methods are employed in an analysis of spiked water samples using bulk electrodes. The robustness of the electroanalytical methods must also be evaluated from the analysis of a great number of environmental samples. In terms of sensor architecture material, a current trend is the preparation of composites of carbon nanotubes with another allotropic carbon forms, such as carbon black, graphene, or diamond. These classes of carbon composite electrodes are very promissory for electroanalysis purposes, and future electrochemical investigations should be carried out on the sensing and biosensing of pesticides.

10.1.3 Biosensors

A biosensor is an analytical device, used for the detection of an analyte, combining a biological component (bioreceptor represented by biomolecules or synthetic molecules obtained using biological scaffolds) with a physico-chemical detector, as well as an associated electronic system, which amplifies, process and display the detected signal. A successful biosensor must use a highly specific biocatalyst, stable in various stirring, pH, and temperature conditions (most often enzymes) (Schöning and Poghosian, 2002), give a dose-dependent and, desirably, real-time response, be cost-effective, portable, easy to use (Grieshaber et al., 2008).

Biosensors are used in a wide range of applications for the quick and easy detection of pesticides and water contaminants. Gheorghe et al. (2017) present an extensive review of biosensors including:

- Electrochemical biosensing techniques used for pesticides detection
- Optical and imaging biosensing methods
- Immunosensors
- Whole-cell based biosensors

Considering the electrochemical biosensing techniques, Ramnani et al. (2016) report that biosensors based on carbon nanostructures are suitable for the design of portable and point-of-use/field – deployable assay kits. Carbon allotropes such as graphene and carbon nanotubes, have indeed been incorporated in electrochemical biosensors for highly sensitive and selective detection of various analytes, due to their many advantages for such applications, like high carrier mobility, ambipolar electric field effect, high surface area, flexibility and compatibility with microfabrication techniques. A simple and sensitive electroanalytical method for cyclic voltammetry and differential pulse voltammetry determination using a magnetic nickel ferrite (NiFe_2O_4)/MWCNTs nanohybrid-modified GCE has been developed. The method was used to detect benomyl in real samples with satisfactory results (Wang et al., 2015).

Piezoelectric Biosensors, as immunosensors based on acoustic waves, are of emerging interest because of their good sensitivity, real-time monitoring capability, and experimental simplicity (Jia et al., 2012). Piezoelectric systems have emerged as ones of the most attractive biosensing assays for the biopesticides detection due to their simplicity, low instrumentation costs, possibility for real-time and label-free detection and generally high sensitivity. Piezoelectric crystals such as quartz vibrate

with characteristic resonant frequency depending on their thickness and cut under the influence of an electric field. The resonant frequency will modify when different molecules adsorb or desorb from the surface of the crystal, and the induced changes are detected by an electronic circuit. Biosensors based on the quartz crystal microbalance have been reported in the literature for organophosphate and carbamate pesticide analysis (Marrazza, 2014).

As a part of developing new systems for continuously monitoring the presence of pesticides in groundwater, a microfluidic amperometric immunosensor was developed for detecting the herbicide residue 2,6-dichlorobenzamide (BAM) in water. A competitive immunosorbent assay served as the sensing mechanism and amperometry was applied for detection. Both the immunoreaction chip (IRC) and detection (D) unit are integrated on a modular microfluidic platform with in-built microflow-injection analysis (μ FIA) function. The immunosorbent, immobilized in the channel of the IRC, was found to have high long-term stability and withstand many regeneration cycles, both of which are key requirements for systems utilized in continuous monitoring. Detection of BAM standard solutions was performed in the concentration range 0.0008-62.5 μ g/L, which demonstrate the potential of the constructed μ FIA immunosensor as an atline monitoring system for controlling the quality of groundwater supply (Uthuppu et al., 2015).

10.1.4 Paper-based sensors

Busa et al. (2016) present a review of paper-based analytical devices (μ PADs) that incorporate different detection methods such as colorimetric, electrochemical, fluorescence, chemiluminescence, and electrochemiluminescence techniques for food and water analysis. In Table 10.2., different paper-based platforms are presented.

With the goal to devise portable and easy measuring techniques and considering the increasing use of smartphones, the number of μ PAD strategies that incorporate mobile or smartphones for target measurements is increasing. For instance, Sincard et al. (2015) describe a combination of paper-based sensors as an ultra-low cost approach for large-scale monitoring of water quality. The paper-based analytical device (mPAD) produces a colorimetric signal that is dependent on the concentration of a specific target, including organophosphate pesticides in water. A mobile phone equipped with a camera for capturing images of two mPADs e one tested with a water sample and the other tested with clean water that is used as a control, and an on-site image processing app that uses a novel algorithm for quantifying color intensity and relating this to contaminant concentration (Figure 10.1). The mobile phone app utilizes a pixel counting algorithm that performs with less bias and user subjectivity than the typically used lab-based software, ImageJ. The use of a test and control strip reduces bias from variations in ambient lighting, making it possible to acquire and process images on-site. The cell phone is also able to GPS tag the location of the test, and transmit results to a newly developed website, WaterMap.ca™, that displays the quantitative results from the water samples on a map. We demonstrate our approach using a previously developed mPAD that detects the presence of organophosphate pesticides based on the inhibition of immobilized acetylcholinesterase by these contaminants. The objective of this paper is to highlight the importance and potential of developing and integrated monitoring system consisting of mPADs, cell-phones and a centralised web portal for low-cost monitoring environmental contaminants at a large-scale.

Table 10.2: Summary of pesticides and insecticides for food and water analyses on paper-based platforms (after Busa et al., 2016)

| Target | μ PAD Wall Fabrication Method | Paper Substrate | Detection Method | Linear Detection Range | LOD | Real Sample Application | Reference |
|------------------------------------|-----------------------------------|--------------------------------------|------------------|---|--|--|-----------|
| 2,4-D | - | Whatman No. 1 chromatography paper | CL | - | 1.0 pM | Tap water, lake water | [1] |
| Paraoxon, Malathion | Wax printing | Whatman No. 1 filter paper | Colorimetric | 1×10^{-8} –ca. 1×10^{-6} M | 10 nM | Water quality monitoring | [2] |
| Methyl-paraoxon, Chlorpyrifos-oxon | Polymer screen-printing | Whatman No. 4 filter paper | Colorimetric | 0 – $0.1 \mu\text{g} \cdot \text{mL}^{-1}$, 0 – $60 \text{ ng} \cdot \text{mL}^{-1}$ | $18 \text{ ng} \cdot \text{mL}^{-1}$, $5.3 \text{ ng} \cdot \text{mL}^{-1}$ | For methyl-paraoxon: cabbage, dried green mussel | [3] |
| Dichlorvos | Cutting | Whatman 3MM Chr chromatography paper | CL | $10 \text{ ng} \cdot \text{mL}^{-1}$ – $1.0 \mu\text{g} \cdot \text{mL}^{-1}$ | $3.6 \text{ ng} \cdot \text{mL}^{-1}$ | Cucumber, tomato, cabbage | [4] |
| Dichlorvos | Cutting | Whatman 3MM Chr chromatography paper | CL | $3.0 \text{ ng} \cdot \text{mL}^{-1}$ – $1.0 \mu\text{g} \cdot \text{mL}^{-1}$ | $0.8 \text{ ng} \cdot \text{mL}^{-1}$ | Cabbage, tomato | [5] |
| Methomyl, Profenofos | Cutting | Canson paper | Colorimetric | - | 6.16×10^{-4} mM, 0.27 mM | - | [6] |
| PCP | Wax screen-printing | Whatman No. 1 chromatography paper | PEC | 0.01 – $100 \text{ ng} \cdot \text{mL}^{-1}$ | $4 \text{ pg} \cdot \text{mL}^{-1}$ | - | [7] |
| Methyl viologen (paraquat) | Cutting | Whatman filter paper | FL | $0.39 \mu\text{mol} \cdot \text{L}^{-1}$ – $3.89 \mu\text{mol} \cdot \text{L}^{-1}$ | $0.16 \mu\text{mol} \cdot \text{L}^{-1}$ | - | [8] |

[1] Wang, S.; Ge, L.; Li, L.; Yan, M.; Ge, S.; Yu, J. Molecularly imprinted polymer grafted paper-based multi-disk micro-disk plate for chemiluminescence detection of pesticide. *Biosens. Bioelectron.* 2013, 50, 262–268.

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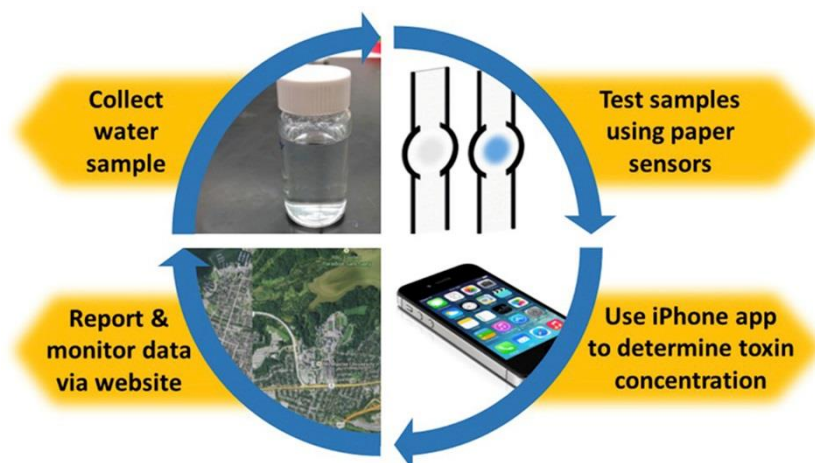


Figure 10.1: Paper-based sensors can change how water quality is tested and monitored globally. Cell phones can be used for data collection and to push data to a website where data is displayed on a map. Areas of contamination become easy to spot and can trigger additional monitoring to take place (after Sicard et al., 2015)

10.2 SENSORS FOR NITRATE MEASUREMENT IN WATER

In their upcoming review on spectroscopic methods for determination of nitrite and nitrate in environmental samples, Singh et al. (2019) extensively described the different laboratory methods referring 229 publications on the topic.

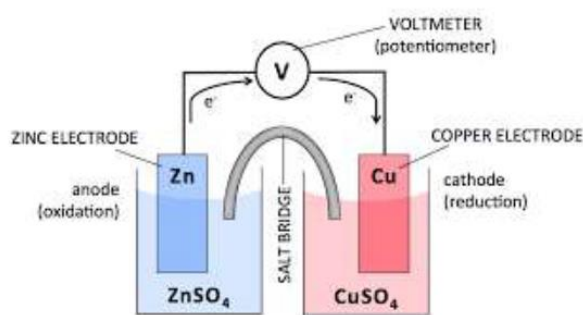
According to Azmi et al. (2017), many researchers in the field of potentiometry, electrochemical, and biosensors have focused on miniaturising their detection systems to enhance the capability of nitrate in-situ measurement. The performance of miniaturised sensor systems is comparable to that of conventional systems.

10.2.1 Potentiometry sensors

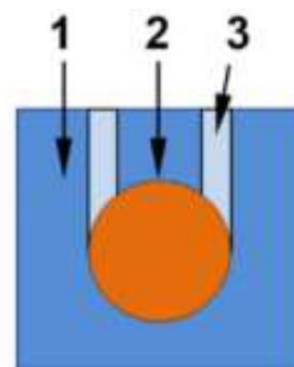
Basically, the conventional architecture of the system consists of two electrodes known as the working electrode and the reference electrode; a salt bridge, and a voltmeter. Figure 10.2(a) illustrates the architecture of the conventional potentiometry system. Meanwhile Figure 10.2(b) illustrates that of the miniaturised potentiometry system.

The advantages of this technique are its low cost (Hassan et al., 2007, Zhang et al., 2015, Mendoza et al., 2014, Paczosa-bator et al., 2014), non-destruction of sample, portable device (Zhang et al., 2015, Mendoza et al., 2014, Chang et al., 2013, Hassan et al., 2007, Santos et al., 2004) with fast response/feedback (Zhang et al., 2015, Li and Li, 2010, Paczosa-bator et al., 2014, Chang et al., 2013, Santos et al., 2004) and the requirement of minimum sample pretreatment.

Research of the potentiometry system has followed several avenues. Early work by Hassan (1976) was concerned with organic nitrate ions and nitramine determination based on the reaction with mercury sulphuric acid mixture. Mendoza et. al. (2014) characterised a nanobiocomposite as Ion Selective Electrodes (ISE) for nitrate ion determination in water. Mahajan et. al. (2007) developed a polymeric membrane by means of Zn (II) complex-based electrodes that work as anion carriers for nitrate anion determination in water. Li and Li (2010) and Nuñez et al. (2013) predict the nitrate contamination level in water based on an artificial neural network (ANN) algorithm.



(a)



(b) [27]

Figure 10.2: (a) Architecture of the conventional potentiometry system and (b) Miniaturised potentiometry system (1) ceramic layer, (2) epoxy-graphite composite and polymeric membrane, (3) microfluidic channel (after Azmi et al., 2017).

Table 10.3 summarises the potentiometry system with limit of detection (LOD).

Table 10.3: LOD of potentiometric system and types of working electrode and membranes (a review by Azmi et al., 2017)

| Working electrode and membrane | Reference electrode | Limit of Detection (LOD) | Nernstian slope (mV/dec) | Application |
|--|---------------------|--------------------------------|--------------------------|--------------------------------|
| Glassy carbon electrode (GCE) and nitrate doped polypyrrole (PPy(NO ₃ ⁻)) | Ag/AgCl | 10-4.8 mol/L | -55.1 ± 1.1 | Soil macronutrient monitoring |
| Glassy carbon electrode (GCE), graphite and tetraoctylammonium nitrate | Ag/AgCl | 10-5.2 mol/L | -57.4 ± 0.8 | Soil macronutrient monitoring |
| Graphite-epoxy and chitosan/bentonite | Ag/AgCl | 2 × 10 ⁻⁴ . M | -54.6 | Nitrate determination in water |
| Platinum wire and trihexyltetradecylphosphonium chloride (THTDPCl) polymeric membrane | Ag/AgCl | 2.8 × 10 ⁻⁶ . mol/L | -60.1 | Nitrate determination in water |

Azmi et al. (2017) remind that the use of a membrane helps the potentiometry system to be selective to nitrate ions and is one of the factors that affects the system's limit of detection (LOD). Bendikov and Harmon (2005) mentioned that doped polypyrrole (PPy(NO₃⁻)) is a highly selective membrane in an ISE system for nitrate determination in water. They revealed that conductive polymer polypyrrole is widely used due to its high conductivity ability and it being relatively stable. As a result, Zhang et al. (2015) took the initiative to apply doped polypyrrole as a sensitive membrane material for the potentiometry system. The polypyrrole could improve selectivity, simplify the recipe procedure, and reduce toxicity compared to the conventional non-porous polyvinyl chloride (PVC) ISE (Zhang et al., 2015). Moreover, this study successfully demonstrated that the use of carbon nanostructure materials between the membrane and the substrate layer in the electrode structure of potentiometric system could prevent the water formation that led to instability. Meanwhile, Mahajan et. al. (2007) developed a polymeric membrane that was made of zinc (II) complex for selective nitrate determination in water. The finding demonstrates that the output of a potentiometry system using zinc (II) complex membrane exhibits better selectivity for nitrate ions than for other inorganic

anions. They highlighted the advantages of zinc (II) complexes, such as stable detection reproducibility and being highly sensitive to nitrate. Wardak (1976) developed an active membrane component using trihexyltetradecylphosphonium chloride (THTDPCI) for polymeric membrane. THTDPCI could enhance the PVC membrane sensitivity by reducing electrical resistance.

The majority of potentiometric nitrate sensors that integrated either true-liquid or liquid polymeric membranes are bulky due to the tubular design with internal reference electrode and internal reference electrolyte solutions. Thus, a micro-fabricated planar potentiometric sensor was introduced (Hassan et al., 2007, Calvo-lópez et al., 2013). The micro-scale sensor could provide several advantages such as small size, simple design, low cost and mass production. Various materials are introduced to produce a micro-scale potentiometric sensor chip. Such materials are screen-printed thick film, silicon transducer chip, silicon nitride base chip and metal printed flexible polyimide film. Current miniaturised micro scale sensors for nitrate detection demonstrate a good response towards nitrate ions.

The miniaturisation of ISEs, while maintaining their selectivity and sensitivity, is a crucial step in the next phase of ISE evolution. Traditionally, in so-called coated-wire ISEs, the ion-selective membrane is placed directly on a solid electronically conductive support, thereby removing the need for an inner solution. However, in these devices, it was observed that the long-term potential stability was quite limited, and they were useful only in specific applications such as capillary electrophoresis or in flow-injection analysis. An important breakthrough in ISE design was achieved by the application of conducting polymers (CPs) as a solid contact layer, i.e. a mediating layer between the electronically conducting substrate and ionically conducting ISE membrane, which was possible due to the mixed conductivity of CPs. Various conductive polymers have been examined as possible internal contact materials that could simultaneously stabilise the overall electrode potential and remove the need for an inner filling solution.

Basically, the conventional architecture of the system consists of two electrodes known as the working electrode and the reference electrode, a salt bridge, and a voltmeter.

10.2.2 Electrochemical sensors

The electrochemical detection of nitrate and nitrite can be divided into a number of categories. Fortunately, these can be broadly grouped within the distinctions of voltammetric and potentiometric systems. Electrochemical systems have the ability to convert the measurement of nitrite ions into the current signal, potential difference and impedance, respectively. In electrochemical systems, various types of electrode were introduced for nitrate detection. Table 10.4 summarises the system performance based on different types of material.

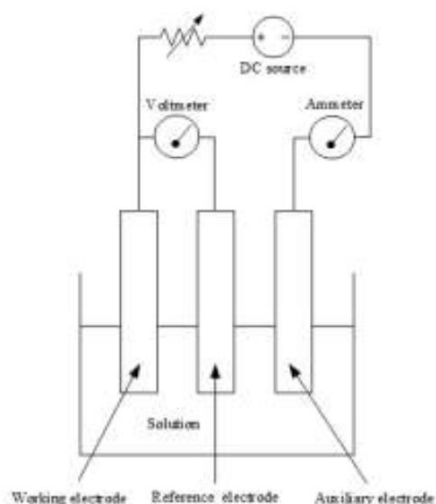
The electrochemical method is widely used due to its high sensitivity to nitrate, simple operation, easy to miniaturise and low power-consumption. However, the conventional electrochemical cell is too massive to be a portable and durable device. Research into electrochemical systems for nitrate detection has followed several avenues (Andreoli et al., 2011, Bhansali and Bhansali, 2013, Can et al., 2013). This is due to the demand for portable devices for continuous monitoring of nitrate concentration in aqueous solutions.

Several researchers have developed a microfluidic base associated with electrochemical sensors for miniaturisation and portable purposes (Li et al., 2011, Li et al., 2012, Li et al., 2013). This combination has promoted many advantages such as the small configuration of electrodes that can be integrated within a microfluidic platform, requiring a minimum instrumentation, small volume of sample, fast response time, and low cost. Moreover miniaturised electrochemical detection is reliable, selective, and highly sensitive to the measured sample. The current architecture of miniaturised electrochemical sensor is designed based on the planar form or flatten of structure. According to Azmi et al. (2017), the performance of miniaturised electrochemical sensor demonstrated good LOD

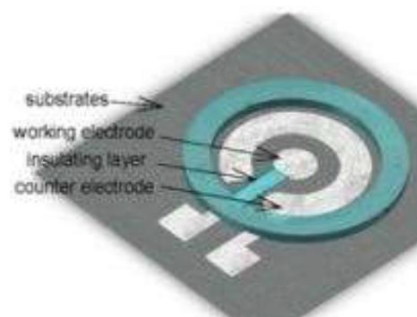
that is comparable to the conventional size of electrochemical system. Figure 10.3(a) illustrates the conventional electrochemical system architecture. Meanwhile, Figure 10.3(b) illustrates the miniaturised electrochemical system architecture.

Table 10.4: LOD of electrochemical/Amperometric/Voltametric system and types of working, counter and reference electrode and application (a review by Azmi et al., 2017)

| Working electrode and membrane | Counter electrode | Reference electrode | Limit of Detection (LOD) | Application |
|---|--------------------------------------|-----------------------------------|--------------------------|--|
| Platinum deposited with copper layer | Platinum deposited with copper layer | Saturated calomel electrode (SCE) | 0.1 mg/L | Total nitrogen (TN) determination in fresh water |
| Platinum deposited with copper layer | Platinum deposited with copper layer | Saturated calomel electrode (SCE) | 5 $\mu\text{mol/L}$ | Nitrate determination in fresh water |
| Silver (Ag)-ultramicroelectrodes (UMEs) | Platinum wire | Ag/AgCl | 3.2–5.1 μM | Nitrate detection in real environmental water samples |
| Copper-micro electrode array | Platinum wire | Ag/AgCl | 1.8 $\mu\text{mol/L}$ | Nitrate detection in water |
| Palladium electrode | Copper electrode | Saturated calomel electrode | 3.6 mg/L | Nitrate ion monitoring in natural water |
| Carbon paste electrode (CPE) | Pt-wire | Ag/AgCl | 0.009 μM | Nitrate and nitrite analysis using microfluidic device |
| Copper wire | Platinum wire | Ag/AgCl | 11 $\mu\text{M/L}$ | Nitrate determination in mineral water |



(a)



(b) [39]

Figure 10.3: (a) Architecture of conventional electrochemical system, and (b) Miniaturised electrochemical system (after Azmi et al., 2017).

10.2.3 Biosensors

A biosensor is one of the direct methods used for nitrate detection in water. In a biosensor system, the concentration of targeted ion in an analyte solution can be determined by employing the biological material, detection system and signal conditioning circuit. The analyte solution is directly exposed to a biological material. The biological material interacts with the targeted ion in the analyte solution. Information on the interaction process is then translated into an electrical signal such as voltage or current by a detection system. The signal is harvested by the signal conditioning circuit in the biosensor system. The signal conditioning circuit such as a digital data acquisition system will recondition the acquired data before being analysed. The concentration of nitrate ion is estimated based on the output signal of the proposed detection system.

Over the last decade, the miniaturisation of biosensor system has been carried out to characterize and quantify the bio molecules. The reduction size of the sensor system can promote lower material cost, lower the power consumption and the system weight. In most biosensors and also chemical and gas sensors, the trace of detection reversible redox species should be implemented by using very small amounts of samples, to descend upon the nanolitre or picolitre range.

Nitrate biosensors have been developed over the last two decades considering the advantage of enzymes that are strongly substrate-selective. Nitrate reductase (NR) is used in the fabrication of nitrate biosensors. However, its multiredox centre responsible for the biological conversion of nitrate to nitrite is generally not very active, and is deeply embedded in the protein structure, thus preventing the direct electron transfer with the electrode.

Carbon nanotubes (CNTs) have emerged as a new class of nanomaterials that are receiving considerable interest owing to their ability to promote electron transfer reactions with enzymes showing low electroactivity. The high conductivity of this carbon material has led to improving electrochemical signal transduction, while its nano architecture imposes an electron contact between the redox centres. CNTs can donate and accept electrons in a wide range of potentials and could therefore be used as mediators in biosensor systems. As a result, Can et al. (2012) investigated the performance of carbon nanotube/polypyrrole/nitrate reductase biofilm electrodes for nitrate detection.

Table 10.5 summarises the different types of biological material, detection systems, LOD and applications of biosensor systems for nitrate ion detection.

Table 10.5: Types of biological materials, detection systems, LOD (a review by Azmi et al., 2017)

| Biological materials | Detection system | LOD | Application | Reference |
|--|--------------------|----------|-------------------------------------|----------------------------|
| Methyl viologen/ Nafion/ nitrate reductase (Aspergillus niger) | Conductometric | 0.005 mM | Nitrate detection in water | Mahajan et al. (2007) |
| Carbon nanotube/polypyrrole/nitrate reductase (NaR) | Amperometric | 0.17 mM | Nitrate measurement | Li et al. (2013) |
| Nitrate reductase (NaR) | Cyclic voltammetry | 200 nM | Nitrate and nitrite detection | Sohail et al. (2012) |
| Escherichia coli | Amperometric | 0.1 mM | Nitrate detection in drinking water | Schnetger & Lehnert (2014) |

10.2.4 Paper-based sensors

Paper-based sensors, so-called paper-based analytical devices (PADs), are a new alternative technology for fabricating simple, low-cost, portable and disposable analytical devices for many application areas environmental monitoring. The unique properties of paper which allow passive liquid transport and compatibility with chemicals/biochemicals are the main advantages of using paper as a sensing platform.

Current paper-based sensors are focused on microfluidic delivery of solution to the detection site whereas more advanced designs involve complex 3-D geometries based on the same microfluidic principles (Figure 10.4). Although paper-based sensors are very promising, they still suffer from certain limitations such as accuracy and sensitivity (Liana et al., 2012). However, it is anticipated that in the future, with advances in fabrication and analytical techniques, that there will be more new and innovative developments in paper-based sensors. In the Netherlands, a monitoring tool based on this technology is tested (Nitrate-app), the measurement is paper based, A phone application scans and analyzes nitrate strips on the paper.

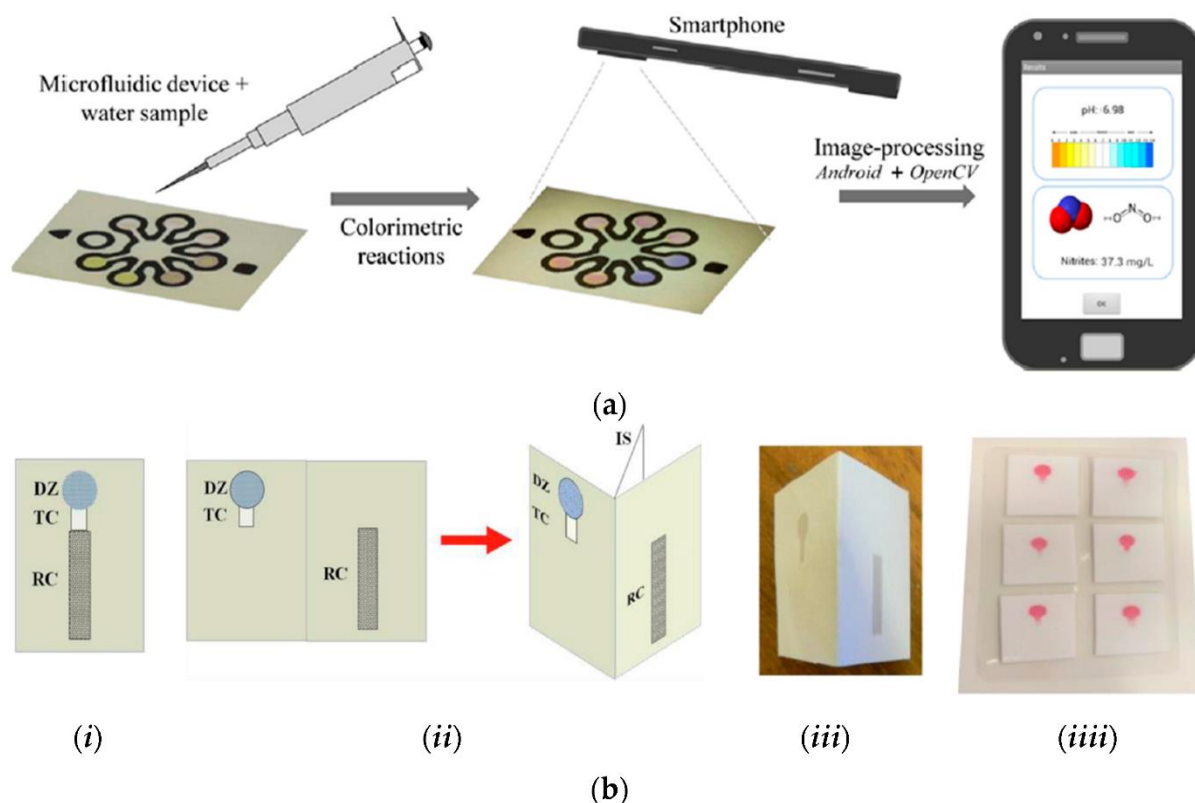


Figure 10.4: Example of a paper-based devices: (a) Griess-color reaction assay-based detection methods for nitrite using a smartphone for image processing (after Lopez-Ruiz et al., 2014, Copyright 2014 American Chemical Society) and (b) Griess-color reaction assay-based detection methods for nitrite and nitrate using 2D (i) and 3D (ii–iv) μ PADs (after Jayawardane et al., 2014, Copyright 2014 American Chemical Society).

Traditional electrochemical sensors often suffer from the effects of fouling due to the adsorption of oxidation products on the electrode surface. That is why paper-based, inexpensive, disposable electrochemical sensors have been developed for nitrite analysis. For example, Wang et al. (2017) present a system based on a simple and efficient vacuum filtration system. Taking advantage of the physicochemical properties of graphene nanosheets and gold nanoparticles, the mass transport regime of nitrite at the paper-based electrode was thin layer diffusion rather than planar diffusion. In comparison with the electrochemical responses of commercial gold electrodes and glassy carbon electrodes (GCE), a considerably larger current signal is seen at the paper-based sensing interface, which significantly improved its sensitivity for nitrite detection. In particular, the paper-based electrode was a disposable sensing device, so that it effectively avoided the fouling effect arising from the adsorption of oxidation products. According to Wang et al. (2017), the paper-based sensing platform made it possible to determine nitrite in environmental and food samples in an accurate, convenient, inexpensive, and reproducible way, indicating that the proposed system is promising for practical applications in environmental monitoring and public health.

10.3 AUTOMATIC SAMPLER TECHNIQUES FOR PESTICIDE AND NITRATE MEASUREMENT IN (SOIL-)WATER

Automatic water sampling systems exist for pesticides and nitrates measured in water samples from ground- or surface waters or extracted from soils.. It is essentially a pump controlled by a clock or other automatic trigger, so that water samples can be pumped from a water source into a bottle at some pre-determined time or event and later collected for analysis (Figure 10.5). Such devices can

be settled to collect water in the saturated zone (piezometer), in streams, rivers and lakes. They can be portable or require an indoor environment. Experimental systems have also been designed to sample percolating water through the vadose/unsaturated zone. These in-house systems mainly consist of suction cups connected to a controlled pump (Hamon et al., 2006; Farsad et al., 2012).

Classically, water samples should be stored in solvent-washed or brand-new (amber) glass bottles verified as uncontaminated, sealed with aluminium foil or Teflon, fitted with new plastic screw-caps and chilled immediately to less than 4°C in a refrigerator (Kennedy et al., 1998). Organic solvent (e. g. dichloromethane) can be added immediately where convenient to limit volatilisation or hydrolysis, although care to prevent leakage is essential. Extraction of water samples with organic solvent should be made within 48 hours and immediately on receipt. Even so, it can be anticipated that samples containing endosulfan isomers will lose chemicals by volatilisation if jars are not properly sealed, ideally with Teflon. A loss of chemicals can also occur by hydrolysis if the pH of the water is above 8.

Due to its instability in over time, automatic water sampling devices require regular human intervention, e. g. to collect water samples (every 24 hours), to fit in new sampling bottles/lysimeters, to change device batteries and for other maintenance work.



Figure 10.5: Automatic water samplers (Campbell Scientific®). Left: The PVS5120D is a portable discrete sampler that deposits its water samples into 1 to 24 containers. This sampler uses a vacuum sampler controller to allow a master device to control and communicate with the water sampler. This sampler is lightweight, portable, and battery-powered. It can fit in a small-sized manhole. Right: The CVS4200D is a discrete, stationary water sampler designed for indoor use(images: Campbell Scientific®).

Another way consist to directly sample the analytes of interest (pesticides and nitrates) rather than water. This is the aim of passive sampling technologies, which have been developed to monitor pollutants in the aquatic environment. The advantage of passive samplers is, that they sample *in situ* without disrupting the environment. They can be used in ground- and surface water. Thanks to their phase or selective membrane, these devices allow to integrate sampling over the time and as a result to concentrate molecules.(Figure 10.6:). Their capacity of accumulation allows to improve the sensibility of the analytical process and so to detect concentrations of micropollutants in concentrations measured in $\mu\text{g/L}$ or even ng/L . Sampling proceeds without the need for any energy sources other than this chemical potential difference. Several types of devices are used depending on targeted compounds. Pesticides can for example be sampled by SPME, SLM, sorbant devices, SPMD, PDBS, POCIS, TRIMPS, dialyse membranes, Chemcatcher, TLC and PISCES devices. These tools require to remain submerged and do not respond well to dry episodes. They are considered from now on as complementary tools with the discrete water sampling techniques.

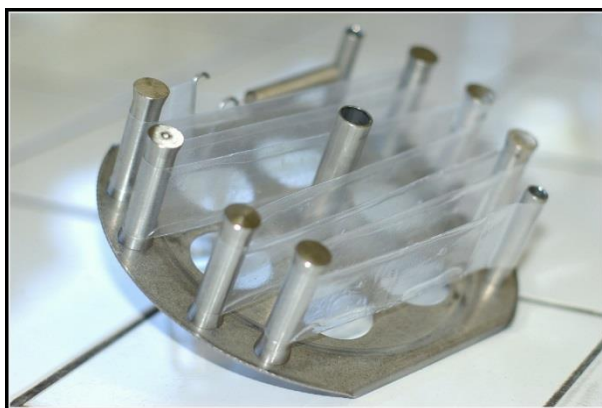


Figure 10.6: Example of a passive sampling device in the BRGM Laboratory © (BRGM - Thomas Alcaraz)

11. PARTICIPATIVE MONITORING: INVOLVEMENT OF CITIZENS

11.1 DEFINITION BASED ON LITERATURE REVIEW

11.1.1 “Citizen science”

For many researchers, participative monitoring is a subset of citizen science that focuses on repeated data collection by non-scientists, often dedicated to identifying trends over time (Etrella and Gaventa, 1998). Although some researchers might disagree with that point of view, this categorization will be used (Eitzel et al., 2017, Lovett et al. 2007). Many definitions have been proposed for “citizen science”. One of the first attempt was in 1995 to describe expertise that exists among those who are traditionally seen as ‘lay people’ (Irwin, 1995). It is one of the broader applications of the term. The term citizen science was added recently to the Oxford English Dictionary in 2014 as:

“Scientific work undertaken by members of the general public, often in collaboration with or under the direction of professional scientists and scientific institutions”

The main tenet of this concept is that members of the public are involved in science as researchers (Conrad, 2011). In order to extend this term to wider public than ‘citizen’ (which may imply a narrower definition, of a native or naturalised member of a state or nation), various terms were proposed: “community science” (Conrad, 2011), and Public Participation in Scientific Research” (PPSR) or “citizen and community science” (Eitzel et al., 2017).

In Europe, scientist as profession is relatively new, emerging slowly throughout the 17th to 19th centuries, with specialization in science. Consequently, the distinction between “scientists” and “citizen scientists” is also relatively new. ‘Citizen scientist’ (meaning scientist independent of institutions) was used at least as early as 1912 (Eitzel et al., 2017). Before, the word “participative monitoring” was establish, the use of “unprofessional” collaborator was common. Many institutions asked vessel captains or crew medical officers to collect plants in newly discovered territory through the 16th and 17th centuries.

The participation of the public/citizens in science decreased during the 19th to 20st centuries with the increase of science specialisation. However, during the second half of the 20st century, thanks to technology development, citizens participations increased again. The fields in which citizen science is used are diverse: ecology, astronomy, medicine and much more. The point of a citizen science project is to facilitate scientist and citizen to collaborate towards a common goal. The collaboration that can occur through citizen science allows investigations at large scales and long time, that can lead to discovery scientists could not have achieved on their own.

Citizen scientists can help with opportunistic and observational studies that do not follow a strict design. These studies can be useful because of the large temporal or geographic scale of the data collection, the rarity of the phenomena observed (e.g., a rare species or infrequent weather event), or the timeliness of the observations (e.g., collecting information for crisis response, such as after earthquakes or oil spills), all of which make data collection difficult (McKinley et al., 2017).

Citizen scientist can participate in various ways in citizen science program by, 1) proposing programs, 2) analysing data and 3) collecting data. The last aspect (collecting data) is what referred to as “Participatory monitoring”.

11.1.2 Participative monitoring

Citizen observation of the environment and collection of data is a very ancient practice, being undertaken informally before the definitions of citizen science and citizen scientist were coined. But

this practice, gradually fade until the 20th century, because the means of data collection was out of reach of many.

It was through association networks (e. g. Nature Conservatory, Earthwatch) that the practice of observing nature maintained its momentum in the second half of the 20th century. In the 1970s, some associations for the protection of birds used citizen science to developed programs of birds watching. Other citizen observation programs quickly follow in the course of the 1990s, involving mostly passionate, professional and amateur naturalists (Conrad and Hilchey, 2011). But, it was not until the 2000s with the advent of the internet, that the movement significantly accelerated and, above all, became open to a much wider audience.

Citizen observations of the environment today, covers a wide range of concerns. The quality of the environment, noise, air pollution, or even the quality of the water have become major concerns for citizens and new tools have facilitated their greater involvement in address these issues. Technology developments have played an important role: the widespread use of smartphones and the ability to produce pollution sensors at a (relatively) low cost opened new horizons for citizen observation of the environment.

The notion of “participative monitoring” has several aspects in literature. As for “citizen science”, various definition are used such as “community based monitoring” (CBM). This expression includes a diversity of projects that involve citizen groups more or less organised in a collective observation and monitoring process of the environment (Conrad and Hilchey, 2011). More recently, participative monitoring programs have also included an increase of the public education (Brossard et al., 2005) and/or an increase of the citizen’s involvement in the environmental decision linked to a specific project. Participative monitoring in its most inclusive form should include stakeholders in decision making but does not always do so even if volunteers tend to have the hope that their efforts will be used to assist in local decision making (Conrad and Daoust, 2008).

Participative projects have several characteristics, including the type of environment observed; the type of public mobilised and the program management. In the FAIRWAY project, we will focus on participative monitoring in a context of a scientific project, in the context of local/regional issue monitoring program.

11.1.2.1 Scientific project monitoring program

Scientific project monitoring programs have, as a principal characteristic, the generation of scientific knowledge. They either mobilise a well informed public, able to carry out a rigorous or data protocols or or else citizens who have been trained to collect data according to the protocol.

These projects are usually driven by one or more research laboratories, often at the national level but also at local scale, and in partnership sometimes with associations or local organisations. Most of the large-scale ecosystem monitoring programs (e. g. bird monitoring programs) tend to be collaborative.

In the field of the environment, collaborative science programs are often developed around the theme of biodiversity. The Anglo-Saxon countries have generally been pioneers in this field. In Britain, for example, the Natural History Museum and the association Royal Society for the Protection of Birds have led for several decades programs of identification and monitoring of common birds by relying on a network made up of thousands of amateurs and professional naturalists (Bing et al., 2008).

The challenge is then to produce a suitable protocol that is 1) sufficiently scientifically rigorous, and 2) not too complex (and ideally enough fun) to enable broad public support.

These monitoring programs involve a central agency (most of the time a government agency or a governmentally funded agency) that requests information from volunteers. The purpose of

monitoring by these volunteers is to provide early detection (by citizens) of issues of environmental concern, which can then be investigated/analysed by scientific experts (Whitelaw et al., 2003, Conrad and Daoust, 2008).

Although often successful in the short term, monitoring by volunteers are often funding dependent and cannot continue on their own without government or doner assistance. Also, these volunteers may not represent a very diverse stakeholder group as they have a vested interested in the issues being address in the monitoring program (i. e. only fishers or only farmers; Conrad and Hilchey, 2011).

In most of the projects, the general principle is to rely on a network of volunteers (citizens) to follow a protocol of data collection with a scientific purpose. Most of the time, a website acts as an interface between scientists and the volunteers. The volunteers have to be able to recognise, count and locate individuals (animals or plants for example), with lots of information being downloaded from internet. Then they defer their comments on a website, the information is then sent directly to the researchers. The findings of the research are generally published on the same website, to inform citizen observers of the findings of the program (Figure 11.1).

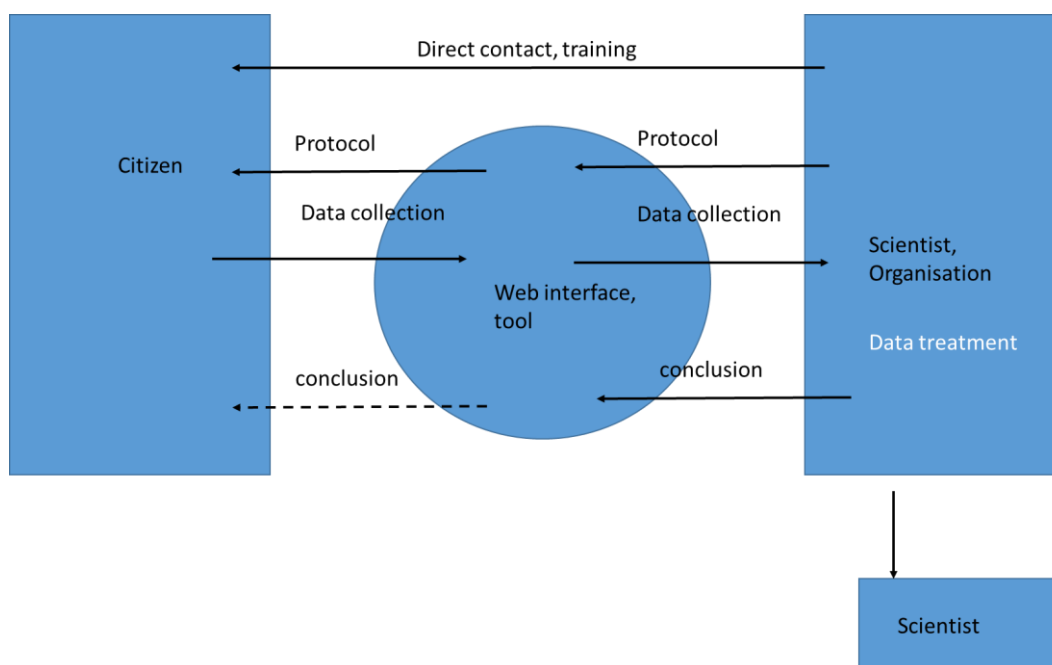


Figure 11.1: Representation of interaction in a scientific project monitoring program (Bing et al., 2008)

11.1.2.2 Local/regional activism monitoring programs

This type of programs often focus on local issues for which actions by governments should be initiated but has not occurred (Conrad and Daoust, 2008). It often focusses on specific issues and sometimes has no private sector or government support (Whitelaw et al., 2003). These participative monitoring projects are characterised by perspectives of joint public action. For these projects, the scientific goal is that data is generated that will inform local citizen to take action on a specific issue.

The general principle of this type of participative monitoring is to mobilise a network of highly motivated volunteers, to collect data. They supply data to an organisation to develop an action program or intervention. As a result, the project manager is rarely a research laboratory, but more often an organisation (administration or association, for example) who seeks to deal with a problem

in a given territory. Such programs can for example provide comments on the invasive species or allergens in order to deploy a program to fight against their dispersion or it can aim to develop an inventory in order to fight against a project planning (Bing et al., 2008).

The monitoring devices used in these projects are similar to those for scientific programs. On one side, the scientists (belonging to an administration or association for example) develop the data collection protocol. On the other side, volunteers collect data using the protocols and equipment supplied by the scientists. Volunteers provide their observations to scientists, directly, or through a website that allows the data entry. These data are then compiled and can lead to concrete action (plan of action, mobilisation, etc.; Figure 11.2).

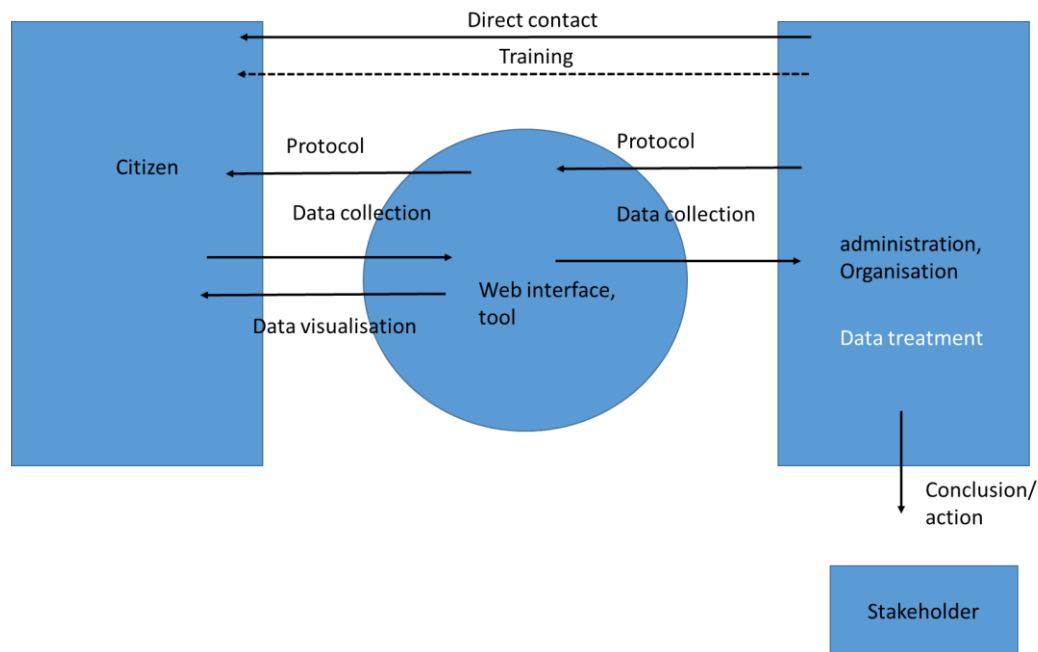


Figure 11.2: Representation of interaction in a Local/regional activism monitoring programs
(Bing et al., 2008)

In some of this “bottom-up” monitoring programs, the local communities do not trust the data provided by the private companies and/or government organisations and want to acquire data by themselves. In many instances, “official” monitoring programs also exist, which may have a high degree of technical credibility, yet generate little credit for the community (World Bank, 2008).

One reason for this is that most monitoring programs are top-down, with the public receiving information that has been collected, analysed, and reported by experts chosen by the project sponsor or company and presented in a way that the public may not understand. In many instances, the information may not even address the real concerns of the community; rather, it may be strictly oriented toward a organisation self interests in relation to compliance with regulations and legal commitments (also an important function of monitoring) (World Bank, 2008).

However, many failures of bottom-up community based monitoring groups are mentioned. These include lack of success due to little organisation credibility and capacity (Bradshaw, 2003). Others suggest that bottom-up participative monitoring programs tend to be unsuccessful on a more organisational level, perhaps due to poor governance structures and no legislation or policy support (Conrad and Daoust, 2008).

11.1.2.3 Global concern monitoring program

The emergence of measurements carried out directly by citizens in open mode and using mobile technologies are gradually taking the shape of networks of "human sensors". This category of participative monitoring includes devices geared towards the general public.

They fit into a perspective of democratisation of the tools for environmental monitoring and are present as complementary to official measures devices (alternative monitoring) to feed and eventually guide public policy. Moreover, they are mostly in the field of "low-dose", i. e. low impact/frequency pollution (pollution of air, water, sound), which they aim to measure and understand for a better control.

These devices provide the ability to have a global networks of sensors, their strength being in the mass production of environmental data. Also, unlike the participative monitoring of "scientific program" or "local issue monitoring program", this type of participative monitoring is little governed by a scientific protocol (which is based on the formulation and testing of hypotheses). They fit into a perspective of democratisation of the tools of environmental monitoring and present themselves as complementary to official measure devices (alternative monitoring) to feed and eventually guide public policy.

The results of measures are data visualisation tool and maps with with generally little corrections or calculations between the measures and the maps/visualisations. The tools to visualise the measure repartition is generally provide with the tools to collect the data (Figure 11.3).

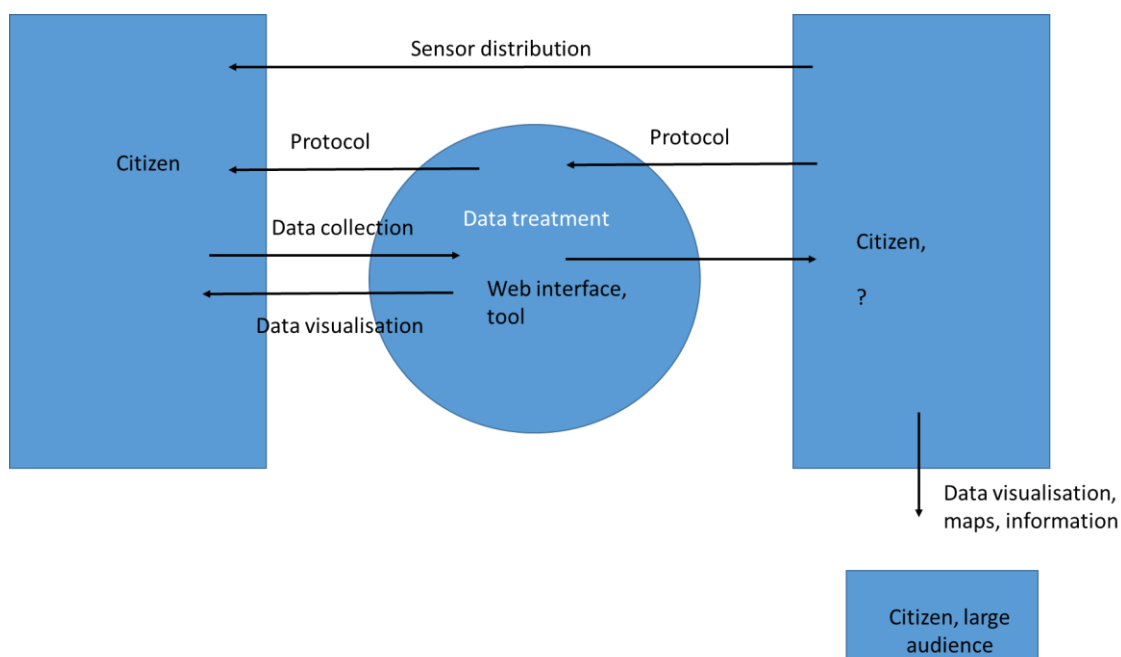


Figure 11.3: Representation of interaction in a global concern monitoring program (Bing et al, 2008)

The complementarity of these devices with those of public administrations is based on two key principles:

- the multiplication of the number of sensors/observers may support a measure based on a limited number of institutional sensors (e. g. sensors payed by government),

- the production of measures of exposure for individuals rather than exposure based on a 'representative' place: participants measure precisely what pollutants they are exposed to in their daily lives.

Issues for "human sensor" monitoring arise during data collection. These include data fragmentation, data inaccuracy, and lack of participant objectivity (Whitelaw et al., 2003). Studies are often lacking in experimental design and do not consider issues such as adequate sample size (through a priori power analysis, for example). This could generate mistrust (by the scientific or government community) in the credibility and capacity of "human sensor" monitoring data (Conrad, 2007).

11.2 WHAT CAN WE EXPECT FROM MONITORING?

11.2.1 Increase cost benefits of action

A key benefit of Participative Monitoring programs is a decrease in the cost of official (i. e. governmentally funded) monitoring programs (almost uniquely) in the field of research

The general decrease in prices of connected tools and the increases of on-line tool are the main drivers behind the recent success of citizen science and participative monitoring programs. However, this is also the case for more 'classic' type monitoring programs. Two decades ago, groundwater level was computed manually every few days whereas now hourly data can be downloaded automatically on a central database. Innovative connected tools (a connected tool received instructions or parameters from the backend, and/or sends to this backend data points collected by its sensors) are not only present in the smartphone field but also in the field of conventional sensors (hourly measurement and hourly transmission are technically achievable and economically accessible).

Connected tools (automated probes) and participatives monitoring have different benefits. Automated approaches have the benefit of regular and frequent (e. g. daily or hourly) measurements whereas the participative monitoring has benefits that counterbalance the lower data frequency, such as engage volunteers and encourage them to become interested in local water resources. Anyhow, the costs are not necessarily lower (Little et al, 2016).

Participative monitoring seems to be a great solution in specific research programs where scientists do not want to (or cannot) spend time or money to realise a task. This kind of monitoring could be valuable in large countries or for monitoring in remote area. In Europe, several network (Lora, GPRS) can be used, so connected tools can be used instead of participative monitoring, and the issue is more a matter of costs than a matter of technical devices.

11.2.2 Modification of volunteers behaviour

Many monitoring programs rely on the idea that making people participate will make them more interested in the topic and more generally in science. However, if specific education and training actions are not planned in the project, the increase of interest is generally marginal as volunteers are usually already interested and motivated individuals people.

Increases of knowledge in a specific domain has been observed in some participative monitoring projects (bird watching) but in other programs the volunteers did not really understand what they measured and misunderstood the results (Land-Zandstra et al., 2016).

In fact, to improve the quality of their data (or increase the reception of their paper in a peer-review journal), the tasks asked to volunteers are generally very simple and do not improve their scientific knowledge. Only teaching and direct contact with scientists has been shown to increase participants general knowledge, and so monitoring activities alone cannot fulfill the hopes of increasing public knowledge. Where it is essential to increase environmental awareness, other more suitable and

efficient methods. like environmental education, can be used to reach this goal (Garcia and Lescuyer, 2008)

Participatory methodologies in the agricultural sciences usually involve limited numbers of farmers, working in collaboration with researchers, and scaling is usually difficult when the aim is to reach a number of larger farmer groups (Beza et al, 2017). The selected farmers (the initial volunteer group) are already conscious of their dependence on their natural resources and are generally willing to change their practices (Dangles et al, 2010). In monitoring, there is no guarantee of environmental efficacy even if the monitoring phase is a success; research message is transferred to farmers who have the role of the adopters or rejectors of innovations developed by others (Probst et al., 2003).

Some of the stakeholders, as well as many farmers do not want to be volunteers because they see monitoring as a way to impose on them new ecological constraints.

11.2.3 Increase administrative action

Because of the common mistrust of public against private companies and government funded monitoring programs and vice versa, the administration mistrust of participative monitoring, monitoring not supervised by administration is rarely used outside of the research world.

Data quality is almost universally recognised as one of the problems that scientists working in case studies need to address (Riesh and Potter, 2014). For example, some studies have shown that monitoring based on visual counting approaches need to take into account specific risks of bias due to the technique itself, volunteer's competences (Crall et al, 2011), the sampling effort and volunteer's missing impartiality (Leopold et al, 2009).

Citizen science and participative monitoring has led to an important number of scientific publications but yet only few administrative decisions (Yank, 2005).

11.2.4 EXAMPLES OF PARTICIPATIVE MONITORING PROGRAMS

The examples below are existing (or previously existing) programs that have reached a broad audience. The projects presented here are mostly from North America because a selection was made on the availability of accessible websites. The selection was also made to present an aspect as wide as possible of different projects on the water. Direct measurement programs for nitrates or pesticides are nevertheless rare.

11.2.4.1 CATTFish

The CATTFish, which stands for Conductivity and Temperature in your Toilet, uses an instrument that measures conductivity in water, allowing citizen in the US to monitor the quality of the water inside their home. It is designed with sensors that sit in a toilet tank. With a push of a button, it takes a measurement each time the tank refills after a flush. The main aim of this program is to measure a potential impact of hydraulic fracturing (www.environmentalhealthproject.org).

11.2.4.2 Rhode Island Water Quality Measure Program

The heart of the program consists of weekly measurements of water quality taken by numerous trained volunteers. The program emphasises watershed scale monitoring, because the water quality of a given body of water is a reflection of the activities in the lands and waters that surround it and lie upstream.

The program encourages citizen to understand the need to cooperatively manage and improve the water quality of water bodies within a watershed. In the program, the most common measured

parameters are: water clarity, algal density, dissolved oxygen, water temperature, alkalinity and pH (<https://web.uri.edu/watershedwatch/program-information/>).

11.2.4.3 Streamselfie and Stream Tracker

These two programs have the same objective: building of a map of a stream using photographs taken by volunteers. In Streamselfie, the aim of the map is to improved stream monitoring so community organisations involved in water monitoring are also part of the projet. The program aims at highlighting streams that are being monitored recently/at present and at developing a national inventory of streams that need to be monitored (<http://www.streamselfie.org/>).

Stream Tracker aims at the improvement of mapping and monitoring smaller, intermittent streams through crowd sourced on-the-ground observations of streamflow presence and absence. Stream Tracker aims at filling in this information gap by combining a network of citizen scientists, sensors, and satellite imagery to track when and where streams flow (<http://streamtracker.org>).

11.2.4.4 NECi's Handheld Photometer

The handheld photometers send nitrate and phosphate data to mobile phones when used with enzyme-based test kits. This tool can be used to obtain accurate nitrate or phosphate concentration in water, soil or plant tissue samples. The enzyme-based test kits provide reliable results while the photometer design ensures accurate translation of the quality data. The design of the photometer enables any citizen scientist to collect accurate nitrate data. The app software allows teams to effortlessly share results and coordinate projects with team members (<http://nitrate.com/store/index.php/nitrate-phosphate-photometer>).

11.2.4.5 Roaring Fork Watershed Stream Temperature Monitoring

This program is based on the citizen growing concern about stream temperatures increases (with flows expected to be lower than average for instance) and its potential impact on fishes and other aquatic species. Citizen scientists will volunteer to take water temperatures in the streams and rivers throughout the Roaring Fork Watershed (in US) so they can detect unusually high temperatures (<http://www.citsci.org/cwis438/websites/citsci/home.php?WebSiteID=7>).

11.2.4.6 KSU "Citizen Science"

The KSU "Citizen Science" program is designed to let community members do their own soil and water testing through the use of accurate test kits. Results can inform if a stream, lake, or another water supply meets water quality standards. They can also be used for the preliminary testing of drinking water, but a certified laboratory should perform follow-up testing if a problem is suspected. A helpful "how to" video for testing water in a local community or as part of a stream monitoring network is presented on the website (www.oznet.ksu.edu/kswater).

11.2.4.7 Know Your Water: Sustainable Groundwater Research

The primary objective of this project, run by a group of postgraduate students, is to model the distribution of modern groundwater across South Africa. In order to achieve this goal, an isotope tracer, tritium (the radioactive isotope of hydrogen), is measured in rainfall and groundwater samples. The sampling trip involves the collection of groundwater samples from pre-determined boreholes, where one can measure the depth to water as well as setting up rainfall collection stations. Citizen scientists who have received their sampling kits in the mail will sample rainfall and their groundwater from boreholes/springs and send them back to the project team for determination of the tritium activity.

11.2.4.8 Nitrate App

A Nitrate App is tested currently in the Netherlands. A reference map is necessary. Surface water and groundwater are analysed with test strips (paper based sensors). Using the App, the result can be scanned and, if desired, shared. The App is in particular designed for people working professionally with water quality such as farmers, water authorities and water companies (<https://www.deltares.nl/en/news/the-nitrate-app-testing-what-you-cant-see/>).

11.3 PARTICIPATIVE MONITORING IN FAIRWAY

11.3.1 Evaluation of a device (tools)

Different tools (devices) that can be used for participatory monitoring of pesticide and nitrates in groundwater and surface water, will be tested during the Fairway project.

Currently in government monitoring programs, are spatially and temporal limited. Using volunteers in a participative monitoring action could increase the number of data available for a specific site (river or spring) or increase the number of points (stream, piezometer) followed.

Participative monitoring's main interest is to gather a community around a concept and/or an issue. In FAIRWAY, participative monitoring will be address in two ways.

- i) Connected probes will be used to measure directly the concentration of nitrates in soils to help farmers to better understand fertilisation impact and then better calibrate fertilisation. The probes are maintained by the farmer and they will be provide with access to a website where there will be provided with support to help with the interpretation of the results collected
- ii) Passive samplers will be evaluated for used in the measurement of pesticides (e.g. MCPA) concentrations instreams. If passive samples the evaluation demonstartes that passive samplers provide an accurate estaimate of the load of pesticides in the stream, then in the future thaey can be used to help farmers to better understand the impact of pesticides application of the drinking water quality in thier area. The management of the passive samplers during the Fairway project will be done directly by farmers, as orginally hoped, but instead by other staksholders within the MAP of the specific case study catchments.

These approaches to participatory monitoring are more valid for surface water than for groundwater (except if springs are present on the catchment).

11.3.2 Evaluation of a method

Education is propably the best way to change stakeholder behavior, with participative monitoring providing supplementary support for this. Significant improvements in stakeholder knowledge are not be expected as a result of this elemet of the Fairway project, as there monitoring program will not be accompanied by and eductaional program However, some training will be provided on site to upskill stakeholder onhandle the device.

Unfortunately, there will be less opportunity than expected to apply participative monitoring in case studies. It was so decided that participative monitoring will be reviewed in 3.2, possible applications on field will be done after a discussion with case studies leaders (WP 3 minutes - meeting Naples 11/2017).

12. CONCLUSIONS

The present report has been written in the context of Work Package 3 (WP3) of the FAIRWAY project. Aim in WP3 is to prioritise and evaluate data-driven indicators for the impact of agriculture activities on drinking water quality, referred to as Agri-Drinking Water Indicators (ADWIs). For this purpose, the ADWIs are defined and reflected on within the DPSIR-framework (Driving forces – Pressure – State – Impact – Response). In addition, Link-indicators are introduced to the framework. These are indicators that describe how nitrate and pesticides leave the agriculture system (Driving forces and Pressure) by leaching or runoff and move on soil surface or through the hydrogeological system (Link) to drinking water resources (State and Impact).

The following aspects for a further prioritisation of ADWI can be deduced from the review:

- Regarding the two kinds of pollutants – nitrates and pesticides – frame conditions are quite different:
 - Nitrate is one single substance, being mobilised and immobilised, leached, transported by runoff and emitted. It is essential for plant growth and omnipresent, even under “natural” conditions.
 - On the contrary, around 250 so called “active substances” of pesticides are authorised by EFSA. Placement on the market of pesticide product needs national approval. They may only consist of the registered active substances registered on EU-level, pure or in mixture, and of additives, for a better handling of the pesticide. Pesticides are supposed to be – to the greatest possible extent - harmless. They are supposed to degrade or at least to be absorbed by the soil matrix, but not to leach into groundwaters. Improper handling may however lead to runoff or drift and therefore to pollution of surface waters.
- ADWI are useful on all levels: at farm level as an aid in farmer’s consultation, at local or even national level as an evaluation and monitoring tool for administration work and for policy-makers.
- From the number of indicators listed in chapter 5 can be deduced, that indicators, which act in the agricultural sector as Driving forces and as Pressure indicators, are far more numerous than State respectively Impact indicators. The large number of agricultural ADWIs also explains, that from this part of the DPSIR-model, many factors may influence water pollution. State indicators which are used for the evaluation of the water quality are – on the contrary – far more standardised, like the water quality standards they are supposed to monitor.

A survey among the FAIRWAY case studies (Milestone 3-1) was conducted. This survey, and the present review indicate the following results:

- The initial goal of the review was to identify a small number of indicators already in use in several European countries that could be disseminated across the rest of the case studies. The review has shown, that very few ADWIs are really used throughout Europe.
- Aim, size and structure of the different case studies are different, and so are the ADWIs in use.
- ADWIs and the data to calculate them may be available on plot, farm or regional level.
- Those case studies with focus on nitrate pollution do not utilise pesticide indicators and vice versa. In addition, there are specificities of each country/case study, such as climatic and agronomic conditions.
- In the case studies, far more indicators and data related to nitrogen are in use than related to pesticides.
- While in the FAIRWAY case studies common indicators for nitrate risk are simple statistics on animal density, yield or N-budgets, for pesticides only compound indicators are in use (Treatment Frequency Index and Pesticide Load Index).

- Concerning pesticides, the DPSLIR-model can only be used, if data on the Driving force and Pressure side on the use of specific pesticides are available and can be linked to the State/impact side. Since a regional differentiated data compilation of application data and a consequential estimation of the pesticide inputs is missing, pesticides found in drinking water can only sporadically be related to application data. (SRU, 2016).
- Pesticide contamination in surface waters being reported by EAA (WISE-databank, reports by Member States) are in their large majority due to substances, which are withdrawn from the market some time ago. In most sites, contamination is due to occasionally high quantities of pesticides contained in the water table that feeds surface water.
- Causes of pesticide contamination of ground waters cannot be identified precisely using the WISE-databank, because obviously some of the Member States reported under a collective term, others reported the analyses of certain active substances. Most of the pesticides being reported contaminating groundwaters are not any more approved by EFSA-authorities.
- It is therefore important to use authentic and up-to-date data on pesticide use in a catchment and to adjust the analytical spectrum for detecting pesticides in ground and surface water accordingly.
- As more (in time and space) aggregated data show less standard deviation than the single datasets, correlation with water quality could be stronger between AEI being deduced from data on a regional level than on farm level). This would explain, why Wick et al. (2012) found the Gross Nitrogen Balance a statistically significant predictor for groundwater nitrate concentration, while other authors (Buczko et al., 2010; Lord and Antony, 2002; Rankinen et al., 2007; Sieling and Kage, 2007) calculated less strong relationships for indicators at a smaller scale.
- Correlation analysis with data of the test site showed, that most integrated and aggregated indicators (field budget or Cassis-N surplus) were not the ones with the best correlation. Also Buczko and Kuchenbuch (2010a) consider, that the Nitrate Leaching Indices (NLIs) developed from the agricultural viewpoint usually are restricted to the soil zone (what corresponds to the Driving force and Pressure ADWIs within the DPSLIR-framework in the FAIRWAY project) and estimate the N losses that leave the root zone. As the fate of diffuse nitrogen losses – and their impact on the environment, is very much influenced by the properties of the unsaturated zone beneath the root zone, they conclude, that it is not sufficient to alone estimate the amount of N that leaves the root zone (this is the reason why we introduce the Link indicator for the DPSLIR-framework).
- Especially composite NLIs show – related to the number of single components and their weighting – a low relative sensitivity for changing conditions (Buczko and Kuchenbuch, 2010).
- Further evaluations should specify which indicators are useful under defined circumstances. For example, the agricultural yield could be an indicator in the non-breeding areas of the Paris Basin for nitrate risk to drinking water. In the Netherlands, in areas with intensive breeding activities, N budgets are used for the same purpose.
- Calibration and validation of ADWIs against field data is of high importance, as Buczko and Kuchenbuch (2010a) point out. This is intended within the next steps of WP3 using field data from FAIRWAY case studies.
- Questions on confidentiality of farm data aroused in conjunction with the survey. This is due to uncertainties related to the new regulation on data protection (EU 2016/679), but also due to a tightening of fertiliser legislation in some member states.
- The data acquisition scale may also be a problem, because readily available data categories at the national level are difficult to access at the local level. This review work has allowed to collect a large number of driving force and pressure parameters to be taken into account and to draw the relevant indicators that relate driving force, pressure and state indicators.

- The first statistical tests were carried out with the French case study data. These tests showed that a diversity of time steps are important to take into account. An appropriate approach could be developed. Integration of other case studies data is at work.
- The selection of indicators that can be used in all European countries remains a work in progress. The database currently being developed will help to select indicators for the case studies.

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14. ANNEX

Table A-1: 28 AEI within the DPSIR framework (COM 2006, eurostat 2018)

| Domain | Sub-domain | Nr | Title |
|---------------------|------------------------------|------|--|
| Responses | Public policy | 1 | Agri-environmental commitments |
| | | 2 | Agricultural areas under Natura 2000 (Archived) |
| | Technology and skills | 3 | Agri-environmental indicator - farmers' training and environmental farm advisory services (Archived) |
| | Market signals and attitudes | 4 | Area under organic farming (see Organic farming statistics) |
| Driving forces | Input use | 5 | Mineral fertiliser consumption |
| | | 6 | Consumption of pesticides |
| | | 7 | Irrigation |
| | | 8 | Energy use |
| | Land use | 9 | Land use change (Archived) |
| | | 10.1 | Cropping patterns |
| | | 10.2 | Livestock patterns |
| | Farm management | 11.1 | Soil cover |
| | | 11.2 | Tillage practices |
| | | 11.3 | Manure storage |
| | Trends | 12 | Intensification/extensification |
| | | 13 | Specialisation |
| | | 14 | Risk of land abandonment (Archived) |
| Pressures and risks | Pollution | 15 | Gross nitrogen balance (Archived) |
| | | 16 | Risk of pollution by phosphorus |
| | | 17 | Pesticide risk |
| | | 18 | Ammonia emissions |
| | | 19 | Agri-environmental indicator - greenhouse gas emissions (see Climate change - driving forces) |
| | Resource depletion | 20 | Water abstraction (Archived) |
| | | 21 | Soil erosion |
| | | 22 | Genetic diversity |
| | Benefits | 23 | High Nature Value farmland |
| | | 24 | Renewable energy production (Archived) |
| State/Impact | Biodiversity and habitats | 25 | Agri-environmental indicator - population trends of farmland birds (see Biodiversity statistics) |
| | Natural resources | 26 | Soil quality (Archived) |
| | | 27.1 | Water quality - Nitrate pollution |
| | | 27.2 | Water quality - Pesticide pollution (Archived) |
| | Landscape | 28 | Landscape - state and diversity (Archived) |

Table A-2: MS 3.1 ADWIs used in the FAIRWAY case studies (survey results)

| | | | Case studies region | | | | | | | | | | | | |
|---------------|----------------------------------|---|--------------------------|---------|------------|--------------|-------------|-------------|--------|---------------|-------------|---------------|----------------|-------|---------------|
| | | | DK | DK | FR | GE | GR | NL | N | PT | RO | SL | UK | N-IRL | NL |
| | | | Tunø | Aalborg | La Voulzie | Lower Saxony | Axios river | Overijsse I | Vansjø | Baixo Mondego | Arges Videa | Dravsko Polje | Anglian region | Dreg | Noord Brabant |
| | | | Case studies contaminant | | | | | | | | | | | | |
| | | | N | N, Pest | N, Pest | N | N, Pest | N, Pest | N | N, Pest | N | N, Pest | Pest | Pest | Pest |
| | | | Case studies water | | | | | | | | | | | | |
| Domain | Sub-domain | Indicator | GW | GW | GW | GW | SW/GW | GW | SW | SW/GW | GW | GW | SW | SW | GW |
| Driving force | | Population density | 1 | 1 | | 3 | | | 3 | 3 | | 3 | | 3 | |
| | Societal and economic demands | Connected population percentage and wastewater treatment percentage | 1 | 1 | | | | | 3 | 3 | | 3 | | | |
| | | Costs per kg NO ₃ reduced | 2 | 2 | | | | | | | | | | | |
| | | Costs per unit pesticide reduced | 2 | 2 | 3 | | | | | | | | | 3 | |
| | | Treatment process at the waterworks incl cost | 1 | 1 | 1 | | | | 3 | | | 3 | | 3 | |
| | Resource management and planning | Land uses | 1 | 1 | 3 | 1 | | | 3 | 1 | | 1,2,3 | 3 | 1,2,3 | |
| | | Soil type | 1 | 1 | | 3 | | | 3 | 1,2 | | 2,3 | 3 | 1,2,3 | |
| | | Drainage index (R / RU) | | | | 3 | 2 | | 3 | | 2 | | | 1,2 | |
| | | Rainfall | 3 | 1 | 3 | 3 | 3 | 3 | 3 | 2,3 | 3 | 3 | 3 | 1,2,3 | 3 |
| | | Average yield Crops (t or qx/ha) | 2 | 2 | 2 | 2 | 2 | 2 | | 1 | 2 | 3 | 1 | | |

| | | | Case studies region | | | | | | | | | | | | | |
|-----------------|--|--|---|---------|------------|--------------|-------------|-------------|--------|---------------|-------------|---------------|----------------|-------|---------------|---|
| | | | DK | DK | FR | GE | GR | NL | N | PT | RO | SL | UK | N-IRL | NL | |
| | | | Tunø | Aalborg | La Voulzie | Lower Saxony | Axios river | Overijsse I | Vansjø | Baixo Mondego | Arges Videa | Dravsko Polje | Anglian region | Dreg | Noord Brabant | |
| | | | Case studies contaminant | | | | | | | | | | | | | |
| | | | N | N, Pest | N, Pest | N | N, Pest | N, Pest | N | N, Pest | N | N, Pest | Pest | Pest | Pest | |
| Farm management | | | Case studies water | | | | | | | | | | | | | |
| | | | Mineral fertilisation (kg N /ha /yr on an area of reference) | 3 | 3 | 3 | 1 | 1,2,3 | 2 | 3 | 1,2 | 1,2,3 | | 1 | | |
| | | | Average mineral fertilisation per crops (kg N per crop /ha /yr on an area of reference) | 2 | 2 | 3 | 1,2 | 1,2,3 | 2 | | 1,2 | 1,2,3 | | 1 | | |
| | | | Livestock density (LU/ha /yr on an area of reference) | 2 | 2 | | 2 | 1,2,3 | 2 | 3 | 1 | 1,2,3 | 2,3 | 1 | | |
| | | | Days of Presence in the pasture (day of LU/ha/yr on an area of reference) | | | | 2 | | 2 | | | 2 | | 1 | | |
| | | | Livestock excretion (kg N/ha/yr on an area of reference) | 2 | 2 | | | | 2 | | 1 | 2 | 2,3 | 1 | | |
| | | | Organic fertilisation (kg N/ha/yr on an area of reference) | 2 | 2 | | 1 | 2 | 2 | | 1,2 | 2 | | 1 | | |
| | | | Average organic fertilization per crops (kg N per crop/ha /yr on an area of reference) | 2 | 2 | | 1 | 2 | 2 | 3 | 1 | 2 | | 1 | | |
| | | | Total fertilisation (kg N /ha/yr on an area of reference) | 2 | 2 | 2 | 1 | 2 | 2 | 3 | 1 | 2 | 2,3 | 1 | | |
| | | | Average total fertilisation per crops (kg N per crops/ha /yr/ on an area of reference) | 2 | 2 | 2 | 1 | 2 | 2 | | 1 | 2 | | 1 | | |
| | | | Treatment Frequency Index (TFI) – (Pesticide doses used by the farmers/standard dose) | 2 | 2 | 2 | | | | | 1,2 | | | 2 | 1,2 | 1 |

| | | | Case studies region | | | | | | | | | | | | | | |
|---|------------------------|--|--------------------------|--|----------------------|--------------|-------------|------------|--------|---------------|--------------|---------------|----------------|-------|---------------|-----|---|
| | | | DK | DK | FR | GE | GR | NL | N | PT | RO | SL | UK | N-IRL | NL | | |
| | | | Tunø | Aalborg | La Voulzie | Lower Saxony | Axios river | Overijssel | Vansjø | Baixo Mondego | Arges Videau | Dravsko Polje | Anglian region | Dreg | Noord Brabant | | |
| | | | Case studies contaminant | | | | | | | | | | | | | | |
| | | | N | N, Pest | N, Pest | N | N, Pest | N, Pest | N | N, Pest | N | N, Pest | Pest | Pest | Pest | | |
| | | | Case studies water | | | | | | | | | | | | | | |
| | | | | Treatment Frequency Index herbicide – (doses of herbicides used by the farmers/ standard dose) | 2 | 2 | 2 | | 1 | | | 1 | | | 2 | 1,2 | 1 |
| | | | | Pesticide load index | 2 | 2 | 3 | | | | | | | | | | |
| | | | Trends | Average yield of crops (t or qx/ha) | 2 | 2 | 2 | 2 | 2 | 2 | | 1 | 2 | 3 | 1 | | |
| | | | Pressure | Leaching quantity | Nitrogen farm budget | 2 | 2 | | | | 2 | | 1 | 2 | | 1 | |
| Nitrogen soil surface budget = net nitrogen budget | 2 | 2 | | | | 1 | | 2 | | 1 | 2 | 3 | 1 | | | | |
| Nitrate concentration (mg NO ₃ /l) in soil leaching (measurements) | 1 | 1 | | | 1 | | | 1 | 3 | | 2,3 | 1 | | | | | |
| Pesticide concentration (mg NO ₃ /l) in soil leaching (measurements) | 1 | | | | | | | | | | | | | | 1 | | |
| Point sources | Point sources | 1 | | 1 | 2 | | | | 3 | 3 | | 3 | | | | | |
| Arial immission | Deposition of nitrogen | 3 | | 3 | | 3 | | 3 | 3 | | 2,3 | 3 | 1 | | | | |
| State/Imp pact | Water quality | Annual average nitrate concentration (mg NO ₃ /l) in drinking water collection points | 1 | 1 | 1 | 3 | 3 | 3 | 3 | 3 | 1,2,3 | 3 | | | 3 | | |

| | | | Case studies region | | | | | | | | | | | | | | |
|----------------------------|---------------|--|--|---|------------|--------------|-------------|-------------|--------|---------------|-------------|---------------|----------------|-------|---------------|-----|---|
| | | | DK | DK | FR | GE | GR | NL | N | PT | RO | SL | UK | N-IRL | NL | | |
| | | | Tunø | Aalborg | La Voulzie | Lower Saxony | Axios river | Overijsse I | Vansjø | Baixo Mondego | Arges Videa | Dravsko Polje | Anglian region | Dreg | Noord Brabant | | |
| | | | Case studies contaminant | | | | | | | | | | | | | | |
| | | | N | N, Pest | N, Pest | N | N, Pest | N, Pest | N | N, Pest | N | N, Pest | Pest | Pest | Pest | | |
| | | | Case studies water | | | | | | | | | | | | | | |
| | | | Public health and regulatory compliances | frequency of exceedance quality standards (%) in drinking water collection points | 1 | 1 | | 3 | 3 | 3 | | 3 | 3 | 3 | 3 | | 3 |
| | | | | Nitrogen maximal concentration in drinking water collection points | 1 | 1 | 1 | 3 | 3 | 3 | | 3 | 3 | 3 | 3 | | 3 |
| | | | Transit time | Soil infiltration | 1 | 1 | 1 | | 3 | | 3 | 1 | 3 | 3 | | 1,2 | |
| | | | | Water unsaturated zone Transfer time | 1 | 1 | 3 | | 3 | | | | 3 | 3 | | 1 | |
| Groundwater residence time | 1 | 1 | | 3 | | 3 | 3 | 3 | | 3 | 3 | | | 3 | | | |
| Link | Source tracer | Number of substances that exceed water quality standards at least once the year | 1 | 1 | 1 | | 3 | 3 | | | 3 | 3 | 3 | 1,3 | 3 | | |
| | | Maximum concentration by substance (if >0.1 µg/l) in drinking water collection points | 1 | 1 | 1 | | 3 | 3 | | | 3 | 3 | 3 | 1,3 | 3 | | |
| | | Maximum concentration for the sum of all individual pesticides in drinking water collection points | 1 | 1 | 1 | | 3 | 3 | | | 3 | 3 | 3 | 1,3 | 3 | | |
| | | Frequency of exceedance quality standards in the drinking water (percentage of the number of samples where the 'drinking water' standard is exceeded) by substance | 1 | 1 | 1 | | 3 | 3 | | | 3 | 3 | | 1,3 | 3 | | |

| Case studies region | | | | | | | | | | | | |
|---|---------|------------|--------------|-------------|-------------|--------|---------------|-------------|---------------|----------------|-------|---------------|
| DK | DK | FR | GE | GR | NL | N | PT | RO | SL | UK | N-IRL | NL |
| Tunø | Aalborg | La Voulzie | Lower Saxony | Axios river | Overijsse I | Vansjø | Baixo Mondego | Arges Videa | Dravsko Polje | Anglian region | Dreg | Noord Brabant |
| Case studies contaminant | | | | | | | | | | | | |
| N | N, Pest | N, Pest | N | N, Pest | N, Pest | N | N, Pest | N | N, Pest | Pest | Pest | Pest |
| Case studies water | | | | | | | | | | | | |
| Water table level (Piezometrical level) in drinking water collection points | 1 | 1 | 3 | | 3 | 3 | | | 3 | 3 | | 3 |
| Vulnerability assessment maps of aquifer and surface water | 1 | 1 | 3 | | 3 | 3 | | | 3 | 3 | | 3 |
| Trends analyses (timeserie analyses) | 1 | 1 | 1 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 1,3 | 3 |
| Depth to nitrate and pesticide interface in the ground or aquifers | 1 | 1 | | | | | | | | | | |





| | |
|---|---|
|  | yes |
|  | no, do not need |
|  | no, do not have data |
|  | no, do not know it/CS were not asked for the availability of these data |
| 1 | data available on plot scale |
| 2 | data available on farm scale |
| 3 | data available on regional or larger scale |

Table A-3: Free available data sources for the calculation of ADWIs

| Sub-domain | Chapter | Indicator | Subindicator | Specification on calculation or data source | Reference |
|---|---------|---|---|---|--|
| Driving force: Resource management and planning | 5.1.1 | Land use (planning) | Land use/land cover | survey (database) | LUCAS-database (Eurostat, 2015, 2018d) |
| | | | Land use change | survey (database) | (Greening/CAP) |
| | 5.1.3 | Agricultural preconditions: climatic conditions | precipitation | database | WorldClim (Hijmans et al., 2005) |
| | | | temperature | database | WorldClim (Hijmans et al., 2005) |
| | | | wind | database | WorldClim (Hijmans et al., 2005) |
| Driving force: Farm management | 5.1.3 | Agricultural preconditions: soil properties | soil type | | LUCAS-database (Eurostat, 2015, 2018d), Ballabio et al. (2015), Panagos et al. (2012b) |
| | | | organic carbon | | Kruijne et al. (2011) |
| | | | clay content | | |
| | | | top soil bulk density | | Ballabio et al. (2016) |
| | | | field capacity | | |
| Driving force: Farm management | | | susceptibility to erosion and compaction | K-factor of the universal soil loss equation | Panagos et al. (2012a/b), NRCS (2009), EPPO (2018), Bunzel et al. (2014) |
| | 5.2.1 | farming standards | organic/conventional | eurostat database [ef_lus_main]; national/regional statistics | Eurostat (2018c) |
| | 5.2.2 | farming intensity | crop yield (average; t or qx/ha) | eurostat database [ef_lus_main]; national/regional statistics | Eurostat (2018c) |
| | 5.2.3 | farm management | cropping patterns | eurostat database [ef_lus_main]; national/regional statistics | Eurostat (2018c), national databases |
| | | | catch crop use | survey (database)? | Greening/CAP national databases |
| Driving force: Farm management | | | method of soil cultivation/tillage practice | | Eurostat (2018c) AEI – tillage practice |
| | | | soil cover | C-factor (cover management factor) | national/regional statistics; LANDUM |
| | | | | | Panagos et al. (2015), Bunzel et al. (2014) |
| Driving force: Farm management | 5.2.4 | N fertilisation | Livestock density (LU/ha /yr on an area of reference) | as livestock units (LU) with LU coefficient | Eurostat (2018c); census data |
| | | | Livestock density (LU/ha /yr on an area of reference) | as animal categories | Regulation EC 1165/2009, census data |

| Sub-domain | Chapter | Indicator | Subindicator | Specification on calculation or data source | Reference |
|------------|---------|-----------------------|---|--|---|
| | | | Livestock feed consumption Livestock excretion (kg N/ha/yr on an area of reference) types of organic fertilisers organic fertilisation/ha; organic fertilisation/crop*ha mineral fertilisation/ha; mineral fertilisation/crop*ha total fertilisation/ha; total fertilisation/crop*ha | census-data in combined with N-excretion/year declaration N-excretion+N from other fertilisers/ha, weighting according to crop need: N from mineral fertilisers/ha organic + mineral N fertilisation | DLG, 2014, KTBL, 2010, Horlacher et al., (2014) Hou et al., 2016) EU 2003/2003, national legislation national/regional statistics on land use and crop yield; N-excretions national sales statistics, i.e. UNIFA (2018), eurostat (2018) see above |
| | 5.2.5 | Pesticide application | Type of Pesticides Chemical properties Consumption of pesticides Application of pesticides/ha (active substances; most frequently used pesticides; most persistent or most toxic pesticides) Splitting/frequency of application Application techniques for pesticides | database database database database/statistics on usage data on pesticides database/statistics on usage data on pesticides database/statistics on usage data on pesticides | PPDB, BPDB (University of Hartfordshire, 2017, 2016) Pelosi et al. (2013), Rossberg (2016), Pesticides Registration & Control Division (2018), Kudsk et al. (2018) Eurostat (2018) EC) No 1185/2009, Rossberg, 2016, Kudsk et al., 2018, Pesticides Registration and Control Division, 2018 EC) No 1185/2009 EC) No 1185/2009 |
| Pressure | 5.7.1 | Surface runoff | Surface transport of nitrogen and pesticides (with soil/fertiliser particles) | database | EPPO (2018) |
| | 5.8.1 | Aerial immission | Pesticide Drift | database | EPPO (2018) |
| | 5.8.2 | | Volatile N-compounds | database | Banzhaf et al., (2015), UBA (2018), EMEP (2018) |

Table A-4.1: 2 Overview of N loss indicator approaches (Buczko and Kuchenbuch, 2010a)

| NLI | Climate/ weather | Soil | Management | N-sources | Off-site and belowground factors | Type of equations | Type of output | Sensitivity (%) | Threshold of NConc or NLoss for “high” vulnerability ^a | Application (A)/ validation (V) |
|---|--|-----------------|------------------------------|---|--|---|---|---|--|---|
| NBal (S1) | – | – | indirect (crop, yield) | NFertApp, NCUpt, (NMin, Denitr) | – | Sums input vs. output of N | Amount kg N ha ⁻¹ (yearly) | Depends on difference between N input and output, often >100% | 60 (sand) to 100 (clay) kg N ha ⁻¹ | A: commonly used in Europe; V: mostly poor correlations with measured N losses |
| EQUIF (S2) | – | – | Indirect (crop, yield) | NFertApp, NCUpt, NMin (humus, crop residues), RSN | – | Sums input vs. output of N, measured data (RSN) | Amount kg N ha ⁻¹ year ⁻¹ , rated into 6 classes | Similar as for NBal | 40 kg N ha ⁻¹ | V: with meas. RSN(h) |
| RSN (S3) | – | – | – | Measured RSN in different soil depths (0– 90 cm) | – | Measured data | Amount kg N ha ⁻¹ at fixed date (before leaching season) | Depends on accuracy of measurements | 40 kg N ha ⁻¹ | A: several countries (Germany, Netherlands, USA); V: NConc(l),(gw) |
| (S4) N application rate (NFertApp) | – | – | – | NFertApp | – | Data provided by farmer | Amount kg N ha ⁻¹ year ⁻¹ | Depends on accuracy of data | 170 kg N ha ⁻¹ year ⁻¹ | A: e.g. France, Netherlands |
| NUE (S5) | – | – | Indirect (crop, yield) | NFertApp, NCUpt | – | NCUpt/NFertApp × 100 | %- Values | Similar as for NBal | na | V: NLoss by leaching, irrigated systems |
| Ncm (S6) | Prec(a) (qualitatively classified as “wet” or “dry”) | – | – | Measured N conc. in plants (maize) (Ncm) | – | Exponential regression Ncm vs. NConc(l), critical Ncm for NConc(l) = 11.3 mg NO ₃ -N l ⁻¹ | Critical Ncm 10.5 (wet years)/7.82 g (dry years) N kg ⁻¹ dry matter | >>100 % | NConc >11.3 mg NO ₃ -N l ⁻¹ | A,V: simulated NConc(l) |
| DRASTIC (TG1) | -(Recharge) | Soil texture | – | – ^b | Depth to groundwater, (recharge), aquifer type (porosity), HC of vadose zone and aquifer, topography | Weighted sum of 7 factors (with scores 1–10) | Scores, range 23–230 | 4–22% (depending on weighting factor) | na | A, V: NConc(gw), different sites worldwide |
| SG (TG2) | SeepRate (recharge) | aWHC(rz) | – | – | Sediment type and thickness of vadose zone layers | Sum of soil and vadose zone terms (scores) | Score, range about 500–2000, higher scores denote lower vulnerability | 20% (sediment, thickness) – 100% (recharge) | na | A, V: NConc(gw) (e.g. Magiera 2002) |
| AVI (TG3) | – | – | – | – | Thickness (d) and HC of vadose zone layers | Sum of ratio d(i)/HC(i) of vadose zone layers (physical units) | Rh (years), log10- values rated into AVI vulnerability classes | >>100% for layers with low HC; for d and high HC < 100% | na | A, V: NConc(gw) (e.g. Magiera 2002) |

Table A-4.2: 2 Overview of N loss indicator approaches (Buczko and Kuchenbuch, 2010a)

| NLI | Climate/ weather | Soil | Management | N-sources | Off-site and belowground factors | Type of equations | Type of output | Sensitivity (%) | Threshold of NConc or NLoss for “high” vulnerability ^a | Application (A)/ validation (V) |
|-----------------------|--|--|---|--|--|---|--|---|--|--|
| MLR (TG4) | – | % Well-drained soils | % Cropland/pasture | NFertApp | Population density (nat. log), depth to water table, fractures in aquifer | Multivariate logistic regression with six variables | Predicted probability of NConc(gw) >4 mg NO ₃ l ⁻¹ | 5% (NFertApp) to 55% (% cropland, depth to water table) | 4 mg NO ₃ l ⁻¹ | A: GW vulnerability map USA; V: NConc(gw) >4 mg NO ₃ l ⁻¹ |
| EF (TS1) | SeepRate (= f(prec(a), ET _{pot})) | WHC(rz) | – | – | – | Transport divided by storage term (physical units) | %-Values (range 0–300) | SeepRate 100%, WHC(rz) depending on magnitude, often >>100% | na | A: Germany, various sites |
| P/RU (TS2) | Prec(ls) | WHC(rz) | – | – | – | Transport divided by storage term (physical units) | Dimensionless, range 1–12 | Prec(ls) 100%, WHC(rz) depending on magnitude, often >>100% | na | A: France, various sites |
| LI (TS3) | Prec(a), prec(ls) | HSG | – | – | – | Nonlinear regression of percolation vs. prec(a) | Index with length units (e.g., inches) | Prec(a), HSG: >>100%; prec(ls) < 100% | na | A, V: USA, various sites |
| CO-VM (CS1) | – | Soil drainage class (index) | Land use, irrigation index | (Land use) | Depth to aquifer, presence of aquifer | Sum of scores | Scores, range 0– 11 | 30%, except irrigation index (8%) and presence of aquifer (100%) | NConc >10 mg NO ₃ -N l ⁻¹ | V: NConc(gw) >5 mg NO ₃ -N l ⁻¹ (n = 576), r ² = 0.78 |
| CO- VMX (CS1) | – | Soil texture | Irrigation efficiency, manure/fertilizer application timing, BMP | NFertApp, NManApp | – | Sum of scores | Scores, range 1– 16 | 25% | RSN >50 kg N ha ⁻¹ | V: with RSN (n = 4), r ² = 0.32–0.95 |
| EnSus (CS2) | Prec(a), ET | Profile available water (≈ aWHC(rz)), organic and hydric soils, factor for low HC | – | Land use as proxy for potential N sources | – | Source term multiplied by transport term | Scores, range 0.4–50 (rated into 5 classes) | 100%; ET >100% for low values | 30 kg N ha ⁻¹ year ⁻¹ (“N pressure”) | A: mapped for New Zealand |
| mNRS (CS3) | – | Preferential flow paths (including subsurface drains) | “Dirty water” applications, cropping system, farmyard risk | Nutrient application rate and timing | Aquifer vulnerability, subsoil type | Source term multiplied by transport term | Scores, range 4– 448 | Source factors 20– 40%; transport factors 100% | Related to crop N requirements | V: grassland, NConc(gw), r ² > 0.35 if N from grazing livestock considered |
| NLHI- IRR (CS4) | – | HC, texture | Irrigation system, crop type | – | – | Multiplication of 3 score terms | Scores, range 1– 80 | 100% | na | A: irrigated agriculture California; V: qualitative |
| NPSAH (CS5) | Precipitation, temperature (“control factor”) | – | Agronomic practices, irrigation (“control factors”) | NFertApp (“hazard factor”) | Slope (“hazard factor”) | Multiplication of 5 score terms | Scaled index, range 1–10 | 100% | na | A: risk map for Cremona province (Italy) |

Table A-4.3: 2 Overview of N loss indicator approaches (Buczko and Kuchenbuch, 2010a)

| NLI | Climate/ weather | Soil | Management | N-sources | Off-site and belowground factors | Type of equations | Type of output | Sensitivity (%) | Threshold of NConc or NLoss for “high” vulnerability ^a | Application (A)/ validation (V) |
|---------------------|-------------------------------|---|---|--|---|---|---|---|--|---|
| OMAFRA- NI (CS6) | – | HSG | Crop type, cover crop, manure application timing | NBal, manure applications after harvest | – | Sum of scores for NBal and manure applications after harvest | Scores, range 0– 12, rating of scores depends on HSG | 50% | 135 kg N ha ⁻¹ year ⁻¹ | A: Ontario, Canada |
| PA-NI (CS7) | – | Soil texture, HC | Method of fertilizer/manure application | NFertApp, NManApp | – | Source term multiplied with transport term (scores) | Scores, range 0– 32 | Source factors: 25%; transport factors: 50% | 150 kg N ha ⁻¹ year ⁻¹ | A: 40 ha experimental watershed in Pennsylvania |
| IROWC-N (CE1) | Prec(a), ET _{pot} | aWHC | – | NBal (NFertApp, NCUpt, NDep, NFix) | – | Ratio of source and transport term (physical units) | NConc(l) | 40–100% | NL >20 kg N ha ⁻¹ and NConc >10 mg NO ₃ -N l ⁻¹ | A: mapped for large parts of Canada |
| PNCL (CE2) | Prec(a), ET _{pot} | – | – | NBal (NFertApp, NCUpt, NDep, NFix) | – | Ratio of source and transport term (physical units) | NConc(l) | NBal 100%; SeepRate variable, >>100% for small values | NConc >50 mg NO ₃ l ⁻¹ (= 11.3 mg NO ₃ -N l ⁻¹) | A: mapped for Germany |
| ALRP (CC1) | Prec(a), prec(l)s | HSG, porosity | – | NBal (NFertApp, NMin, NIrrig, NFix, NCUpt, Denitr, NH ₃ - volat.) | Travel time to aquifer, position of aquifer, vulnerability of aquifer | 4 Components | Scores which are rated into vulnerability classes | 25–50% | 89.6 kg N ha ⁻¹ year ⁻¹ | A: USA, various sites |
| IN (CC2) | SeepRate | Soil water retention, rooting depth | Manure type, application method and timing (for NH ₃ -volat.) | RSN(h), NFertApp | – | Minimum of 4 sub- indicators (scaled between 1 and 10) is defined as IN score | Scores (scaled between 1 and 10) with lower values denoting higher risk | Sub-indicators: 100% when lower than others; separate components for leaching: >>100% | NConc >11.3 mg NO ₃ -N l ⁻¹ | V: sub-indicator for NL (grassland sites in France) |
| MERLIN (CC3) | – | Sensitivity of soils for leaching (similar to HSG) | Cover crops | NFertApp, NCUpt, NMin (humus, crop residues), RSN | – | 3 Sub-indicators, combined by relationship table | 3 MERLIN classes (low, medium, high risk) | 50–100% (3 sub- indicators) | 40 kg N ha ⁻¹ (RSN), NConc >11.3 mg NO ₃ -N l ⁻¹ | V: meas. NLoss (n = 125) |
| NIT-1 (CC4) | Prec(a), prec(l)s | HSG, porosity, bulk density, C _{org} | Rooting depth, crop rotation, fertilizer/manure application method and type, split application, tile drainage, buffer width, irrigation | NBal (NFertApp, NDep, NMin, NIrrig, NFix, NCUpt, Denitr, ammonia volat.) | (Runoff class), travel time to aquifer, position and vulnerability of aquifer, distance to surface water | Sum of 15 score terms (0–8) | Scores, range 0– 124 | 6.2% (for each of the 15 components) | >112 kg N ha ⁻¹ | V: sub-indicators for leaching, NH ₃ volatilization and runoff, sites in USA, Argentina, China |

Table A-4.4: 2 Overview of N loss indicator approaches (Buczko and Kuchenbuch, 2010a)

| NLI | Climate/ weather | Soil | Management | N-sources | Off-site and belowground factors | Type of equations | Type of output | Sensitivity (%) | Threshold of NConc or NLoss for “high” vulnerability ^a | Application (A)/ validation (V) |
|----------------|---------------------|------------------------------|--|---|--|---|---|---|---|--|
| NO-NI (CC5) | (Erosion risk) | Erosion risk ^c | Tillage timing, split application, manure application timing | NBal (NFertApp, NDep, NFix, NCUpt, Incidental NLoss from manure, Denitr), NManApp | Erosion risk | Sum of 3 loss terms: dissolved N (Leaching), particulate N (erosion), incidental N (surface runoff) | N loss in kg N ha ⁻¹ year ⁻¹ | Variable <100% (each of 3 components), dependent on baseline values | na | A: experimental catchment in southeast Norway |

NL=leaching, VZ=flow through vadose zone, AV=ammonia volatilization, DN=denitrification, ER=erosion, SR=surface runoff, GW=groundwater flow, NO=NO (nitric oxide) emission

| Symbol | Unit | Explanation | Symbol | Unit | Explanation |
|-----------|---|--|----------|---|--|
| aWHC | mm | Available water holding capacity | NIrrig | mg NO ₃ -N l ⁻¹ | Measured NO ₃ -N concentration in irrigation water |
| EF | % | Exchange frequency of the soil solution | NL | kg N ha ⁻¹ *year ⁻¹ | Nitrogen leached from the root zone |
| EF(aWHC) | % | Exchange frequency, calculated based on available WHC | NLI | – | Nitrogen Loss Indicator (Index) |
| EF(tWHC) | % | Exchange frequency, calculated based on total | NLoss | kg N ha ⁻¹ *year ⁻¹ | Measured N leaching loss |
| ET | mm year ⁻¹ | Evapotranspiration | NManApp | kg N ha ⁻¹ *year ⁻¹ | N application as manure |
| ETpot | mm year ⁻² | Potential evapotranspiration | NMin | kg N ha ⁻¹ *year ⁻¹ | N mineralisation of organic matter |
| HC | m s ⁻¹ | Hydraulic conductivity | PI | inches (or other length unit) | Percolation index |
| HSG | – | Hydrologic soil group | PNCL | mg NO ₃ l ⁻¹ | Potential nitrate concentration in leachate |
| NAL | kg N ha ⁻¹ *year ⁻¹ | Nitrogen available to leach | prec(a) | mm year ⁻¹ | Annual precipitation |
| NBal | kg N ha ⁻¹ *year ⁻¹ | N balance | prec(Is) | mm year ⁻¹ | Precipitation sum during leaching season |
| NConc(l) | mg NO ₃ -N l ⁻¹ | Measured (or calculated) NO ₃ -N concentration in leachate | Rh | year | Hydraulic resistance |
| NConc(gw) | mg NO ₃ -N l ⁻² | Measured (or calculated) NO ₃ -N concentration in groundwater | RSN | kg N ha ⁻¹ year ⁻¹ | Residual soil mineral nitrogen (=content of mineral N as measured with the “N-min” method) |
| NCUpt | kg N ha ⁻¹ *year ⁻¹ | N uptake by crops | RSN(h) | kg N ha ⁻¹ *year ⁻¹ | Residual soil mineral nitrogen at harvest (autumn) |
| NDep | kg N ha ⁻¹ *year ⁻¹ | Atmospheric N deposition | SeepRate | mm year ⁻¹ A | annual seepage rate (drainage) out of the rooted zone |
| NFertApp | kg N ha ⁻¹ *year ⁻¹ | N application as mineral fertiliser | tWHC | mm | Total water holding capacity |
| NFix | kg N ha ⁻¹ *year ⁻¹ | N fixation by leguminous plants | WHC(rz) | mm | Water holding capacity of the root zone |

Table A-5: Overview of pesticide risk indicators, including specific targets of Member States and level of spatial applicability

| Name of indicator | Country where indicator is used or tested | Field of application | Model parameters included | target | national | regional | farm | Reference |
|--|---|---|--|---|----------|----------|------|--|
| | | | | | | | | |
| Groundwater Ubiquity Score (GUS) | USA, Argentina, Brazil, India, Pakistan, Colombia | an index is derived based entirely on the physical properties of pesticides. Discrimination of "leachers" against "non-leachers" | Koc, DT50 | | x | x | x | (Gianelli and Bedmar, 2017; Hall et al., 2015; Martins et al., 2018; Mendes et al., 2017; Mosquera-Vivas et al., 2016; Novohatska et al., 2018; Sharma et al., 2018; Tahir et al., 2016) |
| Environmental Impact Quotient (EIQ) | UK, Canada | Three components: a farm worker component (aggregating human toxicity), a consumer component (human chronic toxicity), pesticide fate in soil, leaching to groundwater and finally an ecological component adding up effects on aquatic and terrestrial organisms | | Rating system of 1-5 (most harmful). EIQ is average value of 3 components | x | x | x | (Kovach et al., 1992) |
| Pesticides Environmental Risk Indicator (PERI) | Sweden, Finland, Turkey | PERI combines variables from groundwater, surface water, and air compartments in one equation to obtain an environmental risk score (ERS). | PERI uses a system that scores six variables, namely: 1) groundwater ubiquity score (GUS); 2) Henry's constant (Kh); 3) partition coefficient (Kow); 4) lethal concentration value (LC50) for daphnia, and effective concentration (EC50) for algae; 5) LC50 for earthworm; 6) LC50 for bees | ERS score 1-5 | | x | x | (Nilsson, 1999) |

| Name of indicator | Country where indicator is used or tested | Field of application | Model parameters included | target | national | regional | farm | Reference |
|---|---|--|---|--|----------|----------|------|--|
| Toxicity– Human Health– Persistency THP | France, Turkey | The THP rating approach can be used to compare and rate the hazards that pesticides pose to humans, wildlife, and the overall ecosystems through exposure to water and land. | three variables: Toxicity to the aquatic environment (T), hazard to human health by oral intake (H) and the persistence rating value (P), which is related to the probable half-life expressed in days. The recommended application doses and active ingredient amounts are determined for each pesticide | | x | x | x | (OECD, 1982) |
| Environmental Yardstick for Pesticides | The Netherlands | <p>For each pesticide the yardstick assigns environmental impact points for the risk to water organisms, the risk of groundwater contamination and the risk to soil.</p> <p>Three output values: a) acute risk to water organisms (most sensitive organism);b) risk of groundwater contamination; c) acute and chronic risk to soil organisms.</p> <p>The potential risk is expressed in environmental impact points (EIPs). The more EIPs a pesticide gets, the higher its impact on the environment. The EIPs are based on the predicted</p> | chemical properties (persistence and mobility in soil, toxicity) of both active ingredient and principal metabolites; dose rate; organic matter content of the soil; time of application; method of application; distance to surface water | Comparison to MPC for each compartment | x | x | x | (Reus et al., 2002; Reus and Leendertse, 2000) |

| Name of indicator | Country where indicator is used or tested | Field of application | Model parameters included | target | national | regional | farm | Reference |
|---------------------------------|---|--|---------------------------------|----------------------------------|----------|----------|------|----------------------|
| | | environmental concentration (PEC) in a certain compartment and the maximum permissible concentration (MPC). | | | | | | |
| Treatment frequency index (TFI) | Denmark, Croatia, France (additional to other indicators) | The TFI is calculated by the theoretical number of pesticide treatments per hectare, based on standard dose rates of active ingredients, and the amount of pesticides sold yearly. The impact of the pesticide is estimated by the toxicity as measured for certain target-organisms. | Koc, DT50 | Halving the TFI by 2018 (France) | x | x | | (Gravesen, 2003) |
| Pesticide load index (PLI) | Denmark | Environmental behaviour of pesticides, risks of groundwater pollution, effects on human health. The PLI consists of three sub-indicators for human health, ecotoxicology and environmental fate, respectively. For each of the three sub-indicators a pesticide load (PL) is calculated and expressed as the PL per unit commercial product | LC/LD/EC50, DT50, BCF, SCI-GROW | Reach the value 1,96 | x | x | x | (Kudsk et al., 2018) |

| Name of indicator | Country where indicator is used or tested | Field of application | Model parameters included | target | national | regional | farm | Reference |
|---|---|---|--|---|----------|----------|------|---|
| Norwegian Pesticide Risk Indicator (NERI) | Norway | Effect on human health, risk of operator exposure (preparation and application of mixture), mobility, leaching potential, persistence. Effects on various organisms (bees, earthworms, birds, aquatic life, | NERI classifies products into three environmental risk classes. By combining the information on human health and environmental risk classifications products are grouped into 7 pesticide tax classes. Possible risk values are ranging from 0 to 4 | | | x | x | (Stenrød et al., 2008) |
| SyPEP: system for predicting the environmental impact of pesticides | Belgium | The indicator calculates a long-term PEC for groundwater, a short-term PEC for groundwater, and a PEC for surface water. It then divides toxicity information by the PEC in each environmental compartment. | Ranking of pesticides on a 0-5 scale | | | | | (Pussemier, 1999; Pussemier and Steurbaut, 2004) |
| SYNOPS | Germany | Based on pest use, crop stage, application technique, soil type, location, topography of the field, SYNOPS calculates the Predicted Environmental Concentrations (PEC) for different compartments and compare the PEC values to the LC50 and NOEC values for the various target organisms and Exposure Toxicity Ratios (ETR) are calculated for each target | Calculates the Predicted Environmental Concentrations (PEC) for different compartments and compare the PEC values to the LC50 and NOEC values for the various target organisms and Exposure Toxicity Ratios (ETR) are calculated for each target organism in soil, groundwater and surface water | 25 % risk reduction by 2020 compared to the 1996-2005 average | | x | | (Gutsche and Strassemeyer, 2007; Hernández-Hernández et al., 2007; Strassemeyer et al., 2017) |

| Name of indicator | Country where indicator is used or tested | Field of application | Model parameters included | target | national | regional | farm | Reference |
|---|---|--|--|--------|----------|----------|------|---------------------------------|
| | | organism. Compares different pest management strategies. | | | | | | |
| MATF multiattribute toxicity factor model | USA (potato crops) | Ranks toxicity data in order to generate toxicity factor scores for beneficial organisms and humans. It then multiplies these scores by the pesticide's application rate in order to produce toxicity units for each application | | | | x | x | (Benbrook et al., 2002) |
| I-Phy | France | Calculates the risk of surface water contamination, risk of groundwater contamination and risk of air contamination. It relates to the potential environmental impact of the application of a pesticide in a field crop and is defined by four modules. One reflects the presence (rate of application) of the pesticide, the other three reflect the risk for three major environmental compartments (groundwater, surface water, air). | pesticide properties, site specific conditions and application conditions | | x | x | x | (Van Der Werf and Zimmer, 1998) |
| EIS Pesticides | France | The system can effectively analyse some agro-environmental scenarios, and calculate agro-environmental indicators on demand. | time, sprayed surface area, or pesticide type, spatial data, crop type, crop use | | x | x | x | (Vernier et al., 2013) |

| Name of indicator | Country where indicator is used or tested | Field of application | Model parameters included | target | national | regional | farm | Reference |
|--|---|---|---|--------|----------|----------|------|---|
| EPRIP / EPRIP2 | Italy | | Risk score | | | | x | (Oliver et al., 2016; Padovani et al., 2004; Trevisan et al., 2009) |
| Harmonized environmental indicators for pesticide risk (HAIR) | | calculates risk indicators related to the agricultural use of pesticides in EU Member States, by combining databases and models for potential environmental effects | aquatic indicators for algae, daphnia and fish, a groundwater indicator, terrestrial indicators for birds, mammals, earthworms and honey bees, and occupational risk indicators for operators, re-entry workers, bystanders and residents | | x | x | | (Kruijne, 2011) |
| Pesticide Emission Assessment at Regional and Local scales PEARL | | Numerical model of pesticide behaviour in the soil-plant system. Simulates water flow in soil and considers changes in groundwater levels due to rainfall. Soil evaporation and plant transpiration are calculated. | Calculation incorporates convection/dispersion, adsorption, transformation and plant uptake rate. | | | x | x | (Leistra and Boesten, 2010; Leistra and Van Den Berg, 2007; Tiktak et al., 2013) (http://www.pearl.pesticidemodels.eu/) |

Table A-6: Assessments on plot level of the relevance of indicators for the potential of nitrate pollution of ground- and surface waters (CORPEN, 2006, adapted)

| | level of operation: plot | method description (CORPEN, 2006) |
|-------------------------------|---|-----------------------------------|
| Nitrogen fertilisation | organic nitrogen/reference surface (to be defined) | sheet 7 |
| | gap between amount of nitrogen applied and recommended N-fertilisation rate | sheet 19 |
| | mineral nitrogen applied/ha | sheet 9 |
| | plant available nitrogen/ha and year | sheet 10 |
| | number of N-fertiliser applications (organic and mineral) | sheet 11 |
| | percentage of mineral and/or organic nitrogen N applied outside the period of crop growth | sheet 12 |
| | days of pasture (in days LU/ha/year) | sheet 17 |
| | | |
| Soil cover | surface without green cover (bare soil) as annual average | sheet 5 |
| Estimation of nitrogen losses | amount of Nmin in soil after harvest (measures/modelling) | |
| | amount of Nmin in soil after winter (measures/modelling) | |
| | amount of Nmin in soil at the beginning of draining (measures, modelling) | |
| | CORPEN balance (farmgate) | sheet 13 |
| | EQUIF balance (soil surface balance) | sheet 14 |
| | MERLIN method for risks estimation of N-loss by leaching | sheet 20 |
| | IN d'INDIGO model for estimating N-losses by leaching and volatilisation | sheet 21 |
| | DEAC model for estimating N-losses by leaching | sheet 22 |

| agronomic relevance | |
|---------------------|--|
| 1 | indicator not recommended for single use |
| 2 | |
| 3 | |
| 4 | indicator suitable for single use |

Table A-7: Assessments on plot, farm and regional level of the feasibility of indicators for the potential of nitrate pollution of ground- and surface waters (CORPEN, 2006, adapted)

| level of operation | | | method description (CORPEN, 2006) |
|---|---|---|--|
| plot | farm | region | |
| organic nitrogen/reference surface (to be defined) | organic nitrogen/reference surface (to be defined) | organic nitrogen/reference surface (to be defined) | sheet 7 |
| | surface where organic fertilisation is applied/total application area available for organic fertilisation | surface where organic fertilisation is applied/total application area available for organic fertilisation | sheet 8 |
| | Storage capacity for manure existing/necessary*) | | sheet 6 |
| gap between amount of nitrogen applied and recommended N- | | gap between amount of nitrogen applied and recommended N- | sheet 19 |
| mineral nitrogen applied/ha | mineral nitrogen applied/ha | mineral nitrogen applied/ha | sheet 9 |
| plant available nitrogen/ha and year | plant available nitrogen/ha and year | plant available nitrogen/ha and year | sheet 10 |
| plant available nitrogen/ha and year | Number of N-fertiliser applications (organic and mineral) | Number of N-fertiliser applications (organic and mineral) | sheet 11 |
| percentage of mineral and/or organic nitrogen N applied outside the period of crop growth | percentage of mineral and/or organic nitrogen N applied outside the period of crop growth | percentage of mineral and/or organic nitrogen N applied outside the period of crop growth | sheet 12 |
| days of pasture (in days LU/ha/year) | days of pasture (in days LU/ha/year) | days of pasture (in days LU/ha/year) ;extrapolation for the region | sheet 17 |
| surface without green cover (bare soil) as annual average | | surface without green cover (bare soil) as annual average | sheet 5 |
| | surface without green cover (bare soil) during drainage period (winter season) | surface without green cover (bare soil) during drainage period (winter season) | sheet 2 |
| | surface with high leaching potential during drainage period (winter season) | surface with high leaching potential during drainage period (winter season) | sheet 3 |
| | surface under catch crops during drainage period (winter season) | surface under catch crops during drainage period (winter season) | sheet 4 |
| | % UAA (Utilised agricultural area) cultivated as temporary or permanent grassland | | |
| | % UAA converted to temporary or permanent grassland annually | | |
| | % UAA of grassland mowed and not grazed | | |
| | | length of waterways protected/total length of waterways | |
| | | % of surface covered with permanent landscape elements (hedges, woodlots, ponds, buffer strips) | |
| amount of Nmin in soil after harvest (measures/modelling) | | | |
| amount of Nmin in soil after winter (measures/modelling) [measure performed in jan/feb in France] | | | |
| amount of Nmin in soil at the beginning of draining (measures, modelling) | | | |
| CORPEN balance (farmgate balance) | CORPEN/ BGA balance (farmgate balance) | CORPEN balance (farmgate balance) | sheet 13 |
| EQUIF balance (soil surface balance) | EQUIF balance (soil surface balance) | EQUIF balance (soil surface balance) | sheet 14 |
| MERLIN method for risks estimation of N-loss by leaching *) | MERLIN method for risks estimation of N-loss by leaching *) | MERLIN method for risks estimation of N-loss by leaching | sheet 20 |
| IN d'INDIGO model for estimating N-losses by leaching and volatilisation*) | IN d'INDIGO model for estimating N-losses by leaching and volatilisation*) | IN d'INDIGO model for estimating N-losses by leaching and volatilisation | sheet 21 |
| DEAC model for estimating N-losses by leaching*) | DEAC model for estimating N-losses by leaching*) | DEAC model for estimating N-losses by leaching | sheet 22 |
| | Farmgate balance | | sheet 15 |
| | simplified porc farm balance | | sheet 16 |
| | simplified porc farm balance | | sheet 18 |
| | | concentration of nitrates in the water supply**) | sheet 23 |
| *)after parameters are realised | | **)feasibility varies from easy to difficult, according to site characteristics and means available | feasibility |
| | | | 1 |
| | | | 2 |
| | | | 3 |
| | | | 4 |
| | | | implementation of indicator is difficult |
| | | | |
| | | | |
| | | | implementation of indicator is easy |