Analytical and monitoring methods used in catchments

Deliverable 2.1

Work package 2: Predicting catchment-scale nutrient and contaminant fluxes between environmental compartments

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1 Introduction

With the fast-growing human demand on the natural resources, the measurement of the anthropogenic impacts on the environment become over high interest (Parr et al. 2003). Extensive fertilization lead to introduce pollutants into water systems which can pose a threat to the ecosystem and human beings (Vrana et al. 2005). According to Chapman (1996), if the surface waters would not be affected by the human activities, up to 90-99% of the global freshwaters, would maintain the natural chemical concentrations appropriate for aquatic life and human use. Impact of the agriculture on the aquatic environment condition became the focus of the European Union in last years, which resulted in research programs like INSPIRATION ITN (2016 - 2019). To improve the legislative frameworks and directives for farming, the spatially distributed, long-term datasets from water systems are required to be analysed.

The deliverable provides the information on monitoring methods which are currently used to assess water quality in catchment scale and describes monitoring strategies and analytical methods used in three river catchments selected as the objects of investigations in the framework of work package 2 (WS2) within INSPIRATION INT.

2 Monitoring systems

Monitoring is a standardized measurement and observation of the aquatic environment which purpose is to define the status and trends (Chapman 1996). Depending on the monitoring objectives and scientific interest, different duration, frequency and equipment are used.

2.1 Monitoring application

Water systems monitoring is critical for detecting environmental changes influenced by anthropogenic activities and climate changes (Levine et al. 2014). Moreover, it provides information about effectiveness and purposefulness of introduced environmental directives (Lovett et al. 2007), and is a base for change or introduction a new one. Monitoring programmes can be categorized by its duration into short-term and long-term monitoring. The long-term monitoring tends to provide the information about the examined water system from several months to several years. The combination of results from long-term monitoring help to understand factors influencing water parameters, such as precipitation change within the year or temperature hesitations during the day. Long-term monitoring is a good method for gaining knowledge about ongoing processes and general water system's characteristics. The observations from long-term monitoring give the grounds for starting the short-term monitoring (Lovett et al. 2007).

On the other hand, monitoring systems are critical for preventing a human epidemic and the ecosystem pollution by constant check of water parameters such as nutrients concentration, the presence of the bacteria. The monitoring systems used for instant detection of dangerous water composition are called early warning systems and are deployed in water treatment plants or in hazardous facilities such as nuclear power plants or industrial areas. Such kind of system has been working for many years on The River Rhine (Germany) which provides drinking water to 20 millions of people (Chapman 1996).

Monitoring and numerical modelling are inter-linked activities, where monitoring is used to validate the predictions of the numerical models and (Lorz et al. 2003).

2.2 Monitoring system design

Environmental monitoring has evolved in last decades from manual sampling and analysis, through automatic monitoring stations to distributed sensor networks providing real-time measurements of wide range of physical and chemical parameters (Kotamäki et al. 2009). Depending on the scale and purpose of the study, different monitoring techniques can be used.

Water monitoring systems collect scientific data from the preselected geographic locations. The design, deployment, and maintenance of such systems are expensive tasks, therefore they are applied only in the areas of scientific interest or human security importance. The design has to be preceded with the wide range of studies of the geographical features (e.g. terrain's topography, lithology, hydrological, hydro-geological conditioning), human activities (e.g. agriculture, fisheries), water use (urban, industrial facilities). The next step involved carrying out the preliminary surveys by short-term sampling, analysis of contaminants and technical feasibility of complete monitoring programme (Chapman 1996). Based on the results the design decisions are made. The subset of measured parameters has to be selected together with the sampling frequency and the length of the monitoring campaign. The number and the distribution of the sampling points have to be defined.

The monitoring system should provide high-quality data and the samples should be collected and analysed using the same well known and widely accepted methods (Lovett et al. 2007). There exist seven habits regarding the creation of highly effective monitoring programs, which takes into the account reasonableness of the monitoring programme and analysis of quality, consistency, and durability of the data (Lovett et al. 2007).

2.3 Monitoring parameters

Water physical and chemical parameters are determined by climate, geomorphological and geochemical conditions of the drainage basin and underlying aquifer (Chapman 1996). They susceptible to the changing atmospheric conditions within seasons and day times (DPIW 2008). Moreover, field and water use changes during the year influencing the water system conditions. The analysis of monitoring measurements has to take into account those factors to correctly interpret results. Parameters such as water temperature, electrical conductivity, dissolved oxygen, pH can be easily and cheaply measured directly in-field. More difficult and time-consuming is a measurement of ammonia, dissolved organic carbon or some major ions. Very expensive examinations include trace elements and organic pollutants (Chapman 1996).

The most common parameters of surface waters measured directly in-field is water temperature, electrical conductivity, dissolved oxygen and pH (WHO, 2004). The further parameters such as ammonia, dissolved organic carbon and major ions such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-} requires laboratory analysis, therefore the water samples have to be transported and stored in 4°C to prevent undergoing biological processes. Very expensive examinations include trace elements and organic pollutants (Chapman 1996). Similarly to the surface waters, parameters usually measured in groundwater include water temperature, pH, electrical conductivity and concentrations of NO_2^{-} + NO_3^{-}, K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, COD, SiO_2, F. Further analysis is dependent on the monitoring purpose, e.g. in mining or industry areas the important parameters are As, Cd, Hg, Zn (WHO, 2004).

3 Monitoring techniques

3.1 Manual sampling

Many aquatic monitoring programmes rely on collecting discrete water samples at a given time. Depending on the necessities and water quality, larger volumes of water need to be collected to detect trace levels of pollutants. The laboratory analysis provides only a snapshot of the water state at the time of sampling (Vrana et al. 2005). Human inadvertence during manual collection of samples can lead to erroneous results. Therefore, sampling procedure should be defined using well-known, repeatable and fault-tolerant practices to ensure the comparable results across samplings (Lovett et al. 2007). The tool's surface which has a direct contact with the collected sample during yielding has to be firstly rinsed with the water stream from the prospective sampling point. The collected samples should be held in the temperature of 4°C to slow down undergoing biological processes. All samples should be analysed as soon as possible with minimal intervals between analyses each of them to minimize the risk of disrupted results.

Manual sampling is an approach applicable for conducting preliminary studies on rivers. While it does not require the installation of sophisticated instruments in-field, the initial costs are reduced. The new sampling points can be easily added or removed accordingly to the monitoring requirements. The results from consecutive manual sampling campaigns make a base for installation of continuous monitoring stations.

3.2 Automatic continuous monitoring systems

The automatic monitoring systems typically consist of three sub-systems: remote station, monitoring stations and communication system. The remote station retrieves and post-processes the accumulated data. It can be located in a laboratory where more complex measurement takes place but also in early warning computer systems where data is analysed by algorithms. The third sub-system is responsible for providing the communication between the monitoring stations and the remote station. Advanced monitoring systems benefits from remote communication channels such as GSM networks (Rouen et al. 2005). On the other hand, the data can be stored locally by data-loggers and retrieved manually, without a need for neither remote communication system nor the definition of data transmission protocols.

3.2.1 Monitoring station

Automatic monitoring station has to be a self-sufficient system in terms of power energy, sampling and data storing. The construction has to consider its direct deployment in-field and exposition to the changing atmospheric conditions and accessibility by third party. The electronic devices including sensors and storages have to be protected from rain, humility, temperature changes. In order to provide reliable measurements it is critical to separate sensors from the sources of distraction: electromagnetic sources, pollutants, pressure sensor.

Data-logger is an electronic device which stores the measurements off-line. It has limited capacity; when there is no more space left, the new data overrides the oldest (Rouen et al. 2005). Therefore it is important to download recordings periodically. On the market, there is a wide range of devices, suitable for field deployment with waterproof cases and protection against data loss caused by low energy power.

A Power supply is a critical element of every monitoring station. Different energy demand is required depending on the complexity of the station and the number of installed devices. The high-quality power source is required as the electronic devices are sensitive to voltage fluctuations leading to spurious measurements and data consistency loss. For location without access to the energy network, the fuel system or battery storage can be used. That solution requires regular maintenance works, for battery replacement or fuel fill. An alternative energy can be used. Dursun and Ozden (2012), applied photovoltaic systems providing 3.84kW with 48 pieces of solar panels to power water pumping system in Turkey at a lower cost than conventional fuel system. Rouen et al. (2005) used the wind generator to recharge the battery supply on-site.

Sensors. Fast development of wireless technologies facilitated the installation of environmental monitoring stations by deployment of wireless electronic sensors in hazardous or unwired areas (Kotamäki et al. 2009). The collection, storage and share of the data from hundreds of measurements in real time allowed to perform continuous-timed monitoring systems at lower installation and maintenance costs (Kotamäki et al. 2009). Sensors can provide information about water temperature, dissolved oxygen concentration (DO), pH, Conductivity, light extinction (PAR), water level, humidity, precipitation, wind speed and others (Tanwar et al. 2008).

Deployment. Autonomous monitoring station deployment depends on the accessibility of power supply. The usage of high quality batteries supported by alternative energy sources, e.g. solar panels (Dursun, Ozden 2012), allows direct deployment on river (Rouen et al. 2005). Alternatively the water can be abstracted with pump and delivered to the monitoring station laying outside the river stream, where regular power supply is accessible (Rouen et al. 2005).

3.2.2 Communication system

Monitoring stations store the acquired data locally in data-loggers. The data-loggers have limited storage capacity, when the storage is full the new incoming data overwrites the old data. If no automatic transmission system is established, the data have to be copied manually. This solution is used due to its simplicity and when no GSM/Internet networks are available (Rouen et al. 2005).

For the monitoring stations located in the areas where GSM network is present, the automatic transmission can be established. The GSM network is used for transferring the data via GSM providers. For the stations where no GSM coverage is available, the ’shore stations’ can be used. The shore stations are an intermediary between the Remote Station and Monitoring Station. Connection between the Monitoring Station and Shore Station can be provided by low power uhf radio link. The

Shore Station should have connection to the Remote Station (GSM/Internet/Satelite) and the Monitoring Station should connect directly to the Shore Station (Rouen et al. 2005).

The fast growth of the Internet coverage around the globe together with the technological development of power storages and low-power electronical transmitters opened new opportunities for building an on-line sensor networks called Internet of Things. This huge technological step impacted also the monitoring systems, which can now rely on the fast, stable and secure Internet connection accessed by cable, Wi-Fi or GSM network.

3.3 Passive sampling

The groundwater passive samplers are divided into three groups. Equilibrium samplers, which establish equilibrium with groundwater, sorptive samplers which accumulate analytes over time and grab samplers which collect water samples at specific depth and time (Stroo et al. 2014).

Passive sampling is based on free flow of analyte molecules from the sampled medium to a receiving phase. There are different designs of passive samplers, but in general, the accumulated mass of pollutant reflects the concentration at which the sampler is at equilibrium or the time-averaged concentration (Vrana et al. 2005).

One of the main advantages of passive samplers is the lack of power requisition. They can be used to sample groundwater without pumping nor purging, reducing monitoring costs without loss of data quality (Stroo et al. 2014). On the other hand, they cannot automatically send data neither store the results at the specified time which do not qualify them for the modern continuous monitoring networks. The further limitations are that some of the passive samplers do not fit for all analytes, may not collect sufficient sample volume or simply cannot fit into smaller wells (Stroo et al. 2014).

4 Case studies

4.1 Erlauf River Catchment

4.1.1 Site description

The Erlauf River catchment is situated in the northeast of Austria. It is a tributary of the Danube River, which flows into the Black Sea. The total catchment area is 525 km². The Erlauf River is characterized by karst hydrology. The mean discharge calculated for 2006 is 19.3 m³/s, while the average annual rainfall is 860 mm (Strauss 2009). The river is about 50 km length. The northern part is intensively used by agriculture, in contrast to the southern, mountainous part dominated by forest (Fig.1.). The urbanization is low, mainly rural with small villages and few towns not exceeding 10000 habitants (Strauss 2009).

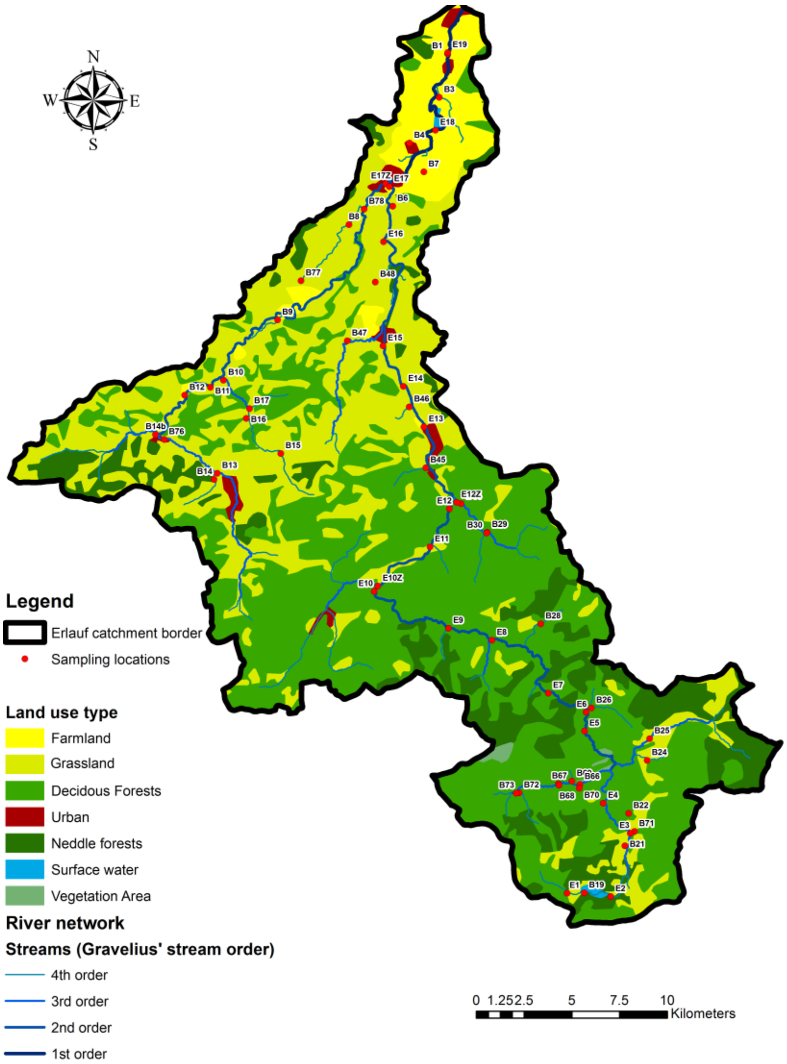

Figure 1 Land use map of Erlauf watershed (EEA, 2014)

4.1.2 Monitoring strategy

Two years monitoring programme in the Erlauf river catchment started in April 2012. Thirty sampling points have been selected, six of them on the Erlauf River and twenty four on the Erlauf River's tributaries. Afterwards, the number of the sampling locations was adjusted on a basis of the data analysis from the sampling campaigns. In total, 60 different locations were investigated during whole monitoring programme. The last campaign ran in January 2014.

After 3 years break, in December 2016, monitoring has been resumed for INSPIRATION ITN purpose, with the planned monitoring duration of one year. The motivation of monitoring resume was to study the agricultural impact on the N-cycling in mesoscale river catchment. Therefore, in April 2017, three new sampling points were added to the sampling programme, in the northern, dominated by agriculture, part of the catchment. Eighteen points from the previous campaigns, mainly in a source area, were considered negligible and skipped. All sampling locations monitored in years 2012 – 2017 are shown in Fig.2.

Due to the changing agricultural practices within a year, and to cover all different seasons, sampling campaigns were scheduled to have placed every second month from April till August, and then in November and January. The samples were collected within two or three days. The last sampling campaign is scheduled for November 2017. Table 2 present the time frame for all sampling campaigns in Erlauf catchment.

Table 1 Time frame for all sampling campaigns in the Erlauf catchment

Sampling campaigns in the Erlauf catchment												
Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2012				X		X		X			X	
2013	X			X		X		X			X	
2014	X											
2016												X
2017				X		X		X			X	

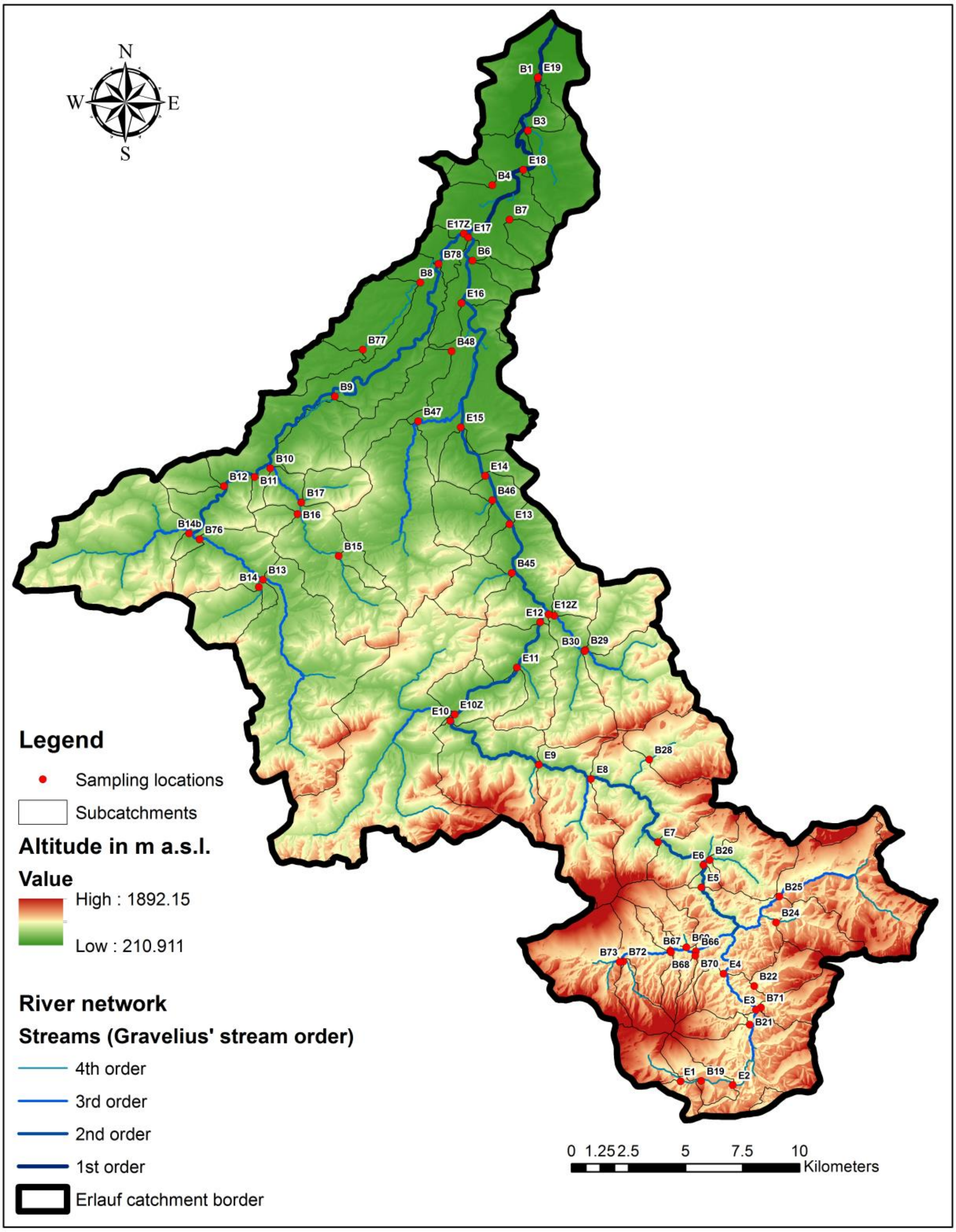

Figure 2 Sampling locations in Erlauf watershed investigated during sampling campaigns conducted from 2012 to 2017

4.1.3 Monitored parameters and analytical methods used

Sampling campaigns consisted of in-field measurements and laboratory analysis. All samples have been collected manually into high-density polyethylene bottles and stored in a fridge. The samples for major ions and isotope signatures (except the samples for $\delta^{34}S$ and $\delta^{18}O$ of sulfate) were filtered using 0.25µm cellulose acetate filters. The further analyses were carried out in the laboratory, within one month from the collection of the samples. The laboratory analysis included the measurements of major anions (Cl^-, SO_4^{2-}, NO_3^-) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and stable isotopes. All samples were analysed for the isotopic composition of dissolved inorganic carbon ($\delta^{13}C$) and dissolved nitrate ($\delta^{15}N$ and $\delta^{18}O$). A mass spectrometer DELTA V Plus in combination with a GasBench II from Thermo Scientific was used for nitrogen and oxygen isotope measurements of nitrate and for carbon isotope measurements of DIC. The isotopic composition of dissolved nitrate was measured by using the denitrifier method with bacteria strains of Pseudomonas chlororaphis (ATCC #13985). Moreover, all samples were analysed for stable isotopes of water (δ^2H and $\delta^{18}O$) by laser-based analyser (L1102-I, Picarro Inc.) with a measurement precision of 1.0 and 0.3‰ for deuterium and oxygen, respectively. Stable isotopes of sulfate ($\delta^{34}S$ and $\delta^{18}O$) were analysed by a mass spectrometer DELTA S Plus in combination with an EA. Due to very low concentration of sulfates in a number of high mountain streams, the isotopic signature of sulfate could not be measured in all sampling locations.

4.2 Bode River Catchment

4.2.1 Site description

Bode River Catchment extends over 3200km2 in the central Germany. The Bode River spring is located in Herz Mountains which take the southern part of the catchment. About 23% of the entire catchment consists of forests and semi-natural areas, while 70% is dominated by agriculture and 7% by urbanization (Kunkel, Sorg 2017).

The catchment has middle European climate with wet summers and cold dry winters (Mueller et al. 2016a). The precipitation in the mountain part of the catchment has an average of 660mm/year and can reach up to 1600mm/year in the southern mountainous part, and about 450mm per year in the middle and lowlands (Kunkel, Sorg 2017).

The Bode River has a moderate to poor ecological status (Mueller et al. 2016a). The survey carried out that 76% of the river system has a high nutrient load and heavily modified river morphology. The whole catchment area consists of four groundwater aquifers, from which 3 are classified having a bad chemical condition (Kunkel, Sorg 2017, Wollschläger et al. 2017).

The entire Bode River catchment area is under long-term meteorological and hydrological monitoring programme within Terrestrial Environmental Observatories (TERENO) network, hosted by Helmholtz Association of German Research Centres. Additionally, the local authorities perform long-term water quality monitoring, some of them for more than 50 years now. The Bode River catchment is divided into five intensive test sites, where different research studies are developed. Meteorological and hydrological monitoring programme within Terrestrial Environmental Observatories (TERENO) was described by Wollschläger et al. (2017).

4.2.2 Monitoring strategy

In March 2012, the stream water monitoring programme started. One hundred thirty-three sampling locations were determined across all Bode's main tributaries and took part of spatial high-resolution sampling. Figure 3 presents all sampling locations investigated during sampling campaigns conducted from 2012 to 2014.

During summer time, some of the streams were dry and could not be sampled. In November 2012, the monthly precipitation monitoring programme started. Field precipitation water collectors were installed in 25 points across catchment area. In 2013, 25 sampling points were selected for more intensive, monthly spatial low-resolution sampling (Mueller et al. 2016b). The points distribution was not steady, a southern part had more sampling points due to the high number of mountain streams (Mueller et al. 2016a).

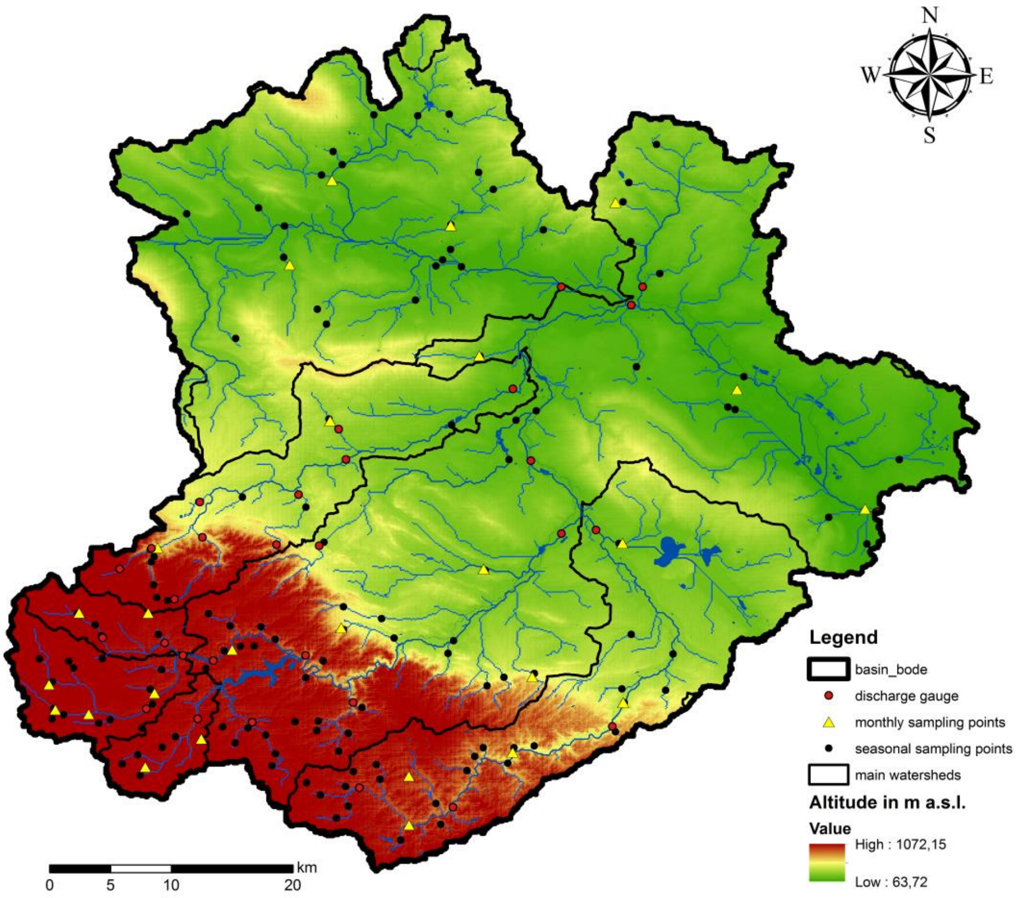

Figure 3 Sampling locations in Bode watershed investigated during sampling campaigns conducted from 2012 to 2017

Table 2 Sampling campaigns in Bode catchment

Sampling campaigns in Bode catchment												
Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2012			RS	X			RS	X	X	RS		
2013		X	X	X	X	X	X	RS	X	X	X	RS
2014	X	X	X	X	X	X	X	X	X	X	X	X
2015		X					X	X			X	
2016		X		E				E	E	E	E	E
2017	E	E	E	E	E	E	E	E	E			

RS – regional survey, 133 surface water monitoring sampling locations
X – 25 representative sampling sites, including precipitation water samples
E – event based monitoring, including precipitation water samples

4.2.3 Monitored parameters and analytical methods used

Electrical conductivity, pH, and temperature were measured directly in-field after the extraction from the sampling point. All samples were filtered in-field with 0.25µm cellulose acetate filters, stored in high-density polyethylene bottles and stored in a refrigerator. Further analysis was carried out in the laboratory within a month from the campaign, where main anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-), cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and isotopes compositions were measured. Untill that time, water samples were kept in the refrigerator. The nitrate concentration was measured using ion chromatography with a Dionex ICS-2000 combined with AS50. The isotopic composition of dissolved nitrate ($\delta^{15}N$ and $\delta^{18}O$) was determined using denitrifier method with Pseudomonas Chlororaphis bacteria strains. All samples were analysed for the isotopic composition of dissolved inorganic carbon ($\delta^{13}C$). The spectrometer DELTA V Plus in combination with a GasBench II from Thermo Scientific was used for measurements of nitrate and DIC isotopes. Moreover, all samples were analysed for stable isotopes of water ($\delta^{2}H$ and $\delta^{18}O$) by laser-based analyser (L1102-I, Picarro Inc.) with a measurement precision of 1.0 and 0.3‰ for deuterium and oxygen, respectively. Stable isotopes of sulfate ($\delta^{34}S$ and $\delta^{18}O$) were analysed by a mass spectrometer DELTA S Plus in combination with an EA.

4.3 Geer River Catchment

4.3.1 Site description

The Geer River is 65km long, it is located in eastern Belgium and flows through three regions and two countries (Belgium, Netherlands). The catchment extends over 474 km^2 and it is mostly dominated by agriculture (65%), pasture (15%), urban (13%) and forests (7%) (Fig.5) (Hakoun et al. 2017). The Geer River provides the water to the Liège and surroundings, where around 600 000 people live and the water consumption is about 30 million m^3 per year (Brouyere et al. 2004). The topography is relatively flat, the altitude ranges between 80 m and 206 m (Batlle Aguilar et al. 2007).

The water quality of the Geer River is considered poor due to the excessive amounts of phosphates and nitrogen, which are still lower than the drinking water limit of 50 mg/L (Batlle Aguilar et al. 2007). In the 70s of the 20th century, the Geer River was declared 'dead' due to law biodiversity. Since that time, several restoration projects have run in order to improve the water quality, which is still far from the European standards (AQUADRA 2013).

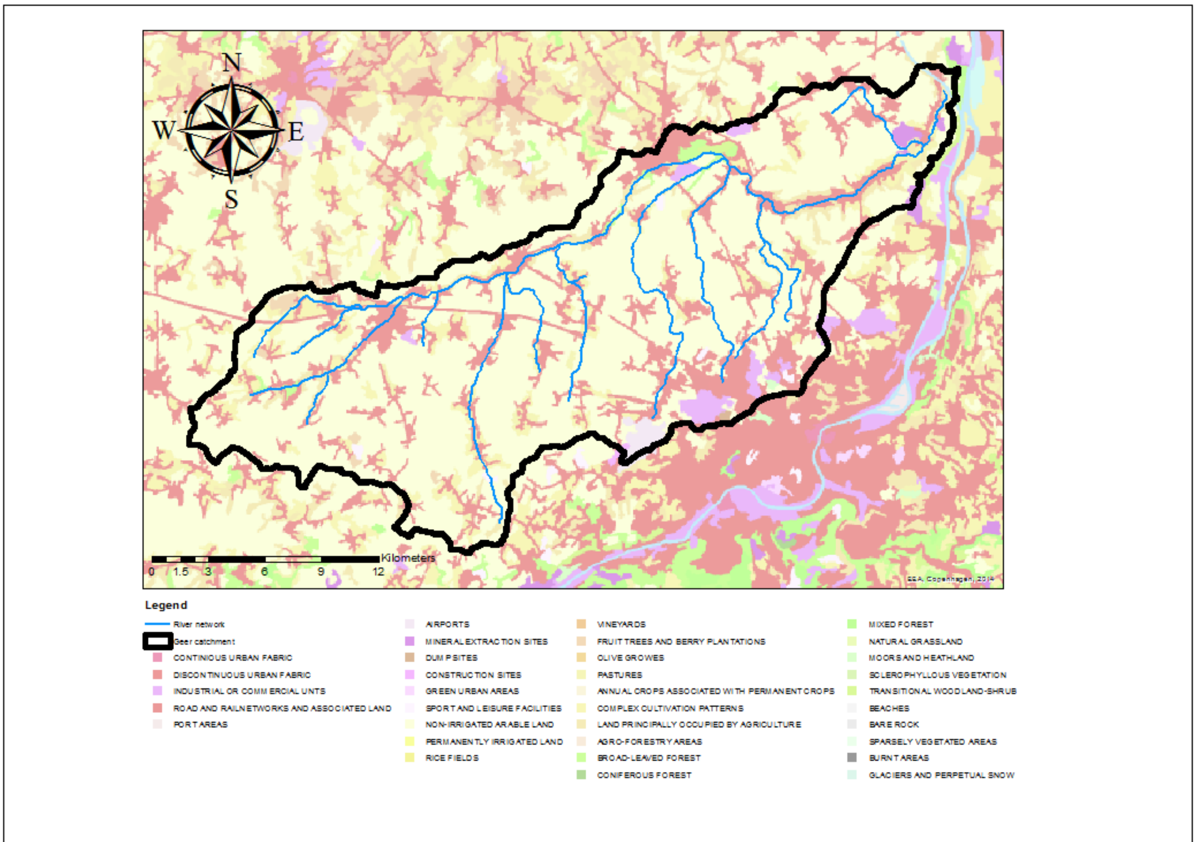

Figure 4 Land use map of the Geer watershed (EEA, 2014)

4.3.2 Monitoring strategy

The monitoring programme in Geer catchment starts in September 2017 and is going to last one year. During that time, the sampling campaigns will occur every second month. During each sampling campaign, 19 surface water samples are going to be collected during 2 days and stored in a refrigerator until further laboratory analysis. In spring 2018, event-based monitoring, during storm events, will be performed. Depending on the weather conditions, several samplings campaigns will take place during storm events. Fig. 6 presents the map with all sampling locations chosen for surface water monitoring.

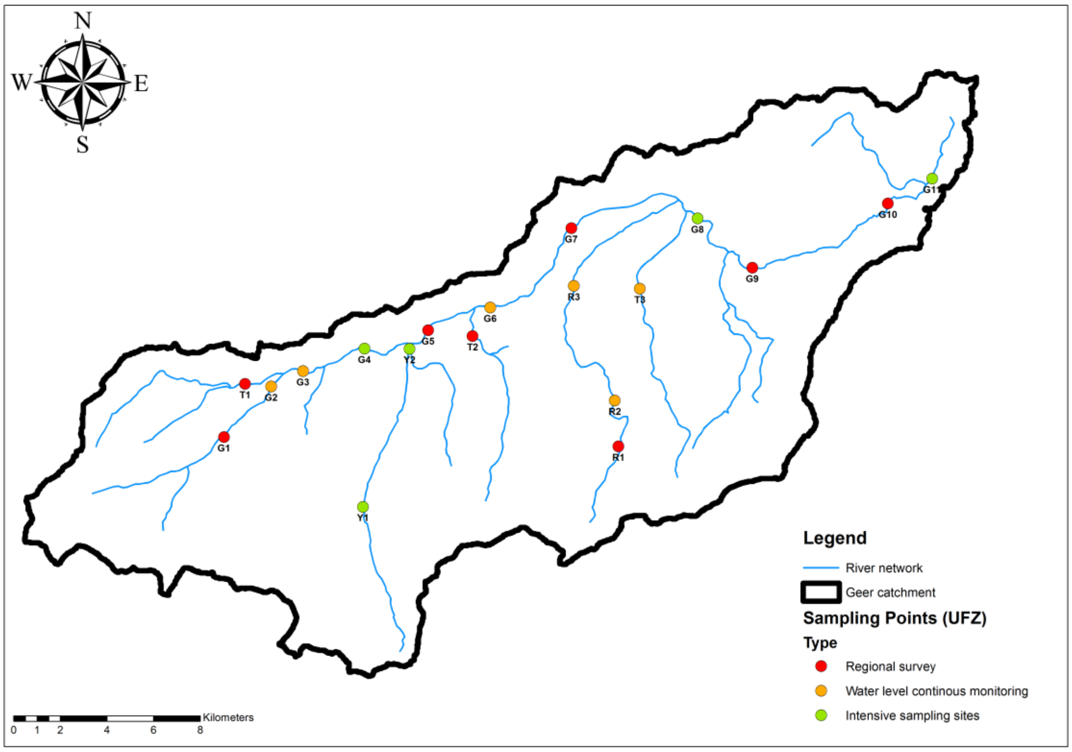

Figure 5 Sampling locations in Geer watershed investigated during sampling campaigns starting in September 2017

Schedule of sampling campaigns in Geer catchment is presented in Tab.3.

Table 3 Sampling campaigns in Geer catchment

Sampling campaigns in Geer catchment												
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017									X		X	
2018	X			X		X		X				

4.3.3 Monitored parameters and analytical methods used

Each water samples will be filtered in-filed just after extraction, with preceding pH, electrical conductivity, alkalinity, DO, and temperature measurements. The further analysis will take place in the laboratory. The concentration of DOC, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+ will be studied and the following stable isotopes signatures will be measured $\delta^{13}C$-DIC (VPDB), $\delta^{34}S$ SO_4 (VCDT), $\delta^{18}O$-SO_4 (VSMOW), $\delta^{15}N$-NO_3 (AIR), $\delta^{18}O$-NO_3 (VSMOW), $\delta^{2}H$-H_2O (VSMOW), and $\delta^{18}O$-H_2O (VSMOW).

5 Summary and conclusion

Water quality monitoring programmes are critical to controlling the current state of the environment. The extensive anthropogenic activities influence entire ecosystems and their impact on water has to be precisely monitored to protect the environment including human beings. The fast technological development of last decades resulted in the appearance of sophisticated measuring apparatus ready for in-field deployment. The alternative energy can now supply power to the autonomous monitoring stations. The growth of Internet coverage opened the opportunity to build sensor networks providing measurement results in real time. The main disadvantage of the automatic monitoring is the high cost of the equipment and maintenance.

The respective study catchment showed the successful application of manual, long-term monitoring programmes in Bode River Catchment and Erlauf River Catchment. Both programmes started in 2012 and successfully run, providing information about the concentration of major anions, cations and isotope composition of $\delta^{13}C$ of DIC, $\delta^{34}S$ and $\delta^{18}O$ of sulfate, $\delta^{15}N$ and $\delta^{18}O$ of nitrate, and $\delta^{2}H$ and $\delta^{18}O$ of water. The similar approach is used in The Geer River catchment, where surface water monitoring is scheduled to start in September 2017 and last one year. The surface water monitoring programmes conducted in all catchments show that manual monitoring is a successful tool for tracing sources and fluxes of matter in agricultural catchments. The advantage of manual monitoring is the reduction of the initial costs. The new sampling points can be easily added or removed accordingly to the monitoring requirements. A repeatable manual sampling remains a cost-effective monitoring method for low-frequency monitoring used still by many scientific centres. The results from consecutive manual sampling campaigns make a base for installation of continuous monitoring stations.

References

AQUADRA (2013): Un project transfrontalier pour le Geer, la Voer, la Berwinneet la Gueule. 4 AFFLUENTS DE LA MEUSE. Aquadra. Rapport final. September 2013.

Batlle Aguilar, Jordi; Orban, Philippe; Dassargues, Alain; Brouyère, Serge (2007): Identification of groundwater quality trends in a chalk aquifer threatened by intensive agriculture in Belgium. In *Hydrogeol J* 15 (8), pp. 1615–1627. DOI: 10.1007/s10040-007-0204-y.

Brouyere, Serge; Carabin, Guy; Dassargues, Alain (2004): Climate change impacts on groundwater resources. Modelled deficits in a chalky aquifer, Geer basin, Belgium. In *Hydrogeology Journal* 12 (2). DOI: 10.1007/s10040-003-0293-1.

Chapman, D. (1996): Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring - Second Edition, pp. 19–133.

DPIW (2008): Site-specific trigger values for physico-chemical indicators monitored under the DPIW Baseline Water Quality Monitoring Program. In *Water Assessment Water Quality Report Series, Report* (WA 08/52.).

Dursun, M.; Ozden, S. (2012): Application of Solar Powered Automatic Water Pumping in Turkey. In *IJCEE* (Vol. 4, No. 2). DOI: 10.7763/IJCEE.2012.V4.471.

EEA (2014): Land Cover. European Environment Agency. Copenhagen. Accessed June 2017.

Hakoun, Vivien; Orban, Philippe; Dassargues, Alain; Brouyère, Serge (2017): Factors controlling spatial and temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium). In *Environmental pollution (Barking, Essex : 1987)* 223, pp. 185–199. DOI: 10.1016/j.envpol.2017.01.012.

Kotamäki, Niina; Thessler, Sirpa; Koskiaho, Jari; Hannukkala, Asko O.; Huitu, Hanna; Huttula, Timo et al. (2009): Wireless in-situ Sensor Network for Agriculture and Water Monitoring on a River Basin Scale in Southern Finland. Evaluation from a Data User's Perspective. In *Sensors (Basel, Switzerland)* 9 (4), pp. 2862–2883. DOI: 10.3390/s90402862.

Kunkel, Ralf; Sorg, Jeurgen (2017): Hydrological Observatory Bode. In *Terrestrial Environmental Observatories*. Available online at http://teodoor.icg.kfa-juelich.de/observatories/HCGL_Observatory/hydrological-observatory-1/page-hydrological-observatory-bode, checked on 1/1/2017.

Levine, Carrie R.; Yanai, Ruth D.; Lampman, Gregory G.; Burns, Douglas A.; Driscoll, Charles T.; Lawrence, Gregory B. et al. (2014): Evaluating the efficiency of environmental monitoring programs. In *Ecological Indicators* 39, pp. 94–101. DOI: 10.1016/j.ecolind.2013.12.010.

Lorz, C.; Hruška, J.; Krám, P. (2003): Modeling and monitoring of long-term acidification in an upland catchment of the Western Ore Mountains, SE Germany. In *Science of The Total Environment* 310 (1-3), pp. 153–161. DOI: 10.1016/S0048-9697(02)00635-6.

Lovett, Gary M.; Burns, Douglas A.; Driscoll, Charles T.; Jenkins, Jennifer C.; Mitchell, Myron J.; Rustad, Lindsey et al. (2007): Who needs environmental monitoring? In *Frontiers in Ecology and the Environment* 5 (5), pp. 253–260. DOI: 10.1890/1540-9295(2007)5[253:WNEM]2.0.CO;2.

Mueller, Christin; Krieg, Ronald; Merz, Ralf; Knöller, Kay (2016a): Regional nitrogen dynamics in the TERENO Bode River catchment, Germany, as constrained by stable isotope patterns. In *Isotopes in environmental and health studies* 52 (1-2), pp. 61–74. DOI: 10.1080/10256016.2015.1019489.

Mueller, Christin; Zink, Matthias; Samaniego, Luis; Krieg, Ronald; Merz, Ralf; Rode, Michael; Knöller, Kay (2016b): Discharge Driven Nitrogen Dynamics in a Mesoscale River Basin As Constrained by Stable Isotope Patterns. In *Environmental science & technology* 50 (17), pp. 9187–9196. DOI: 10.1021/acs.est.6b01057.

Parr, T. W.; Sier, A.R.J.; Battarbee, R. W.; Mackay, A.; Burgess, J. (2003): Detecting environmental change. Science and society—perspectives on long-term research and monitoring in the 21st century. In *Science of The Total Environment* 310 (1-3), pp. 1–8. DOI: 10.1016/S0048-9697(03)00257-2.

Rouen, M.; Glen, George; Kelly, Jack; Lee, Mike; Moreno-Ostos, Enrique (2005): High-resolution automic water quality monitoring systems applied to catchment and reservoir monitoring. In *Freshwater Forum* 2005 (23), pp. 20–37.

Sawyer, J. (2008): Surface Waters: Ammonium is Not Ammonia. Available online at https://crops.extension.iastate.edu/cropnews/2008/04/surface-waters-ammonium-not-ammonia-%E2%80%93-part-1, checked on 8/25/2017.

Strauss, Peter (2009): River Erlauf, Austria. In *PEER Partnership for European Environmental Research*.

Stroo, Hans F.; R. Hunter Anderson; Andrea Leeson (2014): Passive sampling for groundwater monitoring: technology status.

Tanwar, Pankaj; Nandy, Tapas; Ukey, Pallavi; Manekar, Pravin (2008): Correlating on-line monitoring parameters, pH, DO and ORP with nutrient removal in an intermittent cyclic process bioreactor system. In *Bioresource technology* 99 (16), pp. 7630–7635. DOI: 10.1016/j.biortech.2008.02.004.

Vrana, Branislav; Allan, Ian J.; Greenwood, Richard; Mills, Graham A.; Dominiak, Ewa; Svensson, Katarina et al. (2005): Passive sampling techniques for monitoring pollutants in water. In *TrAC Trends in Analytical Chemistry* 24 (10), pp. 845–868. DOI: 10.1016/j.trac.2005.06.006.

Wollschläger, U., Attinger, S., Borchardt, D., Brauns, M., Cuntz, M., Dietrich, P., ... & Hildebrandt, A. (2017). The Bode hydrological observatory: a platform for integrated, interdisciplinary hydroecological research within the TERENO Harz/Central German Lowland Observatory. Environmental Earth Sciences, 76(1), 29.

World Health Organization. (2004). Guidelines for drinking-water quality (Vol. 1). World Health Organization.