UNIVERSITY OF LATVIA

Doctoral Thesis

Riga, 2023

Inga Retiķe

CHARACTERIZATION OF GEOCHEMICAL COMPOSITION AND POLLUTION IMPACTS ON GROUNDWATER QUALITY IN LATVIA TO ELABORATE MONITORING SYSTEM AND MANAGEMENT APPROACHES

Promocijas darba kopsavilkums

LATVIJAS PAZEMES ŪDEŅU ĢEOĶĪMISKĀ SASTĀVA UN PIESĀRŅOJUMA LĪMEŅU RAKSTUROJUMS MONITORINGA UN AIZSARDZĪBAS NODROŠINĀŠANAI

UNIVERSITY OF LATVIA

FACULTY OF GEOGRAPHY AND EARTH SCIENCES

Inga Retiķe

CHARACTERIZATION OF GEOCHEMICAL COMPOSITION AND POLLUTION IMPACTS ON GROUNDWATER QUALITY IN LATVIA TO ELABORATE MONITORING SYSTEM AND MANAGEMENT APPROACHES

Doctoral Thesis

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Abstract

Sustainable groundwater management is a prerequisite for human and nature well-being. Not only does groundwater provides almost half of the global drinking water supply, but also sustains groundwater dependent ecosystems like rivers, lakes, and wetlands that further provide essential ecosystem services. Moreover, the pressures and reliance on groundwater resources are expected to increase globally as urbanization and climate change escalate surface water scarcity and pollution. Despite the exceptional importance of groundwater in social, economic, and environmental processes, it remains poorly understood, mismanaged, and often neglected leading to poor management decisions. An in-depth understanding of the geochemical characteristics of freshwater aquifers is fundamental to conceptualizing the groundwater evolution paths and identifying groundwater vulnerability to pollution. Such conceptual understanding of groundwater systems is needed to carry out representative groundwater monitoring and gather crucial data for groundwater resources assessment and trend analysis. This study aimed to assess the geochemical and pollution controls on the variability of groundwater chemical composition in Latvia to elaborate groundwater monitoring and management systems considering the requirements of the EU water policies.

The study characterized the most common groundwater types in the active water exchange zone that represent different hydrogeological conditions and pollution impacts based on multivariate statistics and using groundwater geochemistry. The results revealed that freshwater aquifers in Latvia are vulnerable to various human activities like agricultural pollution with nitrates or urban runoff induced groundwater contamination. Moreover, historical pollution like aquifer salinization due to groundwater over-abstraction can be still observed and take decades to recover. At the same time, groundwater quality can be lower due to natural processes like strongly reducing conditions promoting high iron, ammonium, and even arsenic concentrations or gypsum dissolution leading to increased mineralization and highlighted fluorine levels. Natural background levels and threshold values were derived to ensure proper assessment and timely detection of seawater intrusion into the freshwater aquifer in the Liepaja – the groundwater body at risk. An in-depth analysis of EU water policies' requirements versus systematic groundwater monitoring revealed the major discrepancies in the Latvian groundwater monitoring system: the underrepresentation of the shallow and most vulnerable aquifers in the monitoring network and the lack of monitoring points, especially in transboundary areas. Gaps can be rapidly and cost-effectively filled by sampling the existing wells from major groundwater abstraction sites (well fields) and by identifying the most representative springs and including them in the national groundwater monitoring network.

Keywords: groundwater, hydrogeochemistry, groundwater monitoring, EU water policies, groundwater management, groundwater vulnerability, groundwater pollution, seawater intrusion, natural background levels, threshold values.

Contents

Abbreviations

BAB	Baltic Artesian Basin
CIS	The Common Implementation Strategy
CLU	Cluster
CV	Criteria value
DL	Detection limit
DPSIR	Driver, pressures, state, impact, and response methodology
DWD	Drinking Water Directive (2020/2184)
DWPA	Drinking water protected areas
EU	European Union
Fe_{tot}	Total iron, mg/L
GAAE	Groundwater associated aquatic ecosystems
GDE	Groundwater dependent ecosystem
GDTE	Groundwater dependent terrestrial ecosystem
GWB	Groundwater body
GWD	Groundwater Directive (2006/118/EC)
HCA	Hierarchical cluster analysis
HPP	Hydropower plant
IBA	Ionic balance error
LEGMC	Latvian Environment, Geology and Meteorology Centre
Major ions	Cations Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and anions HCO_3^{-}, Cl^{-}, SO_4^{2-}
NBLs	Natural background levels
NVZs	Nitrate vulnerable zones
ORP	Oxidation–reduction potential
PC	Principal component
PCA	Principal component analysis
PoMs	The Programme of Measures
RBD	River basin district
RBMP	River Basin Management Plan
REF	Reference value
SEC	Specific electrical conductivity
TDS	Total dissolved solids
TOC	Total organic carbon
TVs	Threshold values
WFD	Water Framework Directive (2000/60/EC)

Introduction

Groundwater globally ensures water supply, ecosystem functioning, and human well-being, and the overall importance is expected to grow as groundwater is more buffered from seasonal and multi-year climate variability than surface water (UNESCO, 2015, 2020). In Latvia, around 80% of the water supply comes from groundwater resources (RBMPs, 2022). Despite its crucial importance groundwater is frequently referred to as a hidden resource as it becomes naturally visible only in caves, geysers, and in the form of springs – natural groundwater outflows (Koit et al., 2023). Groundwater studies often face various challenges like missing and poor quality data, and a lack of conceptual understanding of groundwater system functioning (Terasmaa et al., 2020). Yet, the increasing groundwater demand to supply drinking water, agriculture, and industry in combination with climate change has highlighted the importance of groundwater management and protection (EEA, 2018; Naranjo-Fernandez et al., 2020; Obergfell et al., 2019; Witte et al., 2019).

The mismanagement of groundwater resources may adversely affect the development of countries, including water and food security, groundwater dependent ecosystems having rich biodiversity, and even possibilities to mitigate climate change (Lapworth et al., 2022; Scheihing et al., 2022). Moreover, groundwater does not follow human-drawn boundaries like country borders and unsustainable activities such as groundwater over-abstraction and pollution in one country may lead to poor groundwater status in another country (Terasmaa et al., 2020), or even escalate water conflicts (Klare, 2020; Rigi & Warner 2020).

As stated by Appelo and Postma (2005), the chemical composition of groundwater is a result of all the processes between water, minerals, and gasses it has been in contact with from recharge to discharge areas. In addition to natural factors, human activities may also affect groundwater quality. For instance, significant groundwater pumping may modify the extension of the freshwater domain and initiate water mixing (Pulido-Velazquez et al., 2022), i.e., seawater intrusion into freshwater aquifers (Bikše & Retike, 2018). The occurrence of some substances in groundwater such as pesticides is a direct indicator of human impact, while inorganic components of geogenic origin (i.e., trace metals) may originate from both natural and anthropogenic sources (Biddau et al., 2017).

An in-depth understanding of the geochemical characteristics of freshwater aquifers is essential to understand the groundwater evolution paths and distinguishing between natural and human-influenced groundwater samples. Urresti-Estala et al. (2013) highlight that a large number of factors responsible for the final groundwater composition means that differentiation between natural conditions and human-introduced changes is a highly challenging task accompanied by many errors and uncertainties. Multivariate statistics can reveal the patterns of groundwater geochemistry and has been successfully applied to hydrogeochemical data sets obtained from local (Koit et al., 2021, 2023; Slama et al., 2022) to regional (Biddau et al., 2017; Bondu et al., 2020; Busico et al., 2018; Cloutier et al., 2008) scales.

The EU water policies are a set of legal acts directly aiming to manage and protect groundwater resources by various means of measures. Latvia has been a member state of the European Union (EU) since 2004 and thus is required to implement the EU water policies. The EU Water Framework Directive (WFD) (Directive 2000/60/EC) requires EU member states to ensure the good quantitative and chemical status of groundwater bodies by timely detection of negative trends posing a risk for resource depletion and deterioration of groundwater dependent ecosystems. The WFD and the "daughter" Groundwater Directive (GWD) (Directive 2006/118/EC) require evaluation of the chemical status of groundwater bodies against threshold values (TVs) locally derived for pollutants responsible for putting groundwater bodies at risk. Natural background levels (NBLs) should be established for parameters that can occur also naturally in a range of concentrations at different hydrogeological conditions (e.g., Cl^-, SO_4^{2-}) (Voutchkova et al., 2021). The EU Nitrates Directive (Directive 91/676/ EEC) aims to reduce water pollution caused by N fertilizers used in agriculture by designating specific nitrate vulnerable zones (NVZs) where the application of N fertilizers is limited. The WFD and the so-called Water Convention (UNECE, 1992) are among the major legal agreements to ensure collaboration on the sustainability of shared (transboundary) groundwater resources.

Good quality data obtained with sufficient frequency from representative groundwater monitoring networks are a prerequisite for any hydrogeological study or local to national scale groundwater resources assessment. Systematic groundwater monitoring in Latvia was launched more than 60 years ago. The data set acquired within the framework of national monitoring is of great value due to the availability of long-term observations with usually good spatial coverage and multi-aquifer representation. However, the presence of such a unique data set has been neglected even though it surpasses any previously accomplished hydrogeological study in Latvia. The usage of such data has been hampered for years because of limited access to databases and a lack of supplementary information about data characteristics and quality. Moreover, systematic groundwater monitoring programmes at a national scale undergo a variety of changes in the form of political and economic reforms. They all affect data sets and put some limitations on their future usage that can be overcome if the changes are well documented, and impacts understood.

Aim of the work

The doctoral thesis **aims** to assess the geochemical and pollution controls on the variability of groundwater chemical composition in Latvia to elaborate groundwater monitoring and management systems considering the requirements of the EU water policies. The thesis has the following **tasks:**

1. To characterize groundwater geochemical composition and identify pollution impacts.
2. To evaluate the systematic groundwater quality and quantity monitoring in Latvia and discuss the perspectives for improvements addressing identified gaps and future needs according to the requirements of the EU water policies.
3. To contribute to the development of methodologies for groundwater surveillance and protection.

The novelty of the research

- For the first time, a comprehensive analysis of the groundwater chemical variability of the active water exchange zone in Latvia was performed using multivariate

statistics and addressing a wide range of parameters (major ions, trace elements, nitrogen compounds).
- Delineated groups with distinct groundwater chemical compositions provide new insights into the usage potential of groundwater in Latvia.
- Established methodological approach for monitoring the development of seawater intrusion into freshwater aquifers for groundwater body at risk in Liepaja.
- The research outcomes support the implementation of groundwater-related requirements of EU water policies in Latvia and can improve the processes of national and transboundary aquifer monitoring, management, and sustainable usage planning.

Scientific and applied significance of the research

- The improvement of the Latvian systematic groundwater monitoring network such as the installation of new monitoring wells or the inclusion of existing wells from groundwater well fields is currently happening based on the recommendations from this research.
- Based on the recommendations new springs will be used to expand the existing groundwater monitoring network in Latvia and to develop transboundary groundwater monitoring networks.
- The compliance analysis of the systematic groundwater monitoring network in Latvia together with recommendations for future groundwater monitoring and assessment improvements according to the EU Water Framework Directive and Groundwater Directive have been included in the 3rd cycle Latvian River Basin Management Plans (RBMPs, 2022), and according to the EU Nitrates Directive have been included in national Nitrates Directive's report (Nitrates report, 2020), and in the Environmental policy guidelines for 2021–2027 (the Republic of Latvia Cabinet Regulation No. 583 "On Environmental Policy Guidelines for 2021–2027").
- Natural background levels derived and threshold values established for groundwater body at risk has been adopted in the national legislative act (3rd October 2016 order No. 257 "On the threshold values of polluting substances and their groups in groundwater bodies at risk" on the basis of the Republic of Latvia Cabinet Regulation No. 42 "Regulations Regarding Procedures for Ascertaining of Groundwater Resources and Quality Criteria").
- The in-depth assessment of systematic groundwater quantity and quality monitoring in Latvia will ease the navigation of historical up to modern hydrogeochemical data sets and will foster future research in topics of hydrogeology and groundwater management.

Approbation of the results

The results of the thesis are described in 10 scientific publications (10 articles and 1 book chapter) all being peer-reviewed and included in Web of Science and/or Scopus databases. Paper I is under review. In total author has 17 publications included in Web of Science and/or Scopus databases. The results of the research were presented in 24 reports internationally and 10 reports at local conferences.

Scientific publications related to the thesis

1. Marandi, A., Demidko, J., Borozdins, D., Valters, K., **Retike, I.**, Bikše, J. & Männik, M. (*under review*). Invisible groundwater between Estonia and Latvia – an analysis of gaps and perspectives for better transboundary aquifer management. Submitted to the *Journal of Hydrology: Regional Studies* (Web of Science / Scopus, Q1, IF_{2022} = 5.437) (further referred as to **Paper I**).
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7. Bikše, J. & **Retike, I.** (2018). An Approach to Delineate Groundwater Bodies at Risk: Seawater Intrusion in Liepaja (Latvia). *E3S Web of Conferences*, 54, 00003. https://doi.org/10.1051/e3sconf/20185400003 (Web of Science/Scopus) (further referred to as **Paper VII**).
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Structure of the thesis

Based on the thesis topic 10 peer-reviewed scientific publications further referred to as Papers I–X have been developed. The major topics covered by the publications are presented in Table 1. Key results of the research work are presented in all sections of the thesis. The thesis consists of 88 pages and is supplemented by 23 figures and 9 tables. The QR codes for published papers are included in the Appendices.

Table 1. Overview of the scientific publications within the scope of the doctoral thesis

Number of Paper	Covered sections in the thesis			
	Analysis of groundwater monitoring	Geochemical characterization of groundwater	Assessment of groundwater pollution	Elaboration on management approaches
I	✓			✓
II	✓	✓		✓
III	✓	✓	✓	✓
IV	✓			✓
V	✓			✓
VI			✓	✓
VII	✓		✓	✓
VIII			✓	✓
IX		✓	✓	✓
X	✓	✓	✓	

Author's contribution

The author had principal responsibility for the majority of data curation and statistical analyses, research conceptualization, and methodological approaches presented and discussed in the doctoral thesis. In the preparation of Papers, I–IV and VI author was responsible for the development of sections addressing Latvia or Baltic states under the supervision of principal investigator *Dr. geol.* Andres Marandi (Paper I), *Ph.D.* Oliver Koit (Paper II), Assoc. Prof., *Dr. geol.* Nils-Otto Kitterød (Paper III), Prof., *Ph.D.* Jaanus Terasmaa (Paper IV) and *Dr.* David Pulido-Verlazques (Paper VI). Detailed author's contribution in preparing scientific publications related to the thesis is as follows:

- **Paper I.** Conceptualization 20%, Writing 20%.
- **Paper II.** Conceptualization 20%, Data analysis 10%, Writing 30%.
- **Paper III.** Conceptualization 10%, Data analysis 10%, Writing 20%, Visualization 10%.
- **Paper IV.** Conceptualization 20%, Writing 20%.

- **Paper V.** Conceptualization 80%, Methodology 40%, Data analysis 10%, Writing 90%, Visualization 10%.
- **Paper VI.** Conceptualization 10%, Methodology 10%, Data analysis 20%, Writing 20%, Visualization 10%.
- **Paper VII.** Conceptualization 30%, Methodology 30%, Writing 90%.
- **Paper VIII.** Conceptualization 80%, Methodology 80%, Data analysis 80%, Writing 100%, Visualization 100%.
- **Paper IX.** Conceptualization 90%, Methodology 90%, Data analysis 90%, Writing 90%, Visualization 100%.
- **Paper X.** Conceptualization 90%, Methodology 90%, Data analysis 90%, Writing 90%, Visualization 100%.

1. LITERATURE REVIEW

1.1. The legislative framework for groundwater protection at the European Union level

The beginning of the European Union's regulatory framework for groundwater can be dated back to the end of the 1970s when the original Groundwater Directive (Directive 80/68/EEC) on the protection of groundwater against pollution caused by certain dangerous substances was adopted and remained the major legislative instrument in the EU until 2013 (European Commission, 2008). Groundwater was for a long time neglected in water legislation addressing mainly rivers and lakes used for drinking water abstraction. Deterioration of groundwater and aquatic ecosystem quality, and depletion of available water resources, including salinization of coastal aquifers, accelerated during the 1980s. The increased efforts to address water pollution resulted in the adoption of two directives in 1991: The Urban Wastewater Treatment Directive (91/271/EEC), which addressed water pollution from all settlements but the small villages, as well as a range of industries with biodegradable wastewater; and the Nitrates Directive (91/676/EEC) which aimed to reduce water pollution by nitrates from agriculture (Blöch, 2001).

In 1991 the Ministerial Seminar on Groundwater held in the Hague called for action to avoid long-term deterioration of the quantity and quality of freshwater resources in the EU. An action program on the integrated protection and management of groundwater was adopted by the European Commission in 1996 pointing out the need for monitoring of freshwater quality and quantity, and control of abstraction. It took a decade-long planning and more than 5 years of discussions and negotiations to agree on the most comprehensive European water legislation – a milestone in the modern history of water policies in Europe. The Water Framework Directive (WFD) (Directive 2000/60/EC) came into force on December 22, 2000, and established a framework for Community action in the field of water policies for all EU member states replacing the previously fragmented water legislation. The WFD "absorbed" more than 12 directives of the 1970s and 1980s, which were later repealed. The concept of groundwater tackled by different pieces of legislation was now fully integrated into the basic measures of the WFD (European Commission, 2007; Quevauviller et al., 2011; Rejman, 2007). For the first time groundwater became a part of an integrated water management system, and, in addition to protecting groundwater as a resource with multiple uses, WFD established that groundwater should be protected for its environmental value as well (European Commission, 2008).

The main goals of the WFD are outlined in Article 4 of the directive. The EU member states are required to protect clean water bodies and, where necessary, restore water bodies to reach good status and to prevent any deterioration of dependent ecosystems. The River Basin Management Plans (RBMPs) and Programme of Measures (PoMs) are the key tools for the WFD implementation and are drawn up after extensive public consultation and are valid for six years. The WFD introduces many innovative concepts into a binding regulatory instrument. The holistic approach expands the scope of water protection to all waters (groundwater, rivers, lakes, and coastal water) and fosters cooperation across borders by making it mandatory (at least for EU member states). Public participation is strengthened through a compulsory public consultation process (usually at least 6 months long) to ensure the active involvement of all businesses, farmers, environmental NGOs, and local communities in the planning process of managing river basin districts (RBD). Finally, the WFD has clear goals to be accomplished within a limited timeframe – to achieve good status for all waters by a set deadline of 15 years (with possible extensions by 2027) while leaving flexibility to member states on how to achieve the goals cost-effectively (European Commission, 2007; Quevauviller et al., 2011).

Maia (2017) effectively summarizes the WFD implementation process as (1) transposition and administrative arrangements; (2) characterization of river basin districts; (3) monitoring and assessment of water bodies; (4) setting of objectives and (5) programme of measures and implementation. The European Commission assesses the implementation progress and currently, there are already six implementation reports published according to major milestones in 2007, 2009, 2012, 2015, 2019, and 2021 (Implementation Reports, n.d.). It should be highlighted that all key milestones of the WFD implementation presented in Table 2 include groundwater as one of the components.

Table 2. Milestones of the Water Framework Directive (2000/60/EC) implementation for EU member states.

<table>
<tr><th></th><th>Actions to be carried out</th><th>Reference in the directive</th><th>Deadline</th></tr>
<tr><td>1</td><td>Set up of administrative structures (river basin districts) and identification of competent authorities, transposition of the directive into national legislation</td><td>Articles 3, 24</td><td>2003</td></tr>
<tr><td>2</td><td>Characterization of river basin districts (pressures, impacts and economic analysis), including a register of protected areas</td><td>Articles 5, 6, Annex II, III</td><td>2004</td></tr>
<tr><td>3</td><td>Establishments of monitoring networks and start of the public consultation process</td><td>Article 8, 14</td><td>2006</td></tr>
<tr><td>4</td><td>Presentation of draft 1st River Basin Management Plans to the public</td><td>Articles 13, 14</td><td>2008</td></tr>
<tr><td>5</td><td>Final 1st River Basin Management Plans, including Programme of Measures developed on appropriate monitoring and characterization of river basin districts</td><td>Articles 13, 11, Annex III</td><td>2009</td></tr>
<tr><td>6</td><td>Introduction of pricing policies</td><td>Article 9</td><td>2010</td></tr>
<tr><td>7</td><td>Making the Programme of Measure operational</td><td>Article 11</td><td>2012</td></tr>
<tr><td>8</td><td>Implementation of Programme of Measures and meeting of environmental objectives, end of the first management cycle, public consultation and final 2nd River Basin Management Plans</td><td>Article 4</td><td>2015</td></tr>
<tr><td>9</td><td>Public consultation and final 3rd River Basin Management Plans, second management cycle ends</td><td rowspan="3">Articles 4 and 13</td><td>2021</td></tr>
<tr><td>10</td><td>The third management cycle and last extension of deadlines end</td><td>2027</td></tr>
<tr><td>11</td><td>Revision of River Basin Management Plans every six years</td><td>2033…</td></tr>
</table>

After the set up of RBDs (in Latvia being Gauja, Daugava, Lielupe, and Venta), the member states had to carry out impacts and pressures analysis to identify major risks of not meeting objectives of good status. For groundwater, the impacts and pressures analysis start with the initial characterization process that relies on the proposed Driver–Pressure–State–Impact–Response (DPSIR) methodology/principle that should develop a conceptual understanding of the hydrological system. DPSIR approach has been extensively used in the framework of integrated groundwater resources management within the EU (Bagordo et al., 2016; Mattas et al., 2014) and outside (Ahmad & Al-Ghouti, 2020; Jia et al., 2019).

To carry out the initial characterization first the member states must delineate groundwater bodies (GWBs) within which the information on aquifer characteristics and vulnerability, dominant pressures (point and diffuse pollution sources, abstraction/recharge), and identified groundwater dependent ecosystems (GDEs) should be reported. The WFD introduces a new term "groundwater body" (GWB) within which effective and sustainable groundwater management shall be carried out and progress reported (European Commission, 2003b). GWB is a reporting unit set to estimate its quantitative and chemical status, and to which environmental objectives under Article 4 of the WFD directive should apply. GWB body is defined as "a distinct volume of groundwater within an aquifer or aquifers" and should be delineated in such a way as to ensure proper status assessment and monitoring, effective management, and future treatment (Kovács et al., 2012; Rejman, 2007). As pointed out by Sánchez et al. (2009) the definition of GWB in WFD does not provide a clear and practical application of the term. Even though practical suggestions for GWB identification under the WFD have been created (European Commission, 2003b), varying environmental conditions and the large heterogeneity of European aquifers makes it difficult to unify the water management process (Rejman, 2007). The final number of GWBs and their sizes vary significantly between Member States and depend on the chosen delineation approach (European Commission, 2004). According to the published 2nd RBMPs (WISE, 2018) Luxembourg, Malta, and Latvia had the smallest number of GWBs, respectively, six, fifteen, and sixteen. In 2018 the boundaries of the initial 16 GWBs in Latvia were reviewed based on the modeling results for the Baltic Artesian Basin (Virbulis et al., 2013) and the number of bodies increased to 25 (Bikše & Retike, 2018).

Following the initial characterization and the application of the DPSIR framework member states shall carry out further characterization for GWBs having transboundary nature (significant groundwater flows across the borders) or identified as being at risk of not meeting WFD's objectives. Characterization and risk assessment process shall provide the basis for the establishment of representative groundwater monitoring networks which in turn shall collect information to provide a comprehensive overview of the GWB chemical and quantitative status.

Finally, the Programs of Measures (PoMs) should be composed and adopted by member states to achieve the environmental objectives of the WFD – good quantitative and chemical status of groundwater bodies. The basic measures are mandatory and can be summarized as a minimum set of requirements to ensure overall good GWB status, e.g., control of groundwater abstraction and pollutants inputs. Supplementary measures (e.g., codes of good practices, remediation, or research activities) can be implemented in addition to basic measures and also included in the final list of PoMs adopted by member states.

All groundwater bodies must achieve good quantitative and chemical status. While the objectives of the quantitative groundwater status are straightforward, namely, to ensure a balance between groundwater abstraction and recharge, the criteria for the chemical status are more complex. Thus, on December 12, 2006, Groundwater Directive (GWD) (2006/118/EC), or the so-called "daughter" directive was adopted to clarify criteria for good chemical status and lay down additional technical specifications for the establishment of national quality standards called "threshold values" (Hinsby et al., 2008; Quevauviller et al., 2011). As highlighted by the European Commission (2008), the GWD represents a scientifically sound response to the requirements of the WFD. Complementing the WFD, the GWD requires member states to establish threshold values (TVs), study pollution trends (identify and reverse the significant upward pollution trends), and introduce measures to prevent and limit inputs of pollutants into groundwater.

The Common Implementation Strategy (CIS) was launched in 2001 to support the implementation of the core legislation of the WFD at EU level and in associated countries. The CIS Groundwater working group is one of the six working groups (Groundwater, Floods, Chemicals, Ecological Status, Data and Information Sharing, Water Reuse) developed to address specific aspects of the WFD by exchange of best practices and by boosting mutual learning among stakeholders. The working groups may produce non-binding guidance documents and technical reports (e.g., European Commission 2003a, b, 2004, 2009) to assist stakeholders with the implementation process by providing an overall methodological approach that further needs to be adapted for each specific case. The thematic documents of CIS are stored in the open access platform CIRCABC – Communication and Information Resource Centre for Administrators, Businesses and Citizens (Maia, 2017).

1.1.1. Groundwater status assessment

A set of relevant classification tests should be applied (Figure 1) to assess the overall status of identified GWBs at risk. There are nine classification tests (five chemical and four quantitative) each designed to address specific aspects of groundwater protection to fulfil the environmental objectives of the WFD. The worst-case classification from any test is reported as the overall status. In addition, the weight of evidence should be set for the final assessment in the form of a high or low confidence level. If the assessment is made with a limited amount or missing monitoring data, the confidence is usually reported as low. The status assessment is performed at the end of the RBMP period to reflect the effectiveness of the PoMs and is carried out using monitoring data collected during the period of RBMP (European Commission, 2009).

The final assessment of the quantitative and chemical status of a GWB is a multistage and complex task. If all the conditions set out in Table 2.3.2 of Annex V of the WFD (Directive 2000/60/EC) are met, the chemical status of a GWB is good. Similarly, if all conditions of the WFD set in Annex V 2.1.2 are met, the GWB is in good quantitative status. In short, the groundwater abstraction should not exceed the available groundwater resources and the chemical composition of a GWB should not be worsening. Moreover, GWB status should not harm any of the environmental or usage criteria.

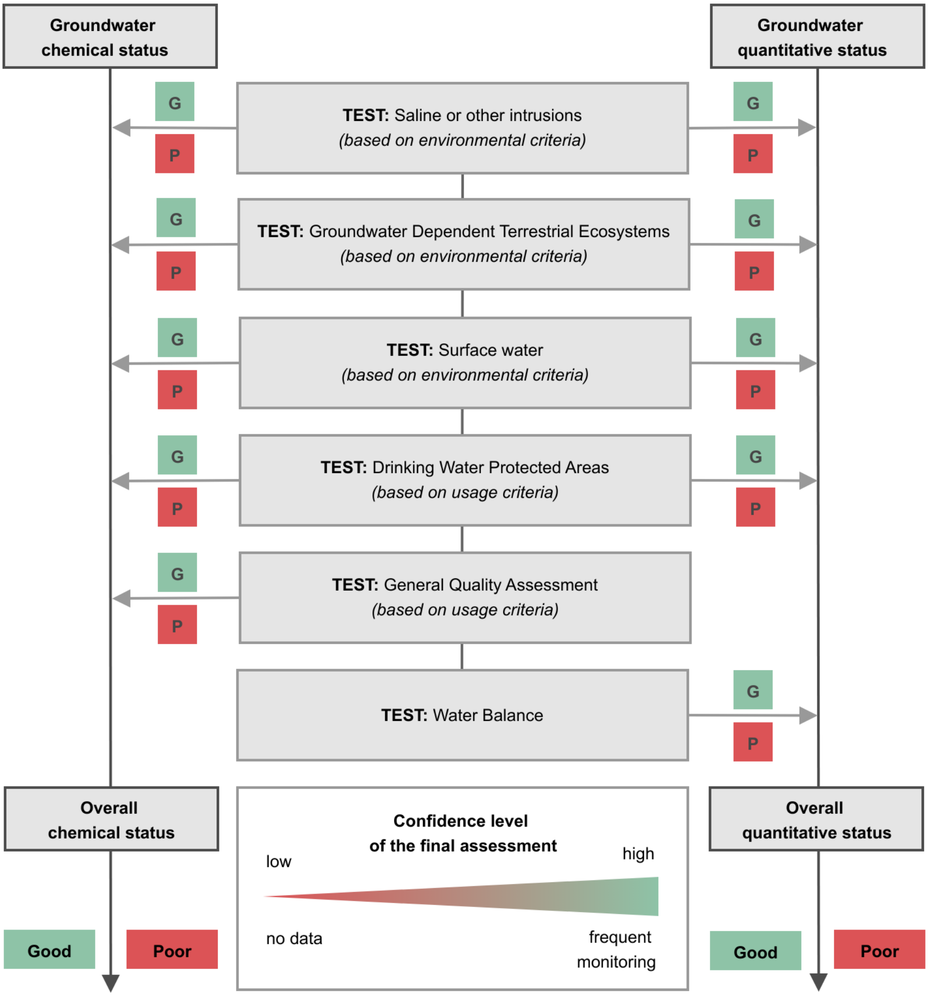

Figure 1. Overview of the groundwater body chemical and quantitative status assessment process and classification tests (modified after European Commission, 2009).

Different processes can cause aquifer salinization and have been discussed within the literature for both coastal and non-costal aquifers (Greene et al., 2016; Marandi & Karro, 2008). The "Saline and other intrusions" test (see Figure 1) refers to a variety of intrusion types with the most common being coastal aquifer salinization and salt-water upconing. First, the quantitative status assessment test should identify areas of intensive groundwater pumping that pose a risk for saline water intrusions. Then, the chemical status test should clarify if threshold values (TVs) are exceeded and anthropogenically increased salinity can be observed. The minimum list of parameters indicative of saline or other intrusions that should be considered in the TV derivation process includes specific electrical conductivity (SEC), sulfates (SO_4^{2-}), and chlorides (Cl^-). It is worth mentioning that aquifers with naturally elevated groundwater salinity are not addressed by this test, therefore aquifer geochemistry should be evaluated in advance – during the initial characterization process (Directive 2006/118/EC; European Commission, 2009).

According to the WFD, a GWB is considered to be in poor status if pressure on groundwater causes significant damage to the related groundwater dependent ecosystem (GDE). GDEs are ecosystems that rely on groundwater supply and a change in groundwater chemical composition or groundwater discharge rate can deteriorate the quality of such ecosystems. GDEs are of high value as they provide habitat for endangered species, support high biodiversity, and provide valuable ecosystem services like water purification, CO_2 capture, or recreation. They are further subdivided into groundwater dependent terrestrial ecosystems (GDTEs) comprising springs and fens, and groundwater associated aquatic ecosystems (GAAEs), namely rivers and lakes (Kløve et al., 2011; Terasmaa et al., 2020), and additionally sinkholes in case of Latvia. The ”Surface water” test assesses the groundwater impacts on surface water bodies or GAAEs, while the “Groundwater Dependent Terrestrial Ecosystems” test mainly addresses wetlands.

The “Drinking Water Protected Areas (DWPAs)” test assesses the deterioration of groundwater aimed for human consumption. According to WFD Article 7.3 (Directive 2000/60/EC), the GWBs identified as DWPAs should aim to avoid deterioration of their quality to reduce the level of purification needed to produce drinking water. Often specific protection measures are focused on the safeguard zones of groundwater abstraction sites (European Commission, 2009). In Latvia, all GWBs are designated as DWPAs as the groundwater in general is used or can be used as the drinking water source (Retike et al., 2016a).

The general assessment of the chemical status of the GWB as a whole is carried out within the “General Quality Assessment” test. It means that good chemical status is met if the ability of GWB to support human uses is not significantly impaired by pollution and that the concentrations of pollutants exceeding the groundwater quality standards or TVs do not present a significant environmental risk (Directive 2006/118/EC). An area criterion is often applied, e.g., if exceedance affects less than 20% of the area (proportion of the total area or volume of the GWB) the whole GWB is not considered as being at poor status (European Commission, 2009).

“The Water Balance” test aims to assess if long-term groundwater abstraction does not exceed aquifer replenishment minus the long-term ecological flow needs. The assessment of groundwater level time series can indicate declining trends, while the results are not always straightforward and the assessment should not rely only on the analysis of groundwater levels (Retike et al., 2022). The water balance test must compare the annual average groundwater abstraction against available groundwater resources using the best available estimates, e.g., calculations from hydrogeological models (European Commission, 2009).

1.1.2. Groundwater quality standards

The EU WFD (Directive 2000/60/EC) and GWD (Directive 2006/118/EC) require member states to evaluate the chemical status of GWBs against EU-wide quality standards for nitrates (NO_3^-, 50 mg/L) and pesticides, for individual 0.1 μg/L and total – 0.5 μg/L (meaning the sum of all individual pesticides detected and quantified in the monitoring procedure, including their relevant metabolites, degradation and reaction products). These standards are uniform with other EU environmental regulations such as the Nitrates Directive (Directive 91/676/EEC), Regulation 1107/2009 concerning the placing of plant protection products on the market, and Regulation 528/2012 concerning the placing on the market and use of biocidal products (Scheidleder & Bogaert, 2022).

The member states are obliged to establish stricter quality standards for NO_3^- and pesticides or establish them for additional pollutants if there is a risk of GWB failing to achieve good groundwater chemical status. Threshold values (TVs) are groundwater quality standards for pollutants set by the individual member states to ensure compliance with the definition of a good chemical status and protection of groundwater dependent ecosystems (both terrestrial and aquatic). The national authorities usually derive TVs as the basis for GWB status assessment (Voutchkova et al., 2021) and use them as criteria to test whether GWB is at good status (Bulut et al., 2020; De Caro et al., 2017). TVs may be used as part of the criteria for the identification of upward trends (worsening of the status) or the starting point for trend reversal and status improvement (Hinsby et al., 2008). Member states are required to publish the established TVs in each River Basin Management Plan as a single value per substance or indicator, or a range of the highest and lowest applied values (Scheidleder, 2012).

TVs must be established for all pollutants and indicators of pollution which have characterized GWB as being at risk of failing to achieve good groundwater chemical status. The general procedure for the establishment of TVs is set in Part A of Annex II of the GWD, while more details can be found in supporting guidance documents (European Commission, 2009). In summary, the TVs should ensure the protection of not only the GWB itself but also human health and the dependent environment (GDEs and GAAEs) (Hinsby et al., 2008). Even though TVs should be based on a variety of interactions and processes, such as interaction with GDEs or interference with actual and intended legitimate uses of groundwater, in practice TVs derived by member states consider national drinking water standards, natural background levels, and sometimes also environmental water quality standards (De Caro et al., 2017; Scheidleder, 2012). TVs can be derived at the national, river basin district (or part of the international district) or GWB (also a group of GWBs) level but should be coordinated in case of shared or transboundary GWBs.

The provisions of GWD on the chemical status of a GWB only apply to anthropogenically altered conditions, thus a fundamental first step in establishing TVs is to derive natural background levels (NBLs). Article 2.5 of the GWD defines NBLs as a concentration of a substance or the values of an indicator in a GWB corresponding to no or minor anthropogenic alterations. Thus, NBLs should be derived only for substances that can naturally occur in a range of concentrations at different hydrogeological conditions (Voutchkova et al., 2021) meaning that NBLs for synthetic substances are automatically set as zero (Müller et al., 2006).

It is important to distinguish between NBLs and the term "baseline level" which are mistakenly used as synonyms. Baseline groundwater quality refers to the range of concentrations derived from entirely natural conditions (Edmunds & Shand, 2008), while NBLs can include minor anthropogenic influences and are set as a single value necessary to derive TVs (Voutchkova et al., 2021). Identification of baseline groundwater characteristics can rely on various approaches such as the use of historical data describing pre-historical or uninfluenced conditions, extrapolation from adjacent areas having a similar geological condition, geochemical modeling, and others (Edmunds & Shand 2008; Voutchkova et al., 2021).

Apelo and Postma (2005) summarize that the hydrochemical characteristics of groundwater are determined by the complex interactions occurring between water, minerals and gases, along the path from recharge to the discharge areas. Such natural factors as climate, rainfall composition and frequency, biochemical processes in the unsaturated zone, water-rock interaction and residence time, as well as mixing contribute to the presence (or absence) of various substances in groundwater (Edmunds & Shand, 2008; Retike et al., 2016b; Sellerino et al., 2019). In addition to natural factors, human activities may also affect groundwater quality. While the occurrence of some substances in groundwater such as pesticides is a direct indicator of human impact, inorganic components (i.e., trace metals) or biogenic elements like NO_3^- and NH_4^+ may originate from both natural and anthropogenic sources (Biddau et al., 2017; Retike et al., 2016b). Urresti-Estala et al. (2013) highlight that a large number of factors responsible for the final groundwater composition means that differentiation between natural processes and human-induced changes is a highly challenging, if possible at all, task accompanied by many errors and uncertainties. Each member state is free to choose the approach how to identify NBLs while the majority (e.g., De Caro et al., 2017; Marandi & Karro, 2008; Pulido-Velazquez et al., 2022; Retike & Bikše, 2018; Sellerino et al., 2019; Vencelides et al., 2010; Wendland et al., 2008) follow the BRIDGE (Müller et al., 2006) methodology (for details see Section 2.5.).

1.1.3. Links with other directives and Water Convention

Groundwater protection has been tackled in a variety of other directives most of which (at least in their initial form) were adopted before the Water Framework Directive (WFD) (Directive 2000/60/EC) and Groundwater Directive (GWD) (Directive 2006/118/EC) came into force. They all contain different instruments which aim to prevent or limit pollutant inputs into the groundwater and are directly or indirectly linked to the WFD or the Groundwater directive (European Commission, 2008). Figure 2 highlights key legal instruments and sectors, as well as DPSIR methodology elements forming the framework of integrated groundwater resources management.

The Nitrates Directive (Directive 91/676/EEC) is the key instrument in Europe in the protection of water against agricultural pressures. It aims to reduce surface and groundwater pollution caused by nitrates used in agriculture and sets out certain steps to be taken by EU member states. Designation of nitrate vulnerable zones (NVZs) is probably one of the major decisions each country must make. Those are areas where NO_3^- concentrations in groundwater (irrespective of its intended use) exceed or are likely to exceed 50 mg/L if no measures are taken (European Commission, 2008). Areas included into NVZs must follow certain rules such as limiting the application of N fertilizers and establishing mandatory action programs which in turn may negatively influence agricultural activities (Kalvāns et al., 2021). Reducing nitrates is an integral part of WFD, and GWD confirms that NO_3^- concentrations in groundwater should not exceed 50 mg/L to reach good chemical status. Action programmes under the Nitrates Directive are one of the basic measures of the WFD and a mechanism for NO_3^- pollution trend reversal under GWD (European Commission, 2008).

The Urban Waste Water Treatment Directive (91/271/EEC) gives the framework for the development of the European wastewater treatment system (Pistocchi et al., 2019) and for the first time in a comprehensive way considered nutrients. It aims to protect the water environment from the adverse effects of discharges of urban wastewater and certain industrial discharges. Member states are required to designate "sensitive areas" which relate to freshwater, estuaries or coastal waters found to be eutrophic or that may become eutrophic soon if no protective actions are taken; surface freshwaters intended for drinking water that contains or is likely to contain nitrates more than 50 mg/L; and areas where further treatment is necessary to comply with other directives. Links with groundwater can be found through obligations to prevent or limit inputs of pollutants into groundwater from potentially contaminated waste waters originating from freshwater sources (Quevauviller, 2005; Quevauviller et al. 2011).

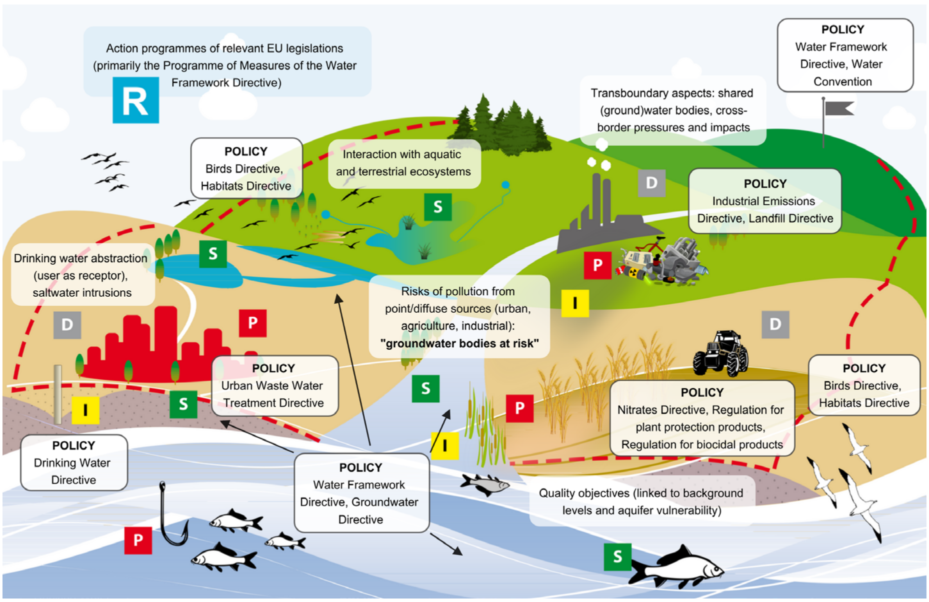

Figure 2. Legal instruments and sectors that are directly or indirectly related to groundwater protection (not exhaustive). "DPSIR" methodology is indicated as D – drivers, P – pressures, S – status, I – impacts, and R – responses (modified after European Commission, 2009).

The Drinking Water Directive (DWD) (98/83/EC) was first adopted in 1998 and has been replaced by the revised one (2020/2184) that entered into force in 2021. The directive concerns the quality of water intended for human consumption and aims to protect human health and ensure that the water used for drinking is wholesome and clean. The directive sets the standard for nitrate in potable water at 50 mg/L and it applies to all distribution systems serving more than 50 people or supplying more than 10 m^3 per day (not exclusive). Under the WFD such sites had to be identified already during the GWB delineation process (Rejman, 2007) and according to Article 7 of the directive all GWBs, in addition, must meet the requirements of the DWD. The linkage with the WFD is expected to increase soon with the revised DWD. Member States now have to transpose it into national legislation by 2027. Introduction of the risk-based approach that requires an in-depth analysis of the whole water cycle from sources to distribution and monitoring of new parameters (emerging pollutants such as endocrine disruptors, Per- and Polyfluorinated substances (PFA's), and microplastics) are the major changes tackling groundwater aspects. The planned activities to promote tap water consumption might have an indirect influence as well.

The Plant Protection Directive 91/414/EEC (repealed by Regulation 1107/2009) and the Biocides Directive 98/8/EC (repealed by Regulation 528/2012) concern the authorization, marketing, use and control of commercial plant protection and biocidal products such as pesticides, fungicides or herbicides within the EU. Authorization of such products is granted only if they have no harmful effect on human health and groundwater (European Commission, 2008). The GWD in Annex I sets maximum permissible concentrations for active substances in pesticides which means plant production products and biocidal products.

The Industrial Emissions Directive (2010/75/EU) aims to minimize air, water and ground pollution from various industrial sources in the EU. The directive applies to various, mainly industrial activities with a high pollution potential (e.g., energy sector, mineral and chemical industries and waste management facilities) and non-industrial activities such as livestock farming. It establishes terms for issuing permits for existing and new installations which include requirements to protect soils and groundwater and set emission limits for pollutants. Measures required under the directive are also a part of the basic measures of the WFD (Annex VI) (Quevauviller et al., 2011).

The Landfill Directive (1999/31/EC) seeks to reduce the negative effects of landfill waste on the environment, including groundwater. It establishes provisions for issuing permits that are based on a range of conditions including impact assessment and is also a part of the basic measures under the WFD (Annex VI). Hydrogeological conditions must be determined for each site and the site itself must be designed in a way to prevent pollution of soil, groundwater and surface water (European Commission, 2008).

The Waste Framework Directive (2008/98/EC) is a central coordination measure for EU waste legislation. It requires waste to be recovered or disposed of without harming the environment without risk to water, air and soil, thus having an indirect link to the groundwater legislation framework (European Commission, 2008).

The Birds Directive (2009/147/EC) and the Habitats Directive (92/43/EEC) protect the most valuable species and habitats in Europe, thus forming a backbone of the EU biodiversity policy. The protected areas designated under these so-called EU nature directives are included in the Natura 2000 network set up under the Habitats Directive. The WFD, GWD and Habitats directives all aim to ensure healthy ecosystems and maintain the balance between water/nature protection and sustainable use of natural resources, but the nexus between directives is often neglected. The synergy between nature and groundwater is clearly stated in the WFD's Article 1 which aims to protect groundwater, which in turn prevents further deterioration and protects and enhances the status of aquatic ecosystems (GAAEs), and regarding their water needs, terrestrial ecosystems and wetlands directly depending on them (GDTEs). Article 6.1 of the WFD stipulates the establishment of a protected areas register which shall include all areas designated for the conservation of species and habitats directly depending on water, and the types of protected areas are covered by Annex IV. It is up to member states to decide which additional areas if any (besides Natura 2000 sites) to include in the register to ensure the protection of water-dependent species and habitats (Schmedtje et al., 2011). The GWD's Article 3 requires that threshold values (TVs) applicable to good chemical status shall be based not only on the protection of groundwater itself but also considering the needs of associated surface waters and directly dependent terrestrial ecosystems and wetlands. Moreover, Article 5 stipulates that member states must reverse trends of pollutants that may harm groundwater dependent ecosystems. In the last decade, the number of studies on GDEs has significantly increased and while the emphasis has been put on GDEs protection (Kløve et al., 2011; Rohde et al., 2011) hydrogeological aspects are incorporated more often (Kalvāns et al., 2021, Koit et al., 2021; Terasmaa et al., 2020).

The Water Convention or "Convention on the protection and use of transboundary watercourses and international lakes" (UNECE, 1992, 2013) is a legally binding instrument and intergovernmental platform that aims to ensure sustainable use of shared surface water and groundwater resources by facilitating transboundary cooperation. Initially planned as a pan-European instrument it has been opened up for accession to all UN Member States since 2016. The similarities between the WFD and the Water Convention are large – both aim to promote sustainable usage of water resources, require establishing common water bodies, and carry out joint management actions (Flem et al., 2022). Convention directly supports the implementation of Sustainable Development Goals, mainly target 6.5. The first and second reporting exercises under the Convention were held in 2017/2018 and 2020/2021 (UNECE, 2021). However, the Convention addresses only transboundary waters or aquifers in the case of groundwater if compared to the WFD. Even though the aims of the EU WFD and the Water Convention are overlapping the understanding of "transboundary" groundwater differs leading to spatially different reporting units. As reported by Terasmaa et al. (2020) more collaboration between water managing authorities, policymakers, and researchers should be initiated to develop a joint understanding of transboundary aquifers thus fostering the monitoring and assessment of shared groundwater resources.

1.2. Evolution of systematic groundwater monitoring in Latvia

The first systematic groundwater observations in the territory of Latvia can be dated back to the end of the 19th century, still, they were local and monitoring initiatives were short-term. At the beginning of the 20th century, the detail and extent of groundwater studies were advanced, while in the middle of 20th century groundwater investigations covered all three water exchange zones (Dēliņa, 2006).

The establishment of a systematic groundwater monitoring network started in 1953 with the first regular observations performed since 1959. At first, the monitoring network consisted of a few dozen wells, most of which were installed in unconfined aquifers. The observations were settled around Riga and Jelgava, as well as Baldone and Kemeri resorts (Juodkazis, 1994). Soon, the network expanded due to the rapid establishment of new well fields around the largest cities along with the extensive installation of piezometers to monitor the rise of water levels near newly built hydropower plants (HPPs) "Plavinas" in the 1960s and "Riga" in 1970s

(Jankins et al., 1993; Juodkazis, 1994; Levina & Levins, 1994). In the later years, the increased knowledge about groundwater formation contributed to an expansion of the groundwater monitoring network around the entire country. Monitoring included regular groundwater level and temperature observations, water sampling for chemistry (major ions and nitrogen compounds) analyses, and even soil moisture measurements (Levins et al., 1998). At the beginning of the 1970s about 130 new wells were installed with the primary aim to study the causes of permanently waterlogged soil conditions in agricultural lands (Jankins et al., 1993).

From 1976 the groundwater monitoring network had two principal branches – regional and local. Regional networks were developed based on the known hydrodynamic properties of large-scale groundwater systems and major pressures to monitor natural and disturbed conditions. Regional networks consisted of monitoring stations (nested wells) installed in transects following groundwater flow lines from recharge to discharge areas and each station had wells with screens at multiple depths to observe water exchange between aquifers. An emphasis was put on monitoring of Riga, Jurmala, and Liepaja vicinities where it was known that overexploitation of aquifers has formed depression cones and deteriorated groundwater quality. Yet, local observation networks were designed in a way to focus on areas strongly influenced by human activities. These were territories near (1) largest groundwater abstraction sites with high potential to aquifer overexploitation, (2) engineering infrastructure objects (e.g., HPPs, open-pit mines, amelioration areas) that disrupt natural water level conditions and may activate surface-groundwater interaction, and (3) heavily contaminated sites that pose a risk to the closest surface water bodies and deeper aquifers used for drinking water supply. Also, water monitoring networks for water balance studies were established in Vienziemite and Maza Jugla river basins to gather data about soil moisture, surface water, unconfined groundwater, and temperature dynamics. Monitoring was carried out for the internationally coordinated hydrological research programme, nowadays – Intergovernmental Hydrological Programme (UNESCO-IHP) (Jankins et al., 1993).

The first optimization of the national groundwater monitoring network took place between 1992 and 1993 after the collapse of the Soviet Union and the subsequent decrease in funding. Thus, several wells were removed from the groundwater monitoring network and overall observation frequency and spatial coverage decreased (Jankins et al., 1993). The wells with poor technical status or insufficient representativity were eliminated first. Also, the local monitoring near open mine pits and polluted sites was canceled (Levina et al., 1995).

In 1993 groundwater sampling techniques significantly improved and approached those to be used today. First, centrifugal pumps (Grundfos) were introduced which prevented aeration and degasification of water during the sampling. Previously a portable grab sampler or bailer was used for retrieving groundwater samples from monitoring wells. Second, the wells were purged before sampling (Jankins et al., 1993). Purging removed stagnant water from a well and caused its replacement by groundwater from an adjacent formation that represents actual aquifer conditions. Water standing in a well for a longer period undergoes changes that can affect water's chemical composition. The changes can impact several parameters including but not limited to pH, alkalinity, hardness, the concentrations of metals, sulfates, total dissolved solids, and dissolved oxygen (OSMRE, 2012). Usually, purging a monitoring well up to two well volumes was considered sufficient. Sample for chemical analyses was taken after stabilization of field parameters – *pH*, specific electrical conductivity (SEC), and temperature (Jankins et al., 1993).

From 1993 until 1998 groundwater chemical monitoring already included a long list of parameters that could vary from year to year: field parameters (temperature, *pH*, SEC), major ions, nitrogen compounds (N/NO_3^-, N/NO_2^-, N/NH_4^+, N_{kop}), color, water hardness, P/PO_4^{3-}, Fe_{tot}, permanganate index, Chemical Oxygen Demand (COD), trace elements (Mn, Zn, Cu, Ni, Pb, Hg).

Until 2002 annual qualitative groundwater monitoring was carried out on a regional basis due to limited funding. Primarily, qualitative monitoring was continued in the territory of Riga and Liepaja to control the development of large-scale depression cones (1993–1996). Secondly, wells with long-time series and monitoring stations having wells with screens at multiple depths were retained (Jankins et al., 1993; Levina & Levins, 1994, 1996, 1997). In addition to Liepāja, in 1997 chemical monitoring was also carried out in the Eastern part of Latvia (Levina et al., 1998), while in 1998 and 2000 in Western and Central parts of Latvia (Levina & Levins, 1999, 2001) in 1999 in Vidzeme (Levina & Levins, 2000), and in 2001 in Eastern and Central parts of Latvia (Levina & Levins, 2002). In 2002 the spatial coverage of groundwater qualitative monitoring almost covered the whole country, except for the northeastern part of Latvia (Levina & Levins, 2003).

During the second inventory (1997–1999) about one-third of the tested wells were found to be in poor status due to clogging, well screen failure, or physical damage. Many wells were installed on private lands leading to conflicts with landowners due to the lack of regulatory legislation. Consequently, access to wells was denied or they were removed by the landowners without proper well plugging (Levina & Levins, 2000). Meanwhile, in 1997 the first digital groundwater database "Groundwater monitoring" was established and continuously improved in the following years by adding historical and actual observations by the State Geological Survey and its successor Latvian Environment, Geology and Meteorology Centre (LEGMC). The database contained groundwater chemistry and level records from 1959 and was developed during a transnational cooperation project with Denmark, which also resulted in sampling and data handling improvements. First, wells having low yields (< 0.1 L/s) were sampled with a smaller pump. Second, field parameters (*pH*, temperature and SEC) were continuously measured during the pumping using WTW multiparameter meters. Then, samples for iron analysis were passed through a 0.45 μm pore diameter filter and acidified to *pH* < 1.5. Finally, the accuracy of water analyses was validated with a ionic balance error (± 10%). Since 1998 total iron (Fe_{tot}) and dissolved oxygen (O_2) has been measured in field conditions (Levina et al., 1998).

The first state groundwater monitoring program was prepared in 1999. Until then the monitoring was continued based on a praxis developed during the Soviet times and without clear objectives and sufficient funding. In 1999 Latvia became a candidate for EU membership, thus the first groundwater monitoring program already tackled recommendations of EU water policies at that time (Levina & Levins, 2000, 2001). Following that, the available funding for groundwater monitoring rapidly increased and its harmonization with the requirements of the Water Framework Directive (Directive 2000/60/EC) and Nitrates Directive (Directive 91/676/EEC), later also with the Groundwater Directive (Directive 2006/118/EC), was started (Retike et al., 2022).

From 2000 groundwater monitoring had two new monitoring types – resource assessment monitoring and specialized monitoring. First one had to provide necessary data for the assessment of groundwater recharge (water balance), and identification of natural and disturbed groundwater level changes at the regional scale. While specialized groundwater monitoring concentrated on the assessment of aquifers near highly populated areas and HPPs (Levina & Levins, 2002). In 2002 the laboratory which had tested groundwater samples since 1995 was changed to the new one which was accredited according to ISO standards. During the laboratory intercalibration, it was identified that the previous laboratory systematically reported around 10–20% lower results for ammonium (Levina & Levins, 2003). However, the results for total nitrogen (TN) delivered by the new laboratory were reported as poor (too low detection limit) until 2003 when TN was determined by alkaline persulfate digestion technique (Levina & Levins, 2004). This is the period when two high-importance hydrogeological databases were merged – database "Groundwater monitoring" representing observations from the national monitoring network and database "Urbumi" holding data mainly about water supply wells (Levina & Levins, 2003). In 2004 thirty (30) springs were included in the national groundwater quality monitoring network to assess the impact of land use and diffuse pollution (Levina & Levins, 2005; Terasmaa et al., 2020). In 2000 the following parameters were measured during the groundwater chemical monitoring: field parameters (temperature, *pH*, SEC, O_2, Fe_{tot}, ORP), major ions, nitrogen compounds (N/NO_3^-, N/NO_2^-, N/NH_4^+, N_{kop}), water hardness, P_{tot}, P/PO_4^{3-}, Chemical Oxygen Demand (COD). Since 2003 additionally, TOC, and ultraviolet radiation A (UVA) were added.

After Latvia entered the EU in 2004 planning of groundwater monitoring programs became periodic. The first monitoring program covered three years (2006–2008) since it had to deliver necessary data for the River Basin Management Plans (RBMPs) in 2009. The second and third monitoring programs were already developed for six-year periods, respectively 2009–2014 and 2015–2020, and matched reporting deadlines of the second and third management cycles of the WFD. Also, in 2008 Latvia had to produce the first four-year report on the implementation of the Nitrates Directive.

The structure of groundwater monitoring programs for the period 2006–2008 was similar to nowadays. It aimed to provide missing data for the initial characterization of groundwater bodies (GWBs) and the improvement of monitoring networks. Technically, it included all key elements of the WFD, GWD and Nitrates Directive, but practically had many drawbacks. For instance, operational monitoring was not carried out due to missing knowledge of dominant pressures on GWBs. Also, monitoring in DWPAs was performed only in surface water bodies that supplied more than 30 000 inhabitants (Daugava and Mazais Baltezers), even though groundwater was and remains the main drinking water source in Latvia (Kitterød et al., 2022). The list of chemical parameters included all major ions and nitrogen compounds, as well as TOC and UV absorption, while *pH*, ORP, O_2, SEC and Fe_{tot} were measured in field conditions. Groundwater levels were measured manually once in the quarter up to twice a week. Major obstacles that delayed the implementation of EU requirements and had to be addressed soon, were technical issues (poor status of wells, imprecise coordinates, and well head records, lack of automatic level measurements) and legislative issues (groundwater monitoring stations and their safeguard zones were not protected by any legal acts). The need for a hydrogeological model at the country scale was highlighted to carry out the Water Balance test (Figure 1) (VMP, 2005).

In 2005 three new monitoring stations (Vecauce, Jaunberze and Mellupite) with 10 shallow wells were installed in the southwestern part of Latvia to monitor diffuse agricultural pressures and deliver necessary data for the implementation of the Nitrates Directive. This was partly an outcome of a cooperation project between Latvia and Denmark (VMP, 2005) and can be dated as the start of groundwater agricultural runoff monitoring organized to support the implementation of the EU water policies in Latvia. The assessment results can be found in the four-yearly reports of the Nitrates Directive (Nitrates Report, 2020). Up to now, the monitoring is carried out and the network is maintained by the Latvian University of Life Sciences and Technologies.

During the modernization of the groundwater monitoring network from 2010 to 2012, 24 new monitoring wells were installed, and 87 existing ones were equipped with automatic level loggers (LEGMC, 2013). This entirely changed the way quantitative monitoring was carried out. Up to that time groundwater levels were measured manually, and observation frequency ranged from one to three times a month for regional scale monitoring and up to 8 times a month for local observation networks. From 2010 groundwater levels in wells having automatic level loggers were measured twice a day and manual control measurements were carried out two to four times a year during data downloads (Retike et al., 2022).

The main objectives of the groundwater monitoring program 2009–2014 were to provide data for the assessment of the chemical and quantitative status of GWBs (including those being at risk), and identification of any negative trends, as well as the implementation of monitoring in protected areas, namely, major water supply sites and support decision-making process (development of PoMs). However, the monitoring program was not implemented as planned due to reduced funding and the negative effects of the global economic crisis in 2007–2008. Still, some overall improvements could be observed during this time, namely, an extended list of parameters to be measured during qualitative monitoring and implementation of operational monitoring and monitoring in protected areas – artificial groundwater recharge areas in Baltezers and NVZs (VMP, 2010). Since 2009 groundwatre chemical monitoring was updated with variety of additional parameters: heavy metals (Cd, Pb, As), trichloroethylene, tetrachloroethylene, pesticides (atrazine, simazine, bentazon, trichloroacetate, 2-methyl-4-chlorophenoxyacetic acid (MCPA)), trichloromethane, 1,2 dichloroethane, volatile aromatic compounds (BTEX).

The strategic objective of the most recent groundwater monitoring program 2015–2020 was to provide necessary data for the status assessment of GWBs. Specific objectives and monitoring design remained the same as in the previous program. The major improvement was an increase in the sampling frequency in springs and shallow wells (< 30 m) which became seasonal and was carried out up to 4 times a year. New parameters for heavy metals (Ni, Hg) and pesticides (permethrin, propazine, 2,4-D, MCPB, isoproturon, aclonifen, bifenox, aldrin, dieldrin, heptachlor, heptachlor epoxide, dimethoate, cypermethrin, alpha-cypermethrin, trifluralin) monitoring were added to the chemical groundwater monitoring. The monitoring program for the first time included an extensive list of techniques applied to check the quality of chemical analysis (VMP, 2015).

1.3. Hydrogeology and groundwater quality in Latvia

The territory of Latvia is located in the central part of the multi-layered sedimentary Baltic Artesian Basin (BAB) – one of the largest groundwater basins in Europe (Lukševičs et al., 2012; Virbulis et al., 2013). Above the crystalline basement (which does not reach the surface) lies the sedimentary cover with a thickness from ~400 m in the northeastern part to over 2000 m in the southwestern part of Latvia (Lukševičs et al., 2012). A simplified geological map of the Baltic states represents the horizontal and vertical distribution of major geological units (Figure 3). From the hydrogeological point of view, groundwater in Latvia can be divided into three major zones which differ by water exchange intensity and aquifer interconnection, water chemical composition, and potential for water usage. All three zones are separated by regional aquitards (Kitterød et al., 2022; Retike et al., 2016b) (see Figure 3, b).

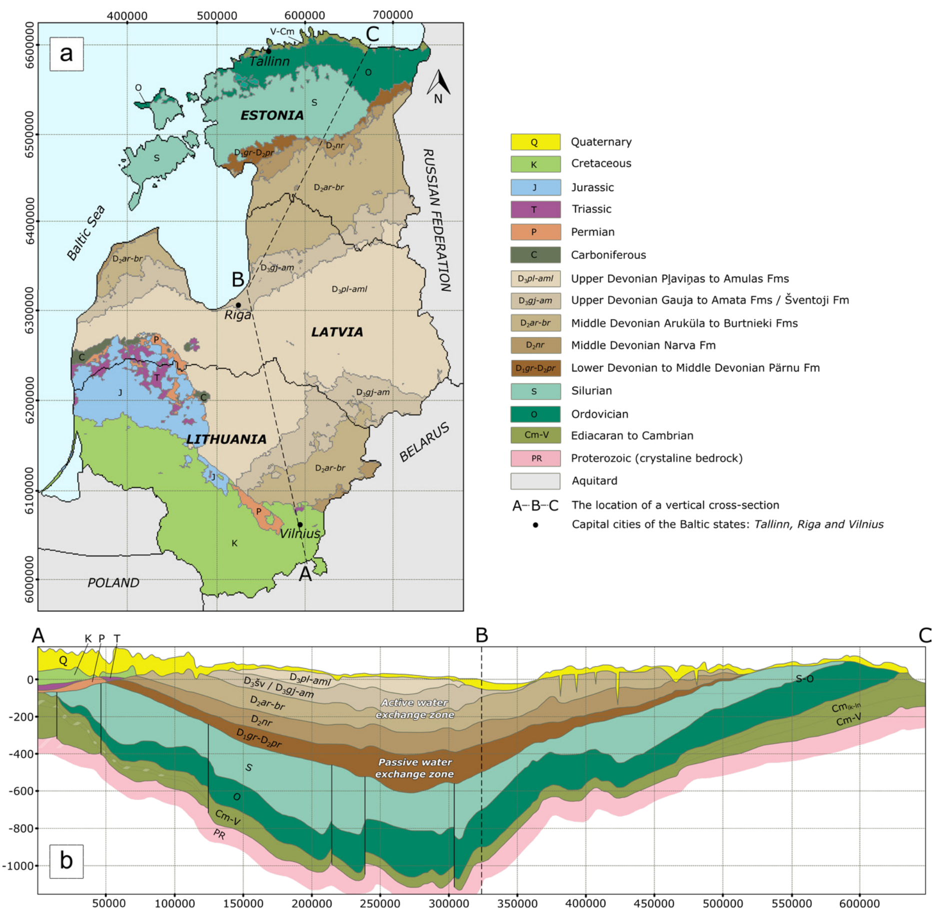

Figure 3. Simplified geological map of the Baltic states: a) spatial distribution and b) cross-section of the main geological units of the Baltic Artesian Basin (black vertical lines indicate faults). Created based on the model Virbulis et al. (2013) model (modified after Kitterød et al., 2022).

The following Ordovician–Silurian sequence consists of marls and clays with occasional limestone and dolostone beds and forms a regional aquitard that separates Cm–V aquifers system (**stagnant zone**) from the next, passive water exchange zone. The thickness of aquitard varies between 280 m in the southeast to 800 m in the west of Latvia (Lukševičs et al., 2012).

The Lower Devonian up to Middle Devonian Pärnu aquifer system forms **the passive water exchange zone** and consists of sandstones, with some admixtures of siltstones, marls, and clays, and reaches a maximum thickness of 200 m in the western part of Latvia. The zone is dominated by Na–Cl (sometimes Na–Cl–SO_4) type saline water with TDS usually ranging from 3 to 10 g/L having elevated trace element content (e.g., Br Bo, Se, Sn, Rb) (Levins & Gosk, 2008; Levins et al., 1998; Retike et al., 2016b) and in Riga and Sigulda such groundwaters are extracted to produce bottled mineral waters. In the 1970s and 1980s saline (TDS 5.5 g/L) and warm (temperature 15° C) Pärnu aquifer was tested for potential usage in trout farming in Ragaciems, Carnikava, and Uzava. The results were promising, however, there is a lack of information if groundwaters are still being used for fish farming (Levins et al., 1998; Retiķe & Dēliņa, 2018). Locally (Riga, Carnikava) a sharp salinity increase (TDS up to 40 g/L) can be observed due to saline water upconing near faults (Babre et al., 2016; Levins et al., 1998). On the contrary, in northern Latvia, the aquifer system contains good quality Ca–Mg–HCO_3 freshwater (TDS up to 600 mg/L) that is used for water supply in cities Salacgriva and Ainazi (Retiķe & Dēliņa, 2018), and recently also being bottled as natural mineral water (SLC "885"). A hypothesis exists that the lower to Middle Devonian aquifer system in western and southwestern parts of Estonia contains glacial paleo-groundwater but further studies are needed (Vaikmäe et al., 2021). Currently, there is no direct evidence of glacial paleo-groundwater in the territory of Latvia, while abnormal groundwater chemical composition has been observed in the northern part of Latvian aquifers with untypically low content Cl^- concentrations (< 3 mg/L). Highlighted barium concentrations exclude the possibility that low Cl^- content is due to recently infiltrated recharge water (Retike et al., 2016b). Even though water stable isotope $\delta^{18}O$ values in the passive water exchange zone in Latvia are around −11.7 ‰ and δ^2H values around −85.3 ‰, thus excluding glacial meltwater presence, the spatial coverage of sampling has been limited (Babre et al., 2016) and the possibility to find glacial meltwater in Latvia is still viable. Narva regional aquitard mainly formed of marl and clay separates the passive water exchange zone from the active water exchange zone. The aquifer is around 100 m thick in the eastern part to 200 m thick in the western part of Latvia (Popovs et al., 2015).

Mostly the sediments of the Middle to Upper Devonian and Quaternary ages form **the active water exchange zone**, while in the southwestern part of Latvia thin layers of Carboniferous, Permian, Triassic, and Jurassic sediments are also present (Lukševičs et al., 2012). The total thickness of the active water exchange zone varies from a few meters in the northwestern edge of Latvia to 650 m in the southern part of Latvia (Retiķe & Dēliņa, 2018). The majority of well fields in Latvia exploit middle Devonian Arukila, Burtnieki, and Upper Devonian Gauja and Amata aquifers (Klints & Dēliņa, 2012), where sandstones predominate at the base of each formation and fine-grained siltstones and clays dominate in the upper part. Above lies Upper Devonian aquifers formed by dolomites and marls and occasional gypsum interlayers in Salaspils and Stipinu aquifers (Lukševičs et al., 2012). The importance of the aquifer system increases in the southwestern part of Latvia where its thickness can reach 300 m, while it is absent in the northern edges of Latvia and the southeast part. Fresh $Ca–Mg–HCO_3$ groundwater with TDS up to 500 mg/L with often elevated Fe_{tot} content (up to 1.5–1.7 mg/L) dominates in the active water exchange zone. However, due to the dissolution of gypsum and water mixing $Ca–Mg–SO_4$ fresh groundwater and $Ca–SO_4$ brackish groundwater with TDS up to 2 g/L can be observed in the central and western parts of the active water exchange zone. Such groundwater is often accompanied by highlighted trace elements – F, Sr, Li and Co content. It is worth mentioning that in Latvia F rarely exceeds the permissible drinking water standard in the EU of 1.5 mg/L as it is controlled by the solubility of CaF_2 (Kitterød et al., 2022; Levins & Gosk, 2008; Retike et al., 2016b).

The whole territory of Latvia is covered by Quaternary, mostly glacial and marine sediments, and its structure is very heterogeneous (Popovs et al., 2015). The thickness of Quaternary deposits varies from a few meters up to 200 m in the areas of buried valleys. Such valleys for instance supply drinking water to the third largest city in Latvia – Daugavpils. Due to shallow occurrence, Quaternary groundwater is often used in rural areas where inhabitants exploit private shallow wells or dug wells (Klavins et al., 1996; Retike et al., 2016a). In the Baltezers vicinity, Quaternary aquifers contain exceptionally good quality $Ca–Mg–HCO_3$ freshwater with TDS less than 200 mg/L and low Fe_{tot} content (< 0.3 mg/L), therefore they are used in the centralized water supply. Part of the centralized water supply in Riga exploits Quaternary deposits in combination with managed aquifer recharge from the lake Mazais Baltezers (Eynard et al., 2000; Lace et al., 2017; Retiķe & Dēliņa, 2018). While around 80% of the water supply in Latvia comes from groundwater resources (RBMPs, 2022). The largest surface water abstraction takes place in the Riga Hydropower Plant reservoir which provides 43% of Riga's centralized water supply (Spriņģe et al., 2021).

1.3.1. Groundwater vulnerability to pollution

Groundwater vulnerability reflects the ability of the groundwater system to maintain natural conditions and its sensitivity to contamination. Hydrogeological characteristics like groundwater depth and type of overlying strata of the watershed control the residence time of groundwater and therefore aquifer vulnerability to pollution (Gomes et al., 2023). Various parameters can be used as vulnerability indicators, for instance, site lithology, hydraulic conductivity, surface/groundwater interaction, and groundwater flow directions, and there is no one standard technique for estimating groundwater vulnerability (Fannakh & Farsang, 2022; Valle Junior et al., 2014). The groundwater vulnerability map (Dēliņa & Prols, 2008) of Latvia often used in water management shows the intrinsic vulnerability of the water table aquifer, but it does not take into account land use or the presence of sporadic shallow groundwater and its quality. Such factors as land use, type of contamination, and groundwater exploitation should also be taken into account when estimating aquifer vulnerability.

The assessment of aquifer vulnerability is a prerequisite for sustainable groundwater management and enables policymakers to improve the decision-making process, for instance, by choosing the best strategies for pollution mitigation or modifying land use activities in the most vulnerable areas (Fannakh & Farsang, 2022). The WFD (Directive 2000/60/EC) requires the identification of the type and magnitude of significant anthropogenic pressures associated with urban, agricultural, forestry, and fishery activities, while the Nitrates Directive (Directive 91/676/EEC) concentrates on the reduction of water pollution caused by nitrates used in agriculture. In Europe, agriculture accounts for the major diffuse pressure on groundwater resources (Gomes et al., 2023) and nitrates are the pollutants most reported as the cause of the poor chemical status of GWBs (EEA, 2018). According to the latest report for the EU Nitrates Directive (Nitrate report, 2020), the highest nitrate concentrations in Latvian groundwater have been found in shallow wells up to 5 meters and springs, occasionally exceeding the threshold value of 50 mg/L up to ~100–200 mg/L. Recent studies show highly variable NO_3^- concentrations for Latvian springs ranging from few mg/L up to 50 mg/L high concentrations (Kalvāns et al., 2021; Koit et al., 2023). Another poorly monitored yet locally identified problem is shallow groundwater, and especially spring water, contamination with pesticides.

In addition, karstic aquifers are known to be especially vulnerable to pollution due to rapid transport and low retention capacity of pollutants (Kalvāns et al., 2021). Karst processes in Latvia are observed in carbonate and sulfate rocks in the central and southern parts of the territory (Delina et al., 2012). Karst rocks like dolomite, gypsum and limestone are present in the Upper Devonian and Permian sediments. Dolomite is widely distributed, while gypsum is mainly found in the Upper Devonian Salaspils formation, but limestone is typical for the Upper Permian formation. Karst processes in Latvia are observed in carbonate and sulphate rocks in the central and southern part of Latvia (Delina et al., 2012), however visual evidence in the form of land subsidence and formation of sinkholes is most often tied to gypsum karst in relatively small vicinities of Skaistkalne and Allazi but karstic features are visually less notable if compared to Birzi vicinity in Lithuania. This might explain why karst processes are still poorly documented and studied in Latvia despite the high vulnerability of such areas to potential groundwater contamination.

From the 1950s until the 1980s each year thousands of tons of acid tar originating from the production of white oils in the petrochemical factories of Riga were dumped in lagoons in Inčukalns. Both northern and southern acid tar lagoons were created in sandy soil without any measures to prevent pollution. Hydrogeological conditions with the discontinuous distribution of the glacial till layer were favorable for tens of meters deep pollution migration to the confined Upper Devonian Gauja aquifer, which in turn slowly transferred the pollution in the Gauja river direction. As a result, this area was characterized as the most polluted site in Latvia, delineated as a separate groundwater body at risk with site-specific threshold values. The remediation of the site was finalized in 2021 (Karušs et al., 2021; Karuša and Demidko, 2018), thus in the upcoming years the improvement of groundwater quality should be monitored frequently and status reevaluated against threshold values.

However, it should be stressed that the studies of groundwater pollution in industrial and waste landfills are few and scattered. There are more than 3500 contaminated or potentially contaminated sites in Latvia, but only 59 of these sites have been investigated (LEGMC, 2021). The majority of explored sites represent historical industrial sites, oil terminals, landfills, and Soviet Union's former military objects, thus the dominant pollutants that contaminate the soil and groundwater are oil products (e.g., PAHs), heavy metals and organochlorines. By now only a few such sites have been properly remediated (Burlakovs et al., 2020; Karušs et al., 2021; Spalvins et al., 2020).

More than 22500 wells have been installed in the territory of Latvia since the 1900s and 21% of them are currently in use (Urbumi, n.d.). However, only 6% of all wells have been decommissioned, while the status of the majority (58.5% or more than 13000 wells) remains unknown. Likely many wells are improperly abandoned and could pose a great risk on groundwater resources as pollution can easily migrate through well casings to aquifers, especially in recharge areas where polluted sites are present.

1.3.2. Aquifer salinization

The WFD (Directive 2000/60/EC) and GWD (Directive 2006/118/EC) require an assessment of the extent of any saline intrusions into the GWB. According to 2nd RBMPs (EEA, 2018) around 9% of all reported GWBs at the EU level are in poor quantitative status due to saline intrusions, and Cl^- is reported as the fifth most common pollutant causing the poor chemical status. The quality of groundwater in coastal areas is frequently affected by seawater intrusion because of intensive groundwater consumption. Overexploitation of coastal aquifers initiates seawater (Na–Cl type saltwater) migration towards fresh groundwater resources and then the water mixture is extracted by water supply systems (Narvaez-Montoya et al., 2023). Seawater intrusion in freshwater aquifers can be easily identified as a shift towards the Na–Cl water type and overall increased salinity. In coastal areas where water supply partly or fully relies on groundwater resources, saltwater intrusion may result in severe negative socio-economic impacts that are expected to worsen when coupled with climate change (Cao et al., 2021; Sola et al., 2013).

Groundwater pumping in former decades has caused a significant seawater intrusion into the Upper Devonian Mūru-Žagares (D_3*mr-žg*) partly confined aquifer with a depth of 38–43 m in Liepaja leading to the deterioration of a relatively wide coastal area. The area affected by seawater intrusion has been delineated as a separate groundwater body at risk (Bikše & Retike, 2018) and according to GWD threshold values must be established for all groundwater bodies to carry out the status assessment (see Section 3.2.3. for results).

Intensive groundwater pumping may also cause aquifer salinization by initiating water mixing between freshwater and more saline groundwater aquifers (Marandi & Karro, 2008). Increased salinity of freshwater aquifers has been observed in the vicinity of Riga where the extensive depression cone was formed during the 1970s due to the overexploitation of major freshwater aquifers (Klints & Dēliņa, 2012). Yet, the source of salinity most likely is not related to seawater intrusion but rather the upconing of deeper-located brackish groundwater from the passive water exchange zone through tectonic faults (Kalvāns, 2012). Solely analysis of major ions does not allow to differentiate between seawater and other saline water intrusion processes as both end members are Na–Cl water type. Therefore, more research is encouraged in this area using other tracers.

2. MATERIALS AND METHODS

2.1. Hydrogeological data

In this study data sets were obtained from various sources, the majority upon a request directly from data owners such as Latvian Environment, Geology and Meteorology Centre (LEGMC) (https://videscentrs.lvgmc.lv/). For each sample, the supplementary information about site characteristics (e.g., well number, station, georeferenced location), represented (hydro)geological environment (such as aquifer and its material, sampling depth), and analytical records (such as sampling/analysis date, detection limits (DL), flags about possible errors) was also collected if available.

A summary of major data sources used to develop the thesis is presented in Table 2. Detailed descriptions of the data sets used or gathered for each specific study can be found in published Papers I–X. Several research stages were carried out to develop the thesis, therefore, the characteristics of data sets (e.g., parameters, time period, sampling sites) vary according to the specific needs of each study and chosen statistical analysis.

Table 2. Summary of hydrogeological data sets used in this thesis with the reference to Papers.

Data source	Retrieved parameters	Data type	Time period	Scientific papers that used the data source
Latvian groundwater monitoring database (Observation database, n.d.)	field parameters, major ions, nitrogen compounds, heavy metals, groundwater levels	MW, MSP	1960–2018	**Paper II–X**
Groundwater register "Urbumi" (Urbumi, n.d.)	field parameters, major ions, nitrogen compounds, heavy metals, trace elements ([1])	WS	1994–2018	**Paper II–X**
Retike et al., 2016b; Levins and Gosk, 2007	field parameters, major ions, heavy metals, trace elements ([1,2])	WS, MSP, SP, PW, DR	1997–2013	**Paper II, IX–X**
Baltic seawater sample (Retike & Bikše, 2018)	field parameters, major ions, Br, As, P_{tot}, NH_4^+	SW	2017	**Paper VIII**

Abbreviations:
MW, monitoring well; MSP, monitoring spring; WS, water supply well; SP, spring; PW, project well; DR, drainage; SW, seawater.
Field parameters (*pH*, temperature, SEC, ORP, Fe_{tot}); major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-)
Nitrogen compounds (NO_3^-, NO_2^-, NH_4^+, N_{tot}); heavy metals (Cd, Pb, Ni, Hg)
Trace elements[1] (F, B, Cr, Cu, Sb, Se), [2] (Al, Ba, Br, Co, Rb, Si, Sr, U, V, Zn, Zr, As)

The data have undergone the basic quality control and homogeneity assessment thus ensuring the use of reliable and representative information for further analysis. Major data pre-processing steps are described in the following Sections.

2.2. External data

This study is the first attempt to provide the missing guidance on how to use and navigate historical to modern data obtained during scattered groundwater monitoring in Latvia. Up to now, Dēliņa (2006) has carried out the most extensive study on the history of groundwater research from the 19th century until 2006 in Latvia, while this study puts an emphasis on the evaluation of systematic groundwater monitoring in Latvia, its characteristics, and changes due to implementation of the EU Water Framework Directive (Directive 2000/60/EC). This study, for the first time, presents a comprehensive evaluation of systematic groundwater monitoring in Latvia from its establishment until nowadays (see Section 3.1.). Reports about the implementation of monitoring programs until 2005 were gathered from the archives of the State Geology Funds (Latvia) where the original copies are kept in printed form only. For modern data links to data sources (if available) were added to the reference list. It should be highlighted that many data sets used in this thesis remain of limited availability and should be requested from the data owners, such as LEGMC.

In Paper IX CORINE Land Cover data (CLC, 2012) were used to analyze the distribution of first-level land use classes within clusters. Geological units of the Baltic Artesian Basin model by Virbulis et al. (2013) were used to develop study site hydrogeological descriptions and conceptual models. The groundwater vulnerability map (Dēliņa & Prols, 2008) of Latvia outlines five vulnerability classes of water table aquifer based on lithological composition, hydraulic conductivity of the sediments, specific yield, and recharge and it was made based on the Quaternary sediments map and map of groundwater recharge modulus to adjust the contours of areas of different vulnerability classes. The map shows the intrinsic vulnerability of the water table aquifer, but it does not take into account land use or the presence of sporadic shallow groundwater and its quality.

2.3. Multivariate statistical analyses

Multivariate statistical methods are almost routinely used in hydrogeochemical studies to ease the classification of groundwater and identify major processes influencing the chemical composition (Cloutier et al., 2008). The application of multivariate statistics has proven to be effective in analyzing hydrogeochemical datasets acquired at various levels ranging from local to regional scales (Biddau et al., 2017; Bondu et al., 2020; Busico et al., 2018; Cloutier et al., 2008; Koit et al., 2021, 2023; Slama et al., 2022). Two well-proven multivariate statistical methods, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used to identify the processes controlling the evolution of groundwater geochemistry in Paper IX and X. Data pre-processing and analyses were carried out using SPSS Statistics 22 and 26.

2.3.1. Data pre-processing

Data sets used were collected from various sources and included historical measurements, thus the first step was to screen for possible errors and remove obvious outliers (like typing errors or duplicates), samples having incomplete records of major ions (including the removal of historical samples that reported sodium and potassium ions as a sum (NaK)), and finally, to check the accuracy of water analysis. A summary of major steps carried out to prepare hydrogeochemical data sets for the multivariate statistical analysis is presented in Table 3.

Multivariate statistical methods require complete data sets, therefore HCA and PCA will automatically exclude a sample if a value is missing for at least one of the variables included in the analysis (Cloutier et al., 2008). Güller et al. (2002) describe various approaches to estimate missing records such as replacing by the means of the variables or calculating from chemical relationships (e.g., HCO_3^- can be calculated from alkalinity values and *pH*). Missing values can be estimated from nearby wells or the electro-neutrality of the samples (Cloutier et al., 2008). Here most samples having missing records were not retained in the further analysis due to a large number of available measurements. Often samples with gaps were taken from monitoring wells having time series (see Table 3) and therefore had a complete water analysis in another sampling event. For instance, in Paper X (Retike et al., 2016b) multiple samples from the same locations comprised 16% of the data set. To sum up, the spatial coverage of observation did not suffer from the exclusion of missing values.

Table 3. Data processing workflow for the multivariate statistical analyses in Papers IX and X (DL – detection limit, IBE – ionic balance error)

Data processing step	Actions carried out	References to similar approaches
Quality and accuracy control	Removal of duplicates, outliers, and samples with missing values	Cloutier et al. (2008)
	Removal of samples with calculated IBE >± 10%	Güler et al. (2002)
Pre-processing	Values under DL replaced by ½ of the DL	Bondu et al. (2020) Farnham et al. (2002) Walter et al. (2019)
	Parameters having small variations within the data set were removed from further analysis	Bondu et al. (2020) Farnham et al. (2002, 2003) Cloutier et al. (2008)
Transformation	Log-transformation toward the normal distribution	Cloutier et al. (2008) Güler et al. (2002)
	Standardization (z scores)	

Typically, water samples having large ionic balance error (IBE) are removed from further assessment and according to Güller et al. (2002) a threshold of more than ±10 % was applied. In a few cases, larger deviations (up to ±20 %) were accepted if water samples had a high concentration of ions not included in the calculation (like NO_3^-, NH_4^+). Depending on the study around 1.6 % in Paper X (Retike et al., 2016b) to 2.8 % in Paper IX (Retike et al., 2016a) of samples were removed from further analyses due to high IBE.

Censored values or values below DL are frequent in water chemistry data sets (Güller et al., 2002). In the second step (Table 3), censored values were replaced by ½ of the DL, which is the most common and best-performing approach (Bondu et al., 2020; Farnham et al., 2002; Walter et al., 2019). It should be highlighted that often DLs were not reported, still, some values were converted to ½ based on expert judgment supported by the knowledge of data storage and analytical peculiarities (see Section 1.2.), e.g., lots of equal, lowest values for a particular parameter at a certain period when such DL was present. As highlighted by Farnham et al. (2002) sensitivity of analytical methods has changed over time and samples taken at different times or analyzed in different laboratories might be challenging to compare. This study also faced a similar challenge with historical data sets, e.g., from the 1970s to 1990s the DL for arsenic was 10 μg/L which is ten times higher than DL nowadays and exceeds the current drinking water threshold in Latvia (Cabinet Regulation No. 671 – Mandatory Harmlessness and Quality Requirements for Drinking Water, and the Procedures for Monitoring and Control Thereof) and most the EU countries. Such data should not be used together with modern data, but due to frequently missing information about DLs identification of such cases was a challenge. The treatment was carried out based on the expert judgment that it is hardly reproducible. However, in previous data pre-processing steps most of the historical data from the 1970s to 1990s were already eliminated (e.g., due to NaK measured as a sum) and expert judgment was applied to a small number of remaining samples.

The replacement of many values under DL with one single value can create noise in the results of multivariate statistics (Walter et al., 2019). Farnham et al. (2003) propose to eliminate parameters with relatively similar concentrations within the data set from further analysis because they weaken the performance of multivariate statistical methods. The optimal proposed threshold value is 30%, after which the PCA results quickly deteriorated (Farnham et al., 2002). Similarly, Bondu et al. (2020) excluded geochemical variables with more than 25% of censored values to avoid artifacts associated with an elevated proportion of data with an identical value. Cloutier et al. (2008) also excluded parameters having a high number of samples below DL (most trace elements) or showing small regional variation. However, no concrete cut-off value was reported, thus the approach can be considered as expert judgment.

In this study trace elements were not included in any of the multivariate statistical analyses mainly because of the large number of missing values that would drastically reduce the spatial coverage of initially huge data sets. In Paper X (Retike et al., 2016b) PCA and HCA were performed based on major ion concentrations (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}). In Paper IX (Retike et al., 2016a) in addition to major ions also nitrogen compounds (NO_3^-, NO_2^-, NH_4^+) were added to the analysis. Samples from the same location having trends in groundwater chemical composition located in the areas and aquifers known to be affected by seawater or saltwater intrusion due to intensive groundwater over-abstraction in former decades were retained in the Paper X (Retike et al., 2016b) to evaluate the temporal changes. While in Paper IX for multiple samples from the same location median values were calculated (Retike et al., 2016a).

The majority of multivariate statistical analyses assume the data follow a normal distribution (Güller et al., 2002), while most hydrochemical data do not (Bondu et al., 2020). In the third step (Table 3) variables were tested for normality to apply the proper transformation. Similar to Cloutier et al. (2008) conclusion, most chemical parameters were highly positively skewed, thus, such data were log-transformed. HCO_3^- and Mg^{2+} distributions were usually close to normal, and these results are alike to those reported by Cloutier et al. (2008). Then standardization was applied to both log-transformed and non-transformed data (for parameters that initially had close to normal distribution) so that each variable weighed equally (Güller et al., 2002). Finally, z scores of the log-transformed data were used as the input into PCA and HCA.

2.3.2. Principal component analysis

Principal component analysis (PCA) is a dimension reduction technique (Davis, 2002) where a set of correlated variables is transformed into a set of uncorrelated principal components (PCs) (Farnham et al., 2002). PCA is used for data reduction and deciphering patterns within large datasets (Farnham et al., 2003). In this study, PCs were obtained through eigenanalysis of the correlation matrix (Farnham et al., 2002). Varimax rotation was used to increase the participation of the variables with a higher contribution and reduce that of the variables with a lesser contribution at the same time (Cloutier et al., 2008; Kaiser, 1958). PCA assumes that each variable follows the normal distribution, outliers are not present, and the sample size is adequate ($N \geq 50$) and balanced (the case-to-variable ratio is at least 5) (Machiwal et al., 2018). In this study, after data pre-processing, all basic requirements were met.

The number of components is usually extracted based on the Kaiser criterion (Kaiser, 1958), which suggests that components with an eigenvalue greater than 1 are the most appropriate ones for interpretation (Cloutier et al., 2008). The first PC explains the most variance within the original data, while each subsequent PC explains progressively less. The loadings were then used to determine the parameters that are responsible for these correlations and parameters with the greatest positive or negative loading accounted for the largest contribution (Farnham et al., 2003). In this study variables with PC loadings greater than ± 0.5 and ± 0.6 were considered significant.

2.3.3. Hierarchical cluster analysis

Cluster analysis is a technique for grouping observations in such a way that each group or cluster is homogeneous concerning certain characteristics and distinct from other clusters regarding the same characteristics (Davis, 2002). Hierarchical cluster analysis (HCA) has been widely used to identify chemical types of groundwater. Widely used combination in HCA is Euclidean or Squared Euclidean distance (as a similarity measure) and Ward's method (for linkage) (Cloutier et al., 2008; Güller et al., 2002; Monjerezi et al., 2012; Surinaidu, 2016). This combination forms distinct and easily interpretable clusters in hydrogeochemical contexts (Güller et al., 2002; Machiwal et al., 2018), thus being applied to this study.

HCA is a semi-objective method that does not require an a priori specification of the number of clusters (Machiwal et al., 2018). The main result of HCA is a dendrogram that groups samples based on their (in this study geochemical) similarities and dissimilarities (Güller et al., 2002). The grouping of samples into clusters was an iterative process. First, the initial number of clusters was visually selected by moving the Phenon line (Güler et al., 2002; Monjerezi et al., 2012) and then justified by interpreting results within clusters (also analyzing parameters not directly included in the analysis) and together with the loadings from PCA. The final number of clusters was subjectively defined by best-matching results. In recent studies, discriminant analysis has been successfully used to verify the number of delineated clusters (Koit et al., 2021; Panagopoulos et al., 2016), but was not applied in this study.

2.3.4. Calculation of saturation indices

Saturation indices of calcite, dolomite, gypsum and halite minerals for Paper X were calculated using the software PHREEQC, version 3 (Parkhurst & Appelo, 2013). The calculation was based on concentrations of major ions, temperature, and *pH* values. Temperature data were not available for 473 samples from a total of 1442 samples. The missing values were substituted with the average groundwater temperature (8.5 °C, standard deviation 1.96 °C) obtained from the rest of the samples with known temperature measurements.

2.4. Seawater fraction calculation

Significant groundwater pumping may modify the extension of the freshwater domain and initiate water mixing, e.g., seawater intrusion into coastal aquifers. The salinization process can be easily observed by increased chloride (Cl^-) content, therefore seawater fraction in groundwater is commonly estimated using Cl^- concentrations (Slama & Bouhlila, 2017). Also, the usage of Na^+, Br, and SO_4^{2-} has been reported (Park et al., 2005; Pulido-Velazquez et al., 2022).

In Paper VIII (Retike & Bikše, 2018) seawater fractions f_{sea} in groundwater samples were calculated based on both chloride (Cl^-) and bromide (Br^-) ions that could be considered as conservative tracers for the Baltic states region according to the following equation (Appelo & Postma, 2005):

$$\frac{m_{x(sample)} - m_{x(freshwater)}}{m_{x(seawater)} - m_{x(freshwater)}} \times 100\% \tag{1}$$

where m_X – concentration of either Cl^- or Br^- concentration in either freshwater, seawater, or groundwater sample. Chloride concentration for the freshwater sample was calculated as average Cl^- content from wells No. 9322 and No. 2254 (Urbumi, n.d.). These wells are inland background monitoring stations installed in the Upper Devonian Mūru-Žagares (D_3*mr-žg*) aquifers and were considered freshwater endmembers, i.e., wells not affected by salinization. The sample taken from the Baltic Sea was used as a seawater endmember in calculations. The seawater sampling area and depth (9 meters) were chosen based on expert judgment – a hypothetical location of the area where seawater could intrude freshwater aquifers.

2.5. Establishment of groundwater quality standards

The quality standards in the form of threshold values (TVs) must be established by each member state for pollutants causing the risk of not achieving good groundwater chemical status. The prerequisite in establishing TVs is a derivation of natural background levels (NBLs) for parameters that can be present in elevated concentrations and whose content might vary significantly from one GWB to another (i.e., SO_4^{2-} rich groundwater in aquifers with gypsum) (Voutchkova et al., 2021).

Very general guidelines for the establishment of threshold values by member states are provided by GWD (Directive 2006/118/EC) Annex II, part A, while more details can be found in the supporting guidance document (European Commission, 2009) – an outcome of the international EU research project "Background cRiteria for the Identification of Groundwater thresholds (BRIDGE)" (Müller et al., 2006). The so-called BRIDGE methodology proposes a simplified approach for the derivation of groundwater TVs which includes NBLs and environmental quality standards (Hinsby et al., 2008). The approach proposes several options for NBL establishment considering the degree of knowledge about geochemical processes and the availability of chemical data (De Caro et al., 2017). In this study (Paper VIII) the commonly applied BRIDGE methodology (Müller et al., 2006) was adapted and used to derive NBLs and further establish TVs for the GWB at risk F5 "Liepaja seawater intrusion".

According to the WFD (Directive 2000/60/EC) member states are required to derive TVs for all pollutants or indicators that put the GWB at risk of not achieving good status (Hinsby et al., 2008). The minimum suggested list for which Member States must consider setting TVs is indicated in Annex II, part B of GWB and includes the following elements that can occur both naturally and/or as a result of human activities (As, Cd, Pb, Hg, NH_4^+, Cl^-, SO_4^{2-}). Based on the hydrogeological conditions of the study site, it was decided to derive NBLs and TVs for Na^+, Cl^- and SO_4^{2-} which are the most representative parameters for the identification of pressures causing the risk (seawater intrusion) on the hydrogeological system. Moreover, these parameters have always been a part of the groundwater quality monitoring in Latvia.

2.5.1. Methodology to derive natural background levels

The BRIDGE methodology is based on the identification of pristine groundwater samples across an available dataset (Molinari et al., 2019) where NBL is derived as a fixed value (Hinsby et al., 2008). Main steps to derive natural background levels for Na^+, Cl^-, and SO_4^{2-} for the GWB at risk F5 are summarized in Table 4.

The BRIDGE methodology suggests a list of minimum criteria to be used to eliminate samples potentially affected by humans (Marandi & Karro, 2008). For this study stricter criteria were applied to eliminate samples potentially affected by (1) any freshwater mixing with more mineralized water (Cl^- criteria > 18 mg/l) or (2) anthropogenic point or diffuse pollution based on a sufficient degree of knowledge about the study area (from Paper IX and X). In this study, median values were calculated for time series at each observation point to assure that time series do not bias the results and all sampling sites contribute equally to the derivation of NBLs as emphasized by Hinsby et al. (2008).

The maximum curvature of the lines on cumulative probability plots reveals inflection points or thresholds between populations – in this case, natural and anthropogenic groundwater samples. The values of a single normally or lognormally distributed population form a straight line, while mixed populations result in a curved line with a pronounced inflection point (Panno et al., 2006). In this study, NBLs were derived at the 90th percentile (Müller et al., 2006) below the inflection point value.

Table 4. Workflow for the derivation of natural background levels.

Data processing step	Actions carried out
Quality and accuracy control	Removal of samples with unknown depth and geographic coordinates
	Removal of samples having missing values, including these with Na^+ and K^+ ions reported as a sum NaK
	Exclusion of samples with IBE > ± 10%
Elimination of human impacts (polluted samples)	Removal of samples having Cl^- > 18 mg/L according to Retike et al. (2016b)
	Removal of samples with NO_3^- > 4 mg/L according to Retike et al. (2016a, b)
Derivation of natural background levels (NBLs)	Median values calculated for the samples taken from the same location
	Detection of the value of the inflection point on groundwater samples according to Panno et al. (2006)
	Validation of the results versus the results from Retike et al. (2016b)
	Determination of the 90th percentile of all freshwater samples below the inflection point value

2.5.2. Establishment of threshold values

As suggested by the BRIDGE methodology, the first step in the establishment of TVs is the selection of relevant criteria or the receptor of groundwater. Criteria can be divided into environmental criteria (such as saline water intrusions and associated aquatic and dependent terrestrial ecosystems) and usage criteria (actual or potential legitimate uses of the function of groundwater). Usage criteria are relevant use base standards, such as drinking water standards or irrigation standards (European Commission, 2009; Scheidleder, 2012). Hinsby et al. (2008) highlight that little is known about the water quality needs of GDEs and recent studies (Kalvāns et al., 2021; Koit et al., 2021) conclude that interaction between groundwater and dependent nature is not straightforward and response to, i.e., inflowing groundwater with high nitrate levels might depend on each ecosystem type. Considering the currently limited knowledge base about the water quality needs of other receptors, this study, like most member states (Scheidleder, 2012), used national drinking water standards (Cabinet Regulation No. 671 – Mandatory Harmlessness and Quality Requirements for Drinking Water, and the Procedures for Monitoring and Control Thereof)) as criteria values (CVs) (Figure 4).

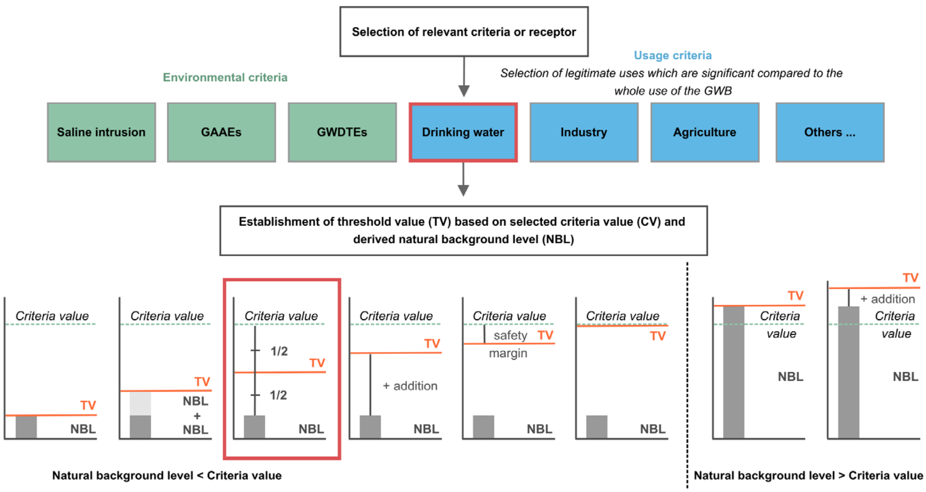

Figure 4. Schematic representation of the methodologies used to derive threshold values in the EU member states. Red boxed indicate the chosen approach for Latvia and this study (adapted from European Commission and Scheidleder, 2012).

According to the GWD (Directive 2006/118/EC) TVs can be derived at the national, RBD (or part of the international RBD) or GWB (also a group of GWBs) level which is the smallest scale allowed for TV derivation. It is up to the member states to set TVs at the most appropriate level. For instance, a purely anthropogenic pollutant more likely will have a TV on a national scale as it does not have an NBL and should not be present in natural conditions. While most inorganic compounds may be present in certain natural conditions (e.g., SO_4^{2-} due to gypsum dissolution in strata) and could vary from one GWB to another or even at GWB scale (European Commission, 2009). In this study, the NBLs for GWB at risk F5 were derived using grouping with hydrodynamically connected GWB F1 (to extend the dataset), but TVs were set only for GWB at risk F5 – Liepaja seawater intrusion (Bikše & Retike, 2018; Retike & Bikse, 2018).

3. RESULTS AND DISCUSSION

3.1. Characteristics and perspectives of groundwater monitoring in Latvia

3.1.1. Systematic groundwater level monitoring

In the majority of Europe systematic groundwater level monitoring started in 20th century (IGRAC, 2020; Jousma & Roelofsen, 2004), while, for instance, The United Kingdom has reported up to 112 years long groundwater level time-series (Bloomfield & Marchant, 2013). The first systematic groundwater level measurements in Latvia can be dated back to 1959 (4 wells) with a clear upward trend in the number of monitoring wells until 1990 (375 wells) (Figure 5). However, the number of monitored wells rapidly decreased from 1991 until 1994, while the number of stations (nested wells) and manual measurements declined only slightly. This observation goes in line with the Jankins et al. (1993) report about the first optimization process (1992–1993) of the groundwater monitoring network shortly after Latvia restored its independence. During the optimization mainly wells with poor technical status and low representativity (e.g., nearby wells installed in the same aquifer) were eliminated and the number of stations was little affected.

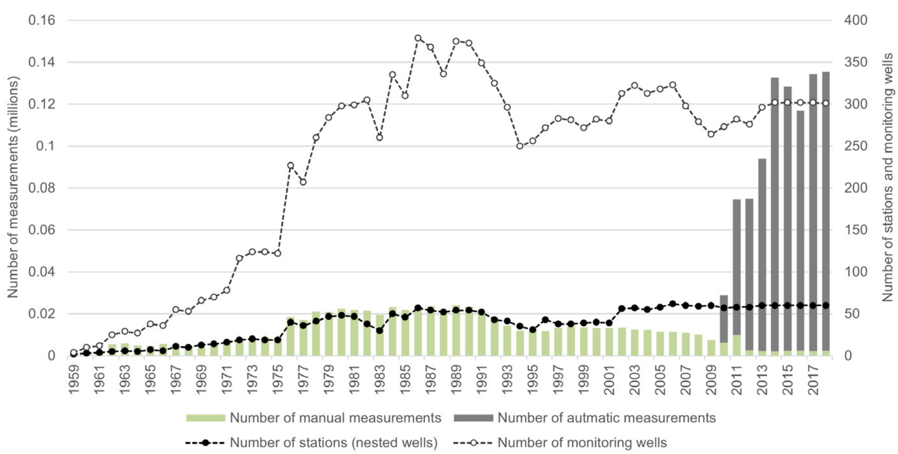

Figure 5. Changes in the systematic groundwater level monitoring from 1959 to 2018 in the territory of Latvia (adapted from Retike et al., 2022).

Levina and Levins (2020) summarized that during the second groundwater monitoring inventory in Latvia (1997–1999) about one-third of tested wells were found to be either damaged, destroyed, or had limited access due to unregulated ownership since many monitoring wells were installed on private lands during the Soviet times. Consequently, the reduction in the number of monitored wells and stations could be expected but was not observed (Figure 5). Moreover, the number of monitored wells and active monitoring stations gradually increased from 1994 (250 wells) until 2006 (323 wells). It could be explained by the fact that Latvia become a candidate for EU membership in 1999 and had to rapidly improve the representativity of the groundwater monitoring network according to EU water policies' requirements (Levina & Levins, 2000, 2001).

Groundwater level monitoring in Latvia experienced dramatic changes with the introduction of automatic level loggers. In 2010 the first automatic level loggers were deployed, and already then, the number of total level measurements increased nearly four times in comparison to 2009 (see Figure 5). Since that time automatic measurements comprise most groundwater level data sets. For instance, from 2012, when deployment of all automatic level loggers was completed (LEGMC, 2013), until 2018 the manual measurements comprised less than 2% of the total groundwater level measurements. In 2018 groundwater level monitoring in Latvia was carried out in 301 wells grouped into 60 monitoring stations (nested wells), and most of the groundwater levels were recorded automatically. Figure 6 represents the spatial changes in the Latvian groundwater level monitoring network during almost 60 operational years. It can be observed that the spatial coverage of groundwater monitoring wells has increased over the whole monitoring period while the changes have been minor since the 1990s.

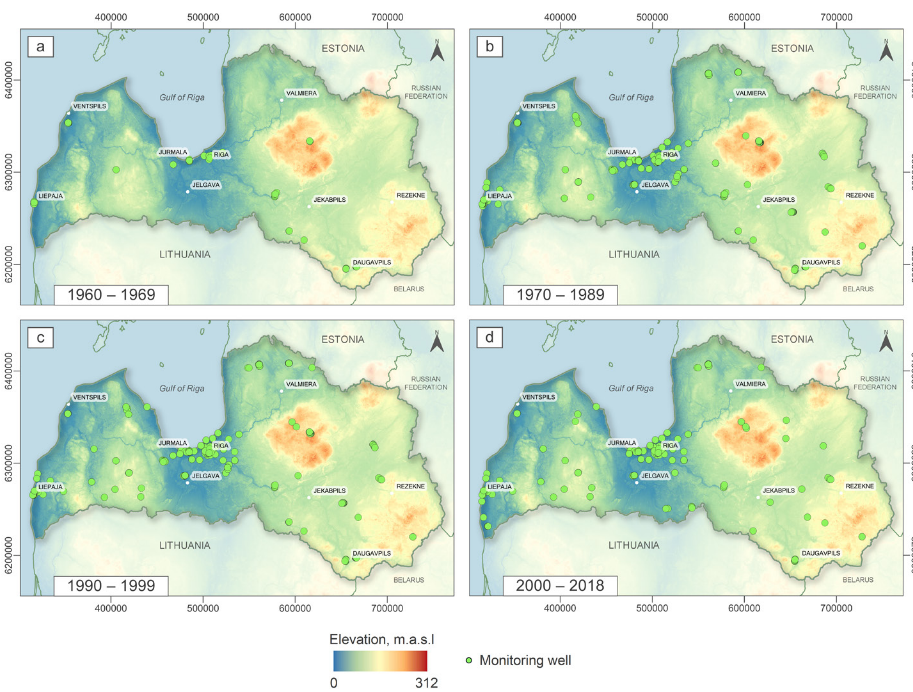

Figure 6. Systematic groundwater quantity monitoring network in the period a) 1960–1969, b) 1970–1989, c) 1990–1999, d) 2000–2018 in the territory of Latvia.

Automatic groundwater level monitoring (often accompanied by manual measurements for verification) is carried out in most European countries, e.g., Estonia, Lithuania, Austria, Denmark, Germany, and others (IGRAC, 2020). On the one hand, the introduction of automatic level loggers has provided new insights into factors affecting groundwater dynamics in Latvia, such as the possibility to investigate groundwater drought episodes (Bikše et al., 2023; Babre et al., 2022). On the other hand, if misplaced or malfunctioning the automatic level loggers have created a new type of error in the time series. Now it is more challenging for national authorities to store and handle such large data sets, as well as identify and treat the errors. The most common errors found in groundwater level time series are summarized in Table 5 and they have affected 88% of the groundwater hydrographs in Latvia (Retike et al., 2022). Currently, downloads of level logger data in Latvia are carried out up to two times per year and often combined with water sampling to save costs. Consequently, any issues with data loggers are discovered only after half a year if not later. As emphasized by Rau et al. (2019) frequent removal of loggers creates errors and should be avoided. Here, the usage of telemetry could be recommended to send groundwater levels automatically to a database as it has been already done, e.g., in the United Kingdom, Argentina, the United States, and Australia (IGRAC, 2020). Automatic groundwater level measurements in Latvia are recorded twice a day due to memory limitations in level loggers. Telemetry would allow for increasing the number of measurements which currently does not allow to capture short-term variations as stressed by Rau et al. (2019).

Table 5. Summary of the characteristic errors found in Latvian groundwater level time series and their handling possibilities (adapted from Retike et al., 2022 – Paper V).

Problems	Possible cause	Characteristic to automatic/ manual measurements	Difficulty to identify/treat the problem
Distinct outlier	The measurement itself or data handling	No/ Yes	Low/ Low
Shift in level	Automatic level misplacement or data handling	Yes/ Sometimes (historical data sets)	Low/ Low
Shift in level followed by recovery	Effects of well itself or nearby pumping/ recharge	Yes/ No	Low/ Median
Data drift	Malfunctioning of level logger	Yes/ No	Low/ Median
Change in level pattern	Data handling or human (anthropogenic) influence	Yes/ Yes	High/ High
Jagged/ toothed level pattern (large deviations)	Measurement itself	No/ Yes	Low/ High
Noise in level observations (a few cm)	Malfunctioning of barometric level logger at freezing temperatures or natural fluctuations	Yes/ No	High/ High
Plateau in level observations	Well completion/ logger installation problems	Yes/ No	Low/High

Around the world, groundwater levels are measured in observation wells for a variety of reasons, for instance, monitoring of long-term changes, assessment of seasonal variations, or evaluation of response to particular stress (IGRAC, 2020). Even though systematic groundwater level monitoring in the Baltic states started almost simultaneously (1959 – Latvia, 1960 – Estonia (Bikše et al., 2023; Terasmaa et al., 2020) and 1963 – Lithuania (Arustiene, 2011) and we share similar hydrogeological conditions (Kitterød et al., 2022), there already are fundamental differences in design and objectives of the monitoring, and each approach has their pros and cons. Latvia and Lithuania use nested well or station principles (wells installed nearby at different depths and/or aquifers) whereas the approach is not used in Estonia, and also not common in other countries. As highlighted by Jørgensen and Stockmarr (2009), nested wells provide an in-depth insight into the local hydrogeological processes, but the upscaling possibilities to the regional levels are questionable. Moreover, nested wells are uncommon for many countries (Jousma & Roelofsen, 2004; Jørgensen & Stockmarr, 2009) and their presence complicates the reporting process to European Commission which often misinterprets nested wells as duplicates.

Another major difference is that most groundwater levels in Latvia and Estonia are measured in confined and deep aquifers, while Arustiene (2011) stated that in Lithuania groundwater level monitoring is focused on shallow aquifers to assess climate change impacts on groundwater recharge. Neglecting the shallow and unconfined aquifers is one of the major drawbacks of the Latvian groundwater level data set. Closest to the surface aquifers are the most responsive to seasonal and inter-annual level fluctuations and therefore the first indicator of climate change (Babre et al., 2022). Also, many GDEs (e.g., wetlands, rivers and lakes) strongly depend on groundwater input, especially from the upper aquifers (Kalvāns et al., 2021; Koit et al., 2021). Finally, the evaluation of surface-groundwater interaction is required to fulfil the EU WFD's requirements (see Figure 1), i.e., to assess the status of a groundwater body (Terasmaa et al., 2020).

Aquifer response to changes in precipitation, temperature, and potential (evapo) transpiration might be reflected in spring discharges, and they have been measured around the world for decades (IGRAC, 2020; Jousma & Roelofsen, 2004), e.g., in Italy up to 100 years long time-series exists (Fiorillo et al., 2020). In Latvia, springs are currently not included in the quantitative groundwater monitoring network. An increase in the number of monitored springs starting from data scarce areas (e.g., transboundary aquifers (Koit et al., 2023)) and equipping with automatic discharge measurements units could fill several identified gaps in Latvian groundwater level monitoring, such as lack of observations for GDEs (Terasmaa et al., 2020), surface-groundwater interaction (Delina et al., 2012; Kalvāns et al., 2020) and nitrate vulnerability assessment (Kalvāns et al., 2021; Retike et al., 2016a). The global decrease in spring discharges has been already associated with climate change (Weissinger et al., 2016), while groundwater abstraction often constitutes a second factor responsible for declining spring discharges (Guo et al. 2005; Sivelle et al. 2021). Terasmaa et al. (2020) pointed out that a change in spring discharge can timely indicate a risk of deterioration of the ecological quality of the GDTE receiving the base flow from the spring. As highlighted by Tóth et al. (2022) the spatial comparison of hydraulic heads of streams and springs can bring insights into surface-groundwater interaction, while in combination with temperature and discharge measurements could unveil the dynamics of groundwater systems at the basin scale. Moreover, the measurement of suggested physical parameters, such as spring temperature and discharge, is a cost-effective solution to cover data scarce areas like cross-border areas between Latvia and neighboring countries (Koit et al., 2023; Marandi et al., In Print).

3.1.2. Systematic groundwater quality monitoring

Nearly 50% of the urban population relies on groundwater (Lapworth et al., 2022) and globally groundwater quality monitoring has been measured for decades (Jørgensen & Stockmarr, 2009). France set up the first groundwater quality network in Europe already in 1902, while in the majority of countries, systematic groundwater quality monitoring started around the 1980s (Jousma & Roelofsen, 2004). Groundwater abstraction in Latvia has a long history and currently groundwater accounts for around 80% of freshwater withdrawal (RBMPS, 2022). As can be observed from Figure 7, systematic groundwater quality monitoring in Latvia can be dated back to 1960 and coincide with the start of groundwater level monitoring (see Figure 5). But the first considerable amount of groundwater samples (49) was collected in 1967. The initial monitoring network was scarce (Figure 8, a) and concentrated around the largest cities and newly built "Plavinas" HPP (Jankins et al., 1993, Juodkazis, 1994; Levina & Levins, 1994).

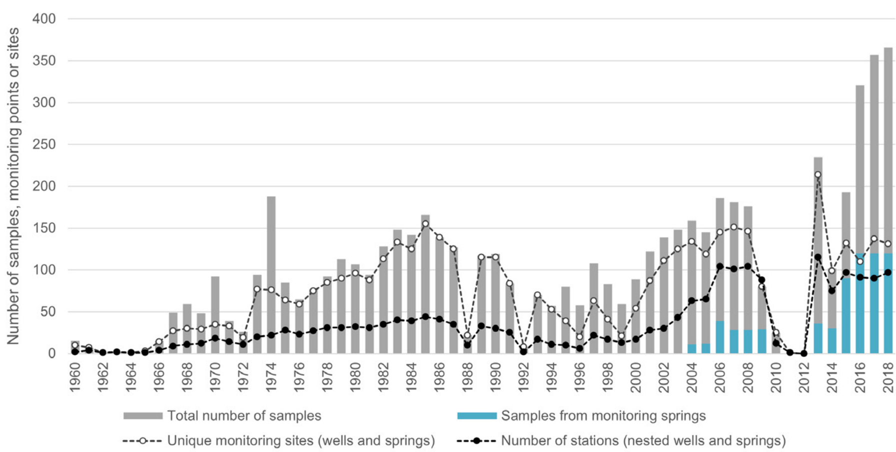

Figure 7. Changes in the systematic groundwater quality monitoring from 1960 to 2018 in the territory of Latvia.

The period from 1973 until 1986 illustrates the establishment of nested wells – several nearby monitoring wells installed at different depths, and the approach has been an integral part of Latvian groundwater monitoring. Nested wells allow monitoring the interaction between shallow and confined aquifers, mixing between freshwater and more mineralized water. The approach yet not common is used in other countries too (e.g., in Denmark (Jørgensen & Stockmarr, 2009) and Lithuania (Arustiene, 2011)) sharing somewhat similar hydrogeological conditions, namely, multi-aquifer systems, or having risk for seawater/saltwater intrusions (Kitterød et al., 2022). Hence, the listed factors might not be exhaustive as, for instance, Estonia does not have nested wells (Terasmaa et al., 2020).

It remains unclear whether the first negative drop in all numbers (Figure 7) was observed in 1988 due to cuts in funding or accidental loss of historical data over time but no similar changes could be observed in the groundwater level monitoring data set (Figure 5). The next negative drop in 1992 coincided with the first documented groundwater network optimization after the collapse of the Soviet Union (Jankins et al., 1993) when the number of monitored wells and sampling frequency decreased. Until 1999 the monitoring continued based on the praxis developed during the Soviet times and with insufficient funding, therefore monitoring was scattered and covered only parts of Latvia. However, for a decade (1990–1999) majority of wells were monitored and only temporal sampling frequency was affected (see Figure 8, c).

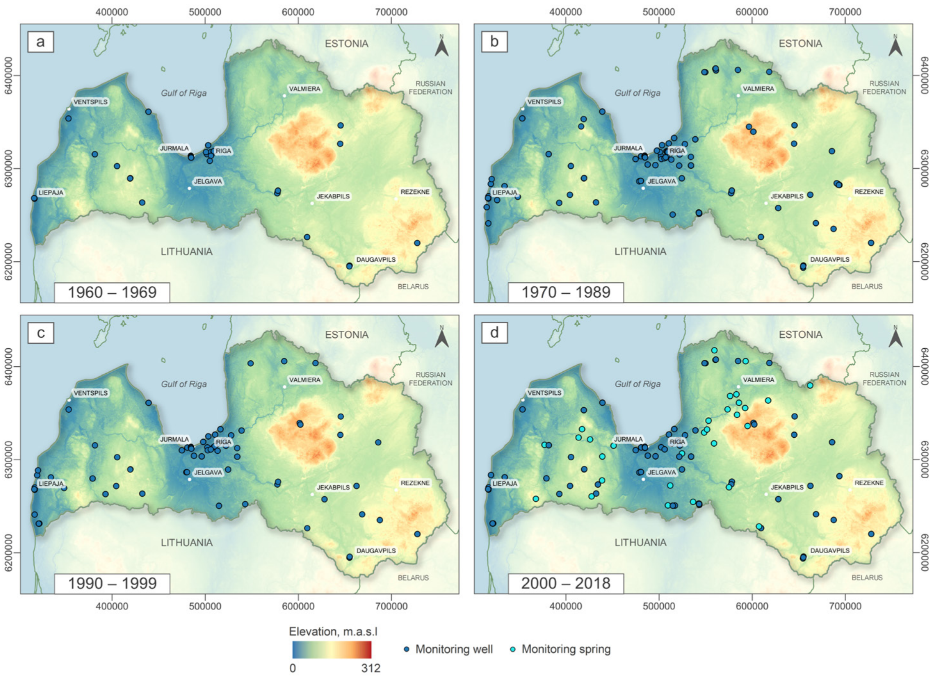

Figure 8. Systematic groundwater quality monitoring network in the period a) 1960–1969, b) 1970–1989, c) 1990–1999, d) 2000–2018 in the territory of Latvia.

A gradual increase in all numbers describing groundwater quality monitoring could be observed since Latvia became a candidate for EU membership in 1999 and entered the EU in 2004. Similar changes were observed in most EU member states trying to rapidly improve national monitoring networks and fulfil EU WFD's requirements (Jørgensen & Stockmarr, 2009; Onorati et al., 2006; Quevauviller, 2005). In comparison with groundwater level monitoring (Figure 5), groundwater quality monitoring improved more rapidly and spatially (Figure 7, Figure 8, d). The number of new stations increased from 13 stations in 1999 to 104 stations in 2008 mainly due to the inclusion of new springs into the groundwater monitoring network. Gosk et al. (2007) first described the vulnerability of Latvia's springs: during the study higher average nitrate concentrations were found in 85 springs compared to 358 shallow wells installed in the same aquifers. It was highlighted that elevated nitrate concentrations were observed also in springs having no evident nitrate source. As a result, 30 high-yielding springs were added to the groundwater quality monitoring network in 2004 to better understand flow patterns and assess the extent of diffuse nitrate pollution.

Since 2009 a dramatic drop in the number of samples taken and sampling sites monitored can be observed (Figure 7) due to the negative impacts of the global economic crisis and consequent cuts in funding. Groundwater quality monitoring In Latvia was cancelled from the middle of 2009 until 2012 and was restarted only in 2013 (VMP, 2010). The impact on groundwater level monitoring was less noticeable (Figure 5) because of recently installed automatic level loggers and generally lower operational costs. The paused groundwater quality monitoring produced essential gaps in data sets and strongly reduced the quality of the following reporting for the WFD (2^{nd} and 3^{rd} cycle RBMPs) as the frequency was not satisfactory to calculate the long-term trends for the majority of monitoring sites (typically 6 to 8 years needed) (Frollini et al., 2021). Similarly, Jørgensen and Stockmarr (2009) reported a reduced budget for the Danish groundwater monitoring programme already in 2007 that negatively affected the number of collected data and analysed parameters and risked the future reporting possibilities to European Commission.

In 2013 the groundwater quality monitoring was restarted, and an attempt was made to fill the gaps developed during the 3.5 years of reduced quality monitoring. As shown in Figure 7, the year 2013 had the historically highest number of monitored sites (214) and stations (115). A sole rise in the total number of samples since 2015 indicated an increase in sampling frequency. It has been reported that from 2015 some springs were sampled seasonally – up to 4 times per year (VMP, 2015). In 2018 systematic groundwater quality monitoring was carried out in 131 monitoring sites grouped into 67 monitoring stations and 30 springs (see Figure 7, Figure 8, d). The sampling frequency on average was 2.8 per year. The most extensive groundwater quality monitoring includes analyses of over 50 different parameters such as major ions, phosphate and nitrogen compounds, heavy metals, pesticides, and their metabolites.

Section 1.2. summarized the major documented changes in groundwater monitoring principles in the territory of Latvia from its beginning to nowadays. Much larger deviations between reported numbers and the actual data were observed for the groundwater quality data set (Figure 7) if compared to the groundwater level data set (Figure 5). Hydrogeochemical databases used and compiled in this study were complex (historical) and consisted of numerous parameters having their own measurement units, detection limits, and even two types of dates – sampling and analysis date. Consequently, more errors compared to the groundwater level database could be expected. Possible deviations could be explained by data processing errors (e.g., typing errors in reports) that generally accounts for a large proportion of errors in databases as highlighted by Kandel et al. (2011) and Liu et al. (2018). Other reasons for the mismatch between reported and actual data could be the loss of historical data during the digitization processes or database merging or unfulfillment of monitoring programmes.

As reported by Gosk et al. (2007) majority of the Latvia's monitoring wells installed during the 1970s and 1980s aimed to control groundwater abstraction, therefore screening deep aquifers exploited for water supply. The average depth of groundwater monitoring well over time ranged from 48.5 to 93.4 m (Figure 9, a) and most wells screened confined Upper and Middle Devonian aquifers (Figure 9, b). Moreover, Figure 9, c illustrates that the majority of monitoring wells currently being operational have been installed in the 1970s and 1980s, while the most recent monitoring wells were installed already a decade ago, in the years 2010 and 2013 (43 wells). Consequently, many valuable data sets have a risk to be interrupted due to well depreciation, thus the technical status of the oldest wells should be verified, and new wells installed.

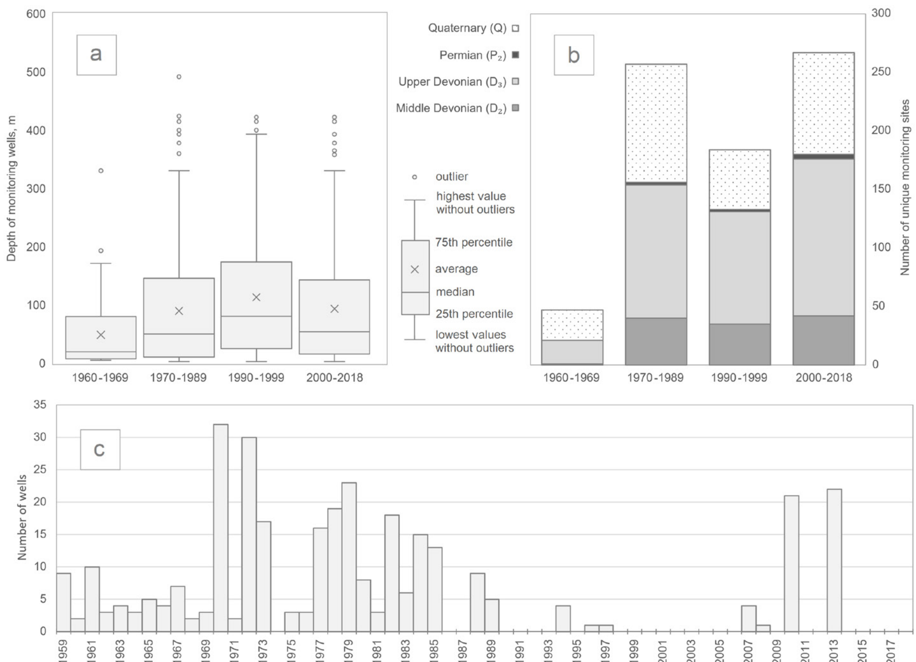

Figure 9. Characteristics of systematic groundwater quality monitoring changes over time from 1960 until 2018, a) depth of monitoring wells, b) represented aquifer systems, c) year of well installation (springs excluded).

The underrepresentation of shallow groundwater and long-term focus only on deep aquifers is one of the major drawbacks of the Latvian groundwater quality monitoring network. Pollution with nitrates and pesticides in the near-surface aquifers has been well documented in the Baltic states and beyond (Kalvāns et al., 2021; Kitterød et al., 2022; Retike et al., 2016a,b; Levins & Gosk, 2008). For instance, Rozemeijer et al. (2021) sampled groundwater with a maximum depth of 5 meters below the surface to evaluate the effects of climate variability on groundwater quality (nitrates). Similarly, the highest NO_3^- concentrations in Latvian groundwater have been observed mainly in shallow wells up to 5 meters and springs (Kitterød et al., 2022; Nitrate report, 2020). As stated by Jørgensen and Stockmarr (2009) monitoring of younger and more vulnerable to pollution groundwater allow timely identification of the movement of pollution front and assessment of the long-term threats to confined aquifers used in the water supply. Besides, the current monitoring design in Latvia cannot ensure a prevention principle and if pollutants are already identified in the confined aquifers, the remediation costs can be huge, and recovery time way beyond the EU WFD's deadline in 2027 (Burlakovs et al., 2020; Karušs et al., 2021; Pulido-Velazquez et al., 2022). It should be considered that there are more than 200 wellfields (extracting more than 100 m^3/d) in Latvia with a good spatial representation of confined aquifers that are obliged to report groundwater quality (around 15 parameters) on annual basis. Many countries worldwide use the existing water supply wells as part of the national groundwater monitoring (IGRAC, 2020), including neighbouring country Lithuania (Arustiene, 2011). Efforts should be made to control and motivate wellfield owners to carry out monitoring, e.g., by covering part of the monitoring expenses or providing training for correct water sampling which are among the major limitations of such data usage.

The rapid expansion of the groundwater quality monitoring network in Latvia is necessary to fulfil the various needs of EU water policies like the establishment of transboundary groundwater monitoring, assessment of the surface-groundwater interaction, nitrate vulnerability, and many more (Quevauviller, 2005). Expansion of the Latvian groundwater quality monitoring network with springs could fill the gaps (Koit et al., 2023) and facilitate the implementation of international legal acts and agreements in Latvia (such as the EU Water Framework Directive, EU Nitrates Directive or Water Convention) (Flem et al., 2022; Terasmaa et al., 2020). Lower sampling/maintenance costs and representation of larger catchments are among the major benefits of spring introduction into monitoring networks, and springs have been used around the world as part of national groundwater monitoring (Bender et al., 2001; IGRAC, 2020; Terasmaa et al., 2020). Spring chemical composition could provide an overview of anthropogenic pressures and pollutant loads present in the catchment area. For instance, high nitrate levels in springs have indicated nitrogen losses from arable lands (Kalvāns et al., 2021; Weber & Kubiniok, 2022). Weber and Kubiniok (2022) identified prohibited plant protection products in spring water thus revealing that applied water protection measures might not be very effective and respected. However, springs can be complex and highly responsive ecosystems reflecting the mixture of natural and anthropogenic forcings and require a preliminary assessment of spring representativeness by the development of conceptual understanding (Farlin et al., 2019; Stevens et al., 2021; Tóth et al., 2022). Such tasks may include watershed delineation and land use assessment (Matheswaran et al., 2019; Stauffer et al., 2005), water quality, temperature, and discharge measurements (preferably, seasonally) to understand the sources and dynamics of springs (Bender et al., 2001; Bozau et al., 2013; Koit et al., 2021; Szczucińska, 2013).

Springs, which are natural groundwater outflows, are a crucial source of drinking water supply, especially in karstic aquifers, in many countries worldwide (Bender et al., 2001; Fiorillo et al. 2020; Kitterød et al. 2022; Lone et al., 2021). Besides the direct value, springs supply GDEs (Kalvāns et al. 2021; Koit et al. 2021; Terasmaa et al., 2020), have a historical and tourism value, deliver educational and awareness-raising services through citizen science (Koit et al., 2023), and are often consumed as drinking water due to their better taste. High naturally occurring iron levels in many Latvian aquifers negatively affect the taste and water colour, thus motivating people to switch to springs or highly expensive bottled water (Retike et al., 2016b; Kitterød et al., 2022).

Springs are the only place where groundwater naturally becomes visible to society. Better communication about groundwater is crucial, and springs are an excellent topic for this purpose (Koit et al., 2023). According to Terasmaa et al. (2020), stakeholder engagement, such as through citizen science, is crucial to raise overall awareness about groundwater protection. A comprehensive review article by Kirschke et al. (2022) has summarized 85 citizen science projects in the field of freshwater quality monitoring. Some of the highlighted effects of citizen science projects were the increase of the temporal and spatial scale of data, awareness raising, or citizen engagement in research and politics. Hydrogeologists should communicate about groundwater with other disciplines, policymakers, and society at large to ensure that decisions are made based on an accurate understanding of groundwater systems (Petitta et al., 2023). Here, springs are the bridge between nature experts via GDEs and water managers as they supply drinking water. Mapping of new spring locations (data gathering) and visual monitoring during the seasons (participatory research) would be the activities that could significantly benefit future hydrogeological studies in Latvia. A more educated and aware society would lead to more groundwater-related actions from local citizens to national and international levels in the form of new research, better monitoring, and more sustainable water policies.

3.2. Characterization of major processes responsible for groundwater chemical composition

3.2.1. Geochemical classification of the active water exchange zone

Three major geochemical characteristics could be extracted by the principal component analysis being responsible for groundwater evolution in the active water exchange zone in Latvia. Initially, the Kaiser criterion suggested only two principal components (PCs) to be retained having eigenvalues greater than 1 (Kaiser, 1958). However, after several tests, three PCs were extracted explaining 84% of the total variance in the data set (Table 6).

PC 1 explains the greatest variance and groups the positive loadings of Na^+, K^+, and Cl^- (Table 6). PC 2 is characterized by highly positive loading of HCO_3^-, Ca^+ and Mg^{2+}. The last, PC 3, explains the least amount of variance and contains highly positive loading of SO_4^{2-} and Ca^{2+}. The results reflect well known groundwater end members observed in the active water exchange zone (Levins et al., 1998), while the explained variance of each type brings new insights. The Ca–Mg–HCO_3 water type represented by PC 2 is the most common groundwater type in the active water exchange zone due to the omnipresent carbonate minerals in the Quaternary cover and the humid climate, and therefore being actively used in water supply (Kitterød et al., 2022), yet PC 2 represents only 20% of the variance. The PC 1 reflects increased salinity and shift towards Na–Cl water type and explains more than 50% of the variance. This type of water is generally found starting from the Middle-Lower Devonian to the Cambrian aquifer, but not being the dominant water type in the active water exchange zone.

Table 6. Principal components loadings and explained variance for three major groundwater geochemical characteristics (components) of the active water exchange zone in Latvia (variables with PC loadings greater than 0.6 are considered to be significant and are marked in bold).

Parameter	PC 1	PC 2	PC 3
Ca^{2+}	0.168	**0.652**	0.667
Mg^{2+}	0.524	**0.625**	0.428
Na^{+}	**0.916**	0.104	0.182
K^{+}	**0.824**	0.139	0.123
HCO_3^-	0.007	**0.933**	–0.139
Cl^-	**0.783**	–0.001	0.381
SO_4^{2-}	0.331	–0.099	**0.878**
Eigenvalue	3.69	1.40	0.79
Explained variance (%)	52.67	20.10	11.30
Cumulative % of the variance	52.67	72.72	83.98

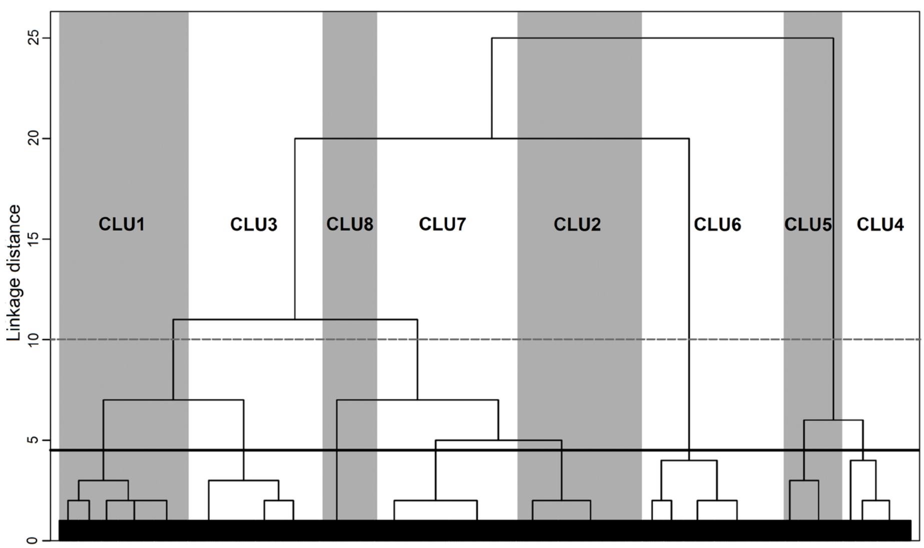

Figure 10. Dendrogram from hierarchical cluster analysis showing the division of groundwater samples into eight clusters (CLU) based on the major ion composition. The black line reflects eight retained clusters for further analysis, dashed line shows the initially delineated four clusters.

Here it is worth mentioning that around 16% of the samples included in PCA were time series (samples from the same locations) typically installed in areas having a risk to water quality depletion (e.g., depression cones, fractures), and could partly account for the deviation. Finally, the PC 3 accounts for the gypsum dissolution process and reflects the Ca–SO_4 water type characteristic to areas where gypsum is encountered in Upper and Lower Devonian aquifers (mainly in the Upper Devonian Salaspils formation), but also can be found in other parts of the active water exchange zone due to water mixing (Levins et al., 1998).

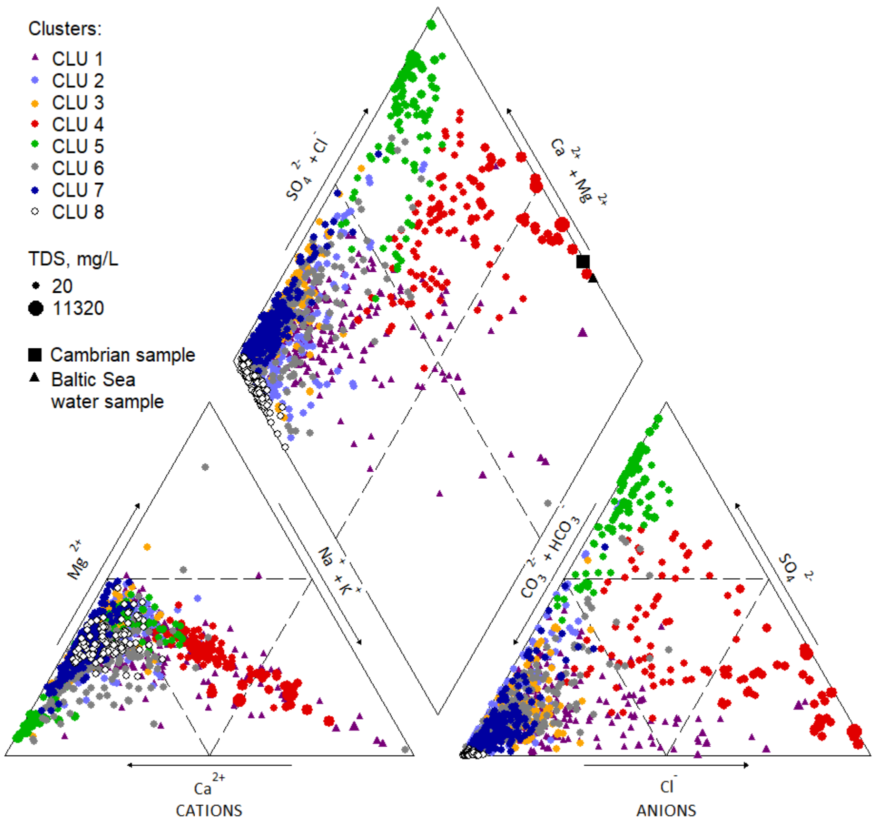

Figure 11. Piper diagram showing the composition of groundwater samples from the active water exchange zone labelled according to delineated clusters (CLU). For the interpretation needs the samples from the Baltic Sea and Cambrian aquifer were added to the diagram. Symbol size is associated with total dissolved solids (except for Cambrian and Baltic Sea water samples).

The main result of hierarchical cluster analysis (HCA) performed on 1442 groundwater samples is a dendrogram (Figure 10) grouping groundwater samples based on their geochemical similarities and dissimilarities. By observing the dendrogram four large groups can be easily identified (see the dashed line in Figure 10) but via an iterative process, it was decided to delineate eight geochemically distinct groundwater groups or clusters (CLUs) by moving the Phenon line in the dendrogram.

There is no rule of thumb on how to choose the final number of clusters rather than a matter of visual observation and interpretation (Cloutier et al., 2008) driven by the aim of the study – here, to bring new insights into major geochemical processes responsible for the evolution groundwater in the active water exchange zone. The dendrogram represents the level of similarity between clusters, for instance, CLU 2 and CLU 7 have the lower linkage distance between eight delineated clusters and thus are expected to be the most alike considering the input data – the major ions. While groundwater samples from CLU 4 and CLU 5 are linked to the other clusters at an elevated distance thus indicating a rather distinct major ion composition if compared to the rest of the clusters.

The Piper diagram (Figure 1) presents groundwater samples belonging to a certain cluster (Figure 10). It can be observed that a large part of the samples falls within Ca–Mg–HCO_3 water type (CLU 2, 3, 6–8) and strongly overlap, while CLU 1, 4, and 5 can be easily separated by visual observation. The groundwater samples from CLU 4 are in the diamond shape area characteristic to shift towards Na–Cl water type and consequently have increased salinity in the form of large TDS (Levins & Gosk, 2008; Cloutier et al., 2008). The upper part of the diamond shape represents a shift towards Ca–SO_4 water type and here are located samples from CLU 5 also having increased TDS values. Finally, the groundwater samples from CLU 1 show enrichment in Cl^- along with no progressive addition of SO_4^{2-} and part of the samples from CLU 1 is in the middle of the diamond-shaped area that indicates the mixing of waters with distinct chemical compositions.

The plot of the principal component scores represents the influence of the components on the groundwater samples (Figure 12). To ease the interpretation the axis in Figure 12, a was labelled as "Na–Cl salinity" versus "Ca–Mg–HCO_3 hardness", while in Figure 12, b as "Na–Cl salinity" versus "Ca–SO_4 salinity". The groundwater samples from CLU 6 are in the lower-left parts of the diagrams and are associated with low salinity and low hardness. On the contrary samples from CLU 4 and CLU 5 are both associated with high salinity but of different origins and are coupled with low (for CLU 4) or low-moderate (for CLU 5) hardness. Groundwater samples from CLU 1 and CLU 3 show similar patterns for hardness but not for salinity components. While the samples from CLU 1 are related to moderate up to high salinity for both salinity types, namely Na–Cl and Ca–SO_4, the samples from CLU 5 occasionally show moderate salinity associated with Ca–SO_4 salinity component only. Majority of the groundwater samples from CLU 2 and 7 fall in the middle of the quadrants showing low to moderate impacts of hardness and both salinities. Finally, the samples from CLU 8 are associated with medium-high hardness coupled with low scores for salinity components.

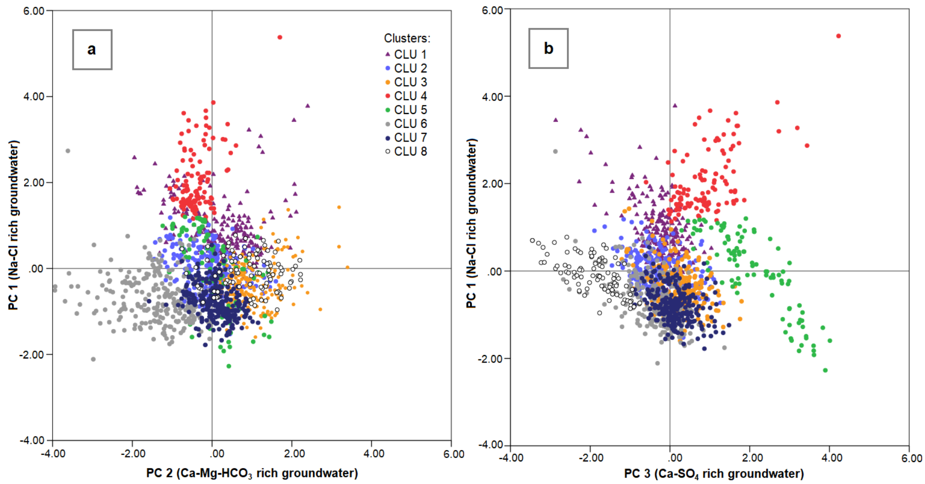

Figure 12. Plot of principal component scores for groundwater samples for the a) first two and b) first and third principal components. For interpretation needs principal component 1 is labelled as "Na–Cl salinity", principal component 2 is labelled as "Ca–Mg–HCO_3 hardness" and principal component 3 is labelled as "Ca–SO_4 salinity" (see Table 6 for all results). Groundwater samples are grouped according to their representative clusters (CLU).

The multivariate statistical analysis (PCA and HCA) and thus the division into eight clusters were performed only on the major ions. One major drawback of this approach is that the elements that are sensitive to human health (such as As, F) often occur in high concentrations only locally (Walter et al., 2019). Therefore, the eliminated parameters (trace elements, nitrogen compounds) were later assessed within each cluster based on much smaller data sets. The chosen approach well supported the number of retained clusters and gave new insights into possible evaluation paths of groundwater in the active water exchange zone (Figure 13), thus can be proposed when dealing with scarce geochemical data sets that have many missing values. The major results are summarized in Table 7, while the information about the variance of groundwater chemical composition within each cluster is presented in Paper X.

Table 7. Main geochemical and hydrogeological characteristics of eight distinct groundwater types (clusters) of the active water exchange zone obtained from the hierarchical cluster analysis (average depth represented as 25th and 75th percentile; MW – monitoring well, WS – water supply well, SP – spring, PW – project well, DR – drainage).

Cluster (sample size)	Dominant sampling source	Average depth, (m)	Aquifer material	Dominant aquifers	Average TDS, (mg/L)	Median water type	Characteristic parameters (median values)
CLU 1 ($N = 218$)	MW, WS, SP, PW	4–100	Sandstone, sand, dolomite, till	Q, D_3*gj*, Middle Devonian	520–700	Ca–Mg–HCO_3	–
CLU 2 ($N = 213$)	MW, WS, PW	4–90	Sandstone, sand, dolomite	Q, D_3*gj*, Middle Devonian	400–500	Ca–Mg–HCO_3	Highest Al
CLU 3 ($N = 223$)	PW, SP, DR	2–7	Till, sand, dolomite	Q, D_3*pl-slp*	570–750	Ca–Mg–HCO_3	Highest Cd, Mn, Ni, Pb, U, Zn, NO_3^-
CLU 4 ($N = 115$)	WS, MW	65–170	Sandstone	Middle and Lower Devonian	780–1520	Ca–Mg–Na–Cl–HCO_3	Highest B, Br, Rb, Sb, Se, V
CLU 5 ($N = 98$)	MW, WS, SP	15–100	Sandstone, dolomite, gypsum	D_3*pl-slp*, D_3*gj*	800–2050	Ca–Mg–SO_4	Highest Cu, F, Li, Sr
CLU 6 ($N = 242$)	PW, SP, MW	3–15	Sand, sandstone	Q, D_3*gj*, D_2*br*	170–300	Ca–Mg–HCO_3	Low trace elements, nitrogen compounds, TDS
CLU 7 ($N = 240$)	SP, PW, WS	3–50	Sand, sandstone, dolomite	Q, Upper and Middle Devonian	410–490	Ca–Mg–HCO_3	–
CLU 8 ($N = 93$)	MW, WS	25–75	Sandstone, dolomite	Upper and Middle Devonian	420–570	Ca–Mg–HCO_3	Highest As, Ba, Fe_{tot}, Si, NH_4^+ and low SO_4^{2-}, Cl^-, NO_3^-

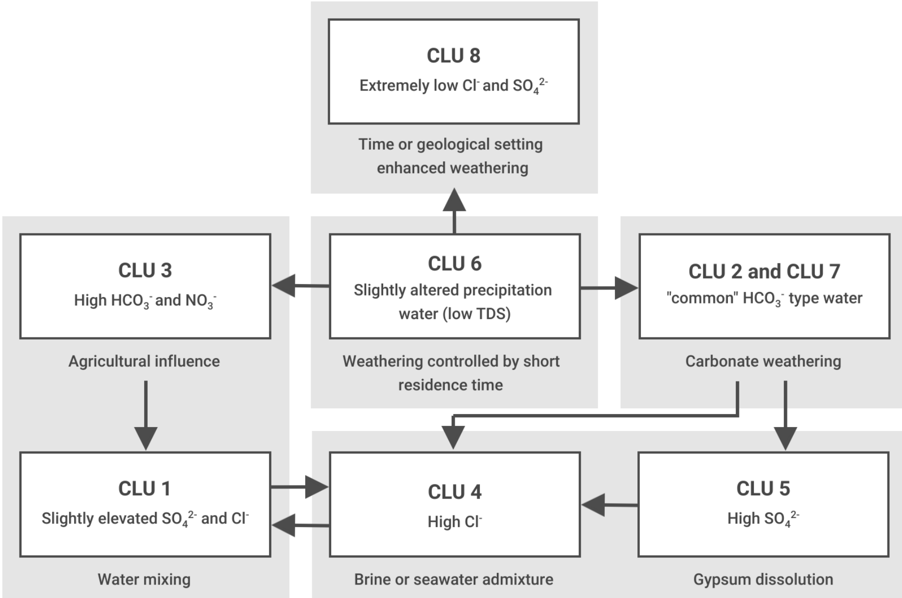

Figure 13. The evolution paths of groundwater geochemistry in the active water exchange zone in Latvia. Grey areas reflect a close linkage distance observed by hierarchical cluster analysis.

Groundwater from CLU 6 has the lowest TDS and major ion values as well as low concentrations of most trace elements (Table 7). Considering the relatively shallow depth and the fact that groundwater is undersaturated to calcite (Figure 14), the groundwater samples from CLU 6 reflect slightly altered precipitation water in the local recharge areas where water has not yet equilibrated with most of the sediment-forming minerals. Consequently, CLU 6 can be considered as starting point or initial composition for any of the following clusters.

Groundwater samples from CLU 2 and CLU 7 both belong to the Ca–Mg–HCO_3 water type commonly found in sandy Quaternary deposits and Upper and Middle Devonian sandstone and dolomite aquifers. Samples are mainly taken from water supply wells having good groundwater quality. The dominance of positive PC 2 (Figure 12) and the fact that groundwater is mainly saturated with respect to calcite (Figure 14) suggests that both clusters result from carbonate dissolution (Cloutier et al., 2008). The major difference between CLU 2 and CLU 7 is average depth (larger for CLU 2) and slightly higher concentrations of major ions Na^+, K^+, SO_4^{2-} and trace elements Sr, Rb, B.

Strontium concentrations increase along the flow path due to incongruent reactions with carbonates and can be used as a residence time tracer, however, Sr also can be added from anhydrite or gypsum dissolution having celestine inclusions (Edmunds & Smedley, 2000). Natural B sources in groundwater are water-rock interaction (carbonate rocks and evaporates) (Karro et al., 2000), therefore higher values could be associated with longer residence time in aquifers. Neither this nor previous studies

(Dēliņa, 2006; Levins & Gosk, 2008) have observed the influence of water-bearing rocks on groundwater composition except for gypsum and carbonates. The reason is the widespread carbonate cement for the sand grains in sandstones. The previous study by Levins and Gosk (2008) also did not identify the widespread Ca–Mg–HCO_3 water type (here observed in CLU 2, CLU 6, and CLU 7) and it is probably due to the inclusion of trace elements and nitrogen compounds into statistical analysis that overwhelmed the natural conditions. Also, the previous studies (Dēliņa, 2006; Gosk et al., 2008; Levins & Gosk, 2008) mainly addressed shallow groundwaters which are typically more affected by pollution than deeper situated, confined aquifers.

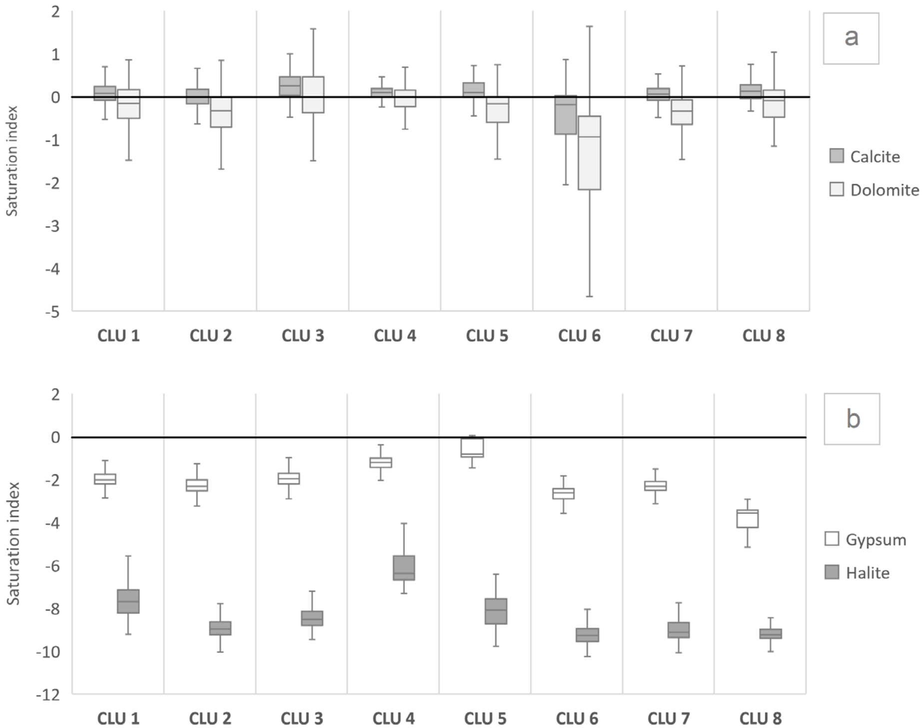

Figure 14. Saturation indices for a) calcite and dolomite and b) gypsum and halite grouped according to eight geochemically distinct groundwater groups (clusters) of the active water exchange zone (outliers not shown). Threshold for saturated samples is above zero indicated with black line.

Groundwater samples from CLU 8 have extremely low SO_4^{2-} and Cl^- concentrations, both under 3 mg/L. High NH_4^+ and low NO_3^- values can be considered indicators for strongly reducing conditions in the aquifer. High Ba content can occur due to low SO_4^{2-} concentrations, otherwise, Ba would be removed from the water solution and precipitated as barite (Mokrik et al., 2009). The distribution of groundwater samples in CLU 8 through the territory of Latvia can be divided into three large groups: (1) fresh groundwater samples from Lower Devonian aquifers in the northeast part of Latvia (aquifers contain brackish or saline water in other parts of Latvia); (2) sampling sites near the city of Daugavpils in the southeast part of Latvia where buried paleo valleys are present; and (3) samples from typical carbonate sediments in the Upper Devonian and Permian aquifers with no gypsum present.

CLU 8 is plotted slightly below the one-to-one equivalent line (Figure 15) and indicates Ca^{2+} and Mg^{2+} replacement with Na^{+} and K^{+}. One of the hypothesis is that groundwater samples from CLU 2, CLU 6, and CLU 7 represent modern groundwater, while CLU 8 represent groundwater that has infiltrated during pre-industrial times when Cl^{-} and SO_4^{2-} concentrations were lower (Edmunds and Smedley, 2000). The highest SO_4/Cl ratios among the clusters accompanied by relatively high Sr values support this assumption. Alternatively, CLU 8 can reflect mature groundwater from well-washed rocks, e.g., local circulation systems, where all the easily soluble components such as Cl^{-} and SO_4^{2-} have been removed from the sediments. The high Fe_{tot} and low Mn values can support this hypothesis. Mn (IV) compounds are reduced before the Fe(III) compounds, giving us the chance to speculate that all the Mn has already been washed out of the sediments. To sum up, here more research is encouraged e.g., using stable isotopes and groundwater age dating (Ženišová et al., 2015).

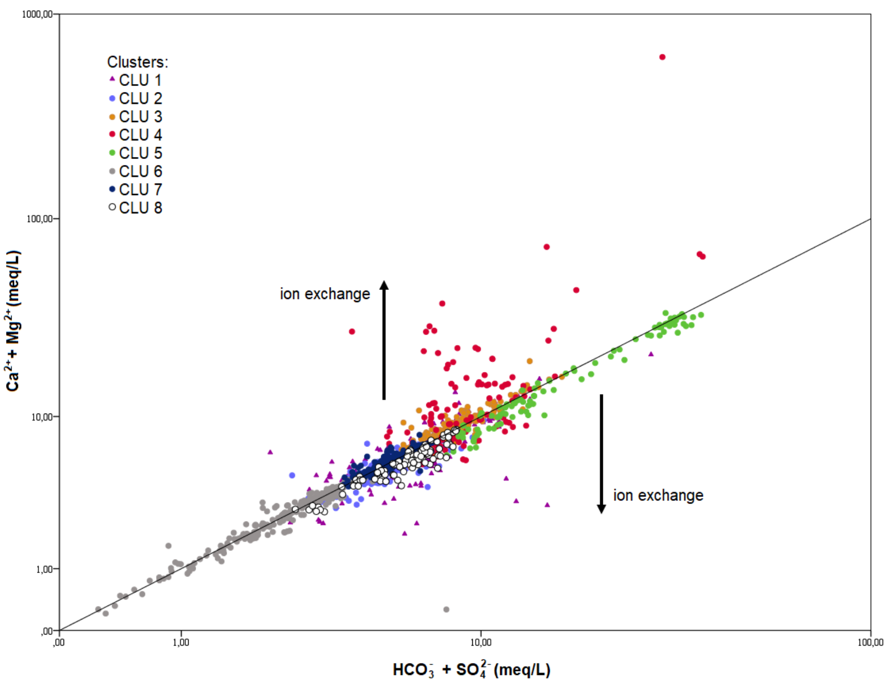

Figure 15. Bivariate plot of relationships between Ca^{2+}+Mg^{2+} and HCO_3^{-} and SO_4^{2-} indicating ion exchange processes.

Groundwater samples from CLU 3 reflect water table aquifers or, in some cases, samples taken from drainage. CLU 3 is characterized by highlighted NO_3^{-} and a variety of trace elements (U, Cd, Mn, Ni, Pb, U, Zn) (see Table 7) which are mainly associated with agricultural influence (Helena, 2000; Levins & Gosk, 2008). The high NO_3^- values in shallow groundwater reflect diffuse contamination and are the result of the nitrification process (Valle Junior et al., 2014) and have been previously observed by Levins and Gosk (2008). Drainage and irrigation processes promote groundwater aeration (Levins & Gosk, 2008) resulting in certain increased trace element values that are more mobile under oxidizing conditions like U. Rather high TDS values for shallow groundwater and the fact that groundwater is saturated with respect to both calcite and dolomite suggest that ploughing has promoted the dissolution of carbonate and gypsum in the soils (Valle Junior et al., 2014). The possible evolution for CLU 3 is directly from CLU 6 (Figure 13).

Samples from CLU 4 reflect two main origins: (1) groundwater with high salinity from or mixed with groundwater from passive or stagnant water exchange zones of greater depth and (2) groundwater highly affected by seawater intrusion in the Riga and Liepaja regions from the Upper and Middle Devonian aquifers (Bikše & Retike, 2018; Kitterød et al., 2022; Pulido-Velazquez et al., 2022; Retike & Bikše, 2018). Groundwater from both origins is saturated with respect to calcite and dolomite, however, only brines are also saturated for gypsum and close to the saturation for halite. The highest values of many trace elements observed in CLU 4 (Table 7) are characteristic of waters having high salinity (Faye et al., 2005; Cloutier et al., 2008). The main processes controlling the chemistry of CLU 4 are gypsum dissolution, groundwater mixing, and ion exchange between Ca^{2+} and Na^+. It can be observed that due to ion exchange the Ca^{2+} amount in groundwater increases (Figure 15).

The samples from CLU 5 belong to or are shifted towards the $Ca–SO_4$ water type. The dominant geochemical process forming CLU 5 is gypsum dissolution which can be justified by sample saturation with respect to calcite and gypsum (Figure 14) and by the highest "$Ca–SO_4$ salinity" scores (Figure 12, b). The majority of samples are located in areas having gypsum in sediments or being known to contain sulfate-rich groundwater (potentially as a result of water mixing). The characteristic trace elements for CLU 5 (Table 7) are known to be incorporated in carbonates or evaporites as secondary minerals, for example, celestine (Faye et al., 2005; Klimas & Mališauskas, 2008). In Latvia, celestine is commonly found in association with gypsum (Lukševičs et al., 2012). Very low Ba concentrations occur mainly because of barite precipitation (Monjerezi et al., 2012), while the presence of F in evaporites does not produce extremely high fluorine concentrations due to typically high Ca^{2+} concentrations in groundwater and consequent fluorite precipitation (Karro & Uppin, 2013). $Ca–SO_4$ water type groundwater typically evolves from $Ca–Mg–HCO_3$ groundwater, therefore the evolution path is from less mineralized bicarbonate waters from CLU 2 or CLU 7 (Figure 13).

CLU 1 potentially reflects the most diverse geochemical processes. Part of the samples belongs to $Ca–Mg–HCO_3$ groundwater from confined aquifers with slightly to high elevated Cl^- concentrations and noticeable ion exchange process (Figure 15). Some of the sampling sites are located in the Riga, Jurmala, and Liepaja vicinities where saltwater intrusion occurs (Bikše & Retike, 2018; Kitterød et al., 2022; Pulido-Velazquez et al., 2022; Retike & Bikše, 2018), thus reflecting a potential connection between CLU 1 and CLU 4 (Figure 13). The placement of some samples close to $Na–HCO_3$ water type (Figure 1), together with samples plotting under the one-to-one equivalent line where Ca^{2+} deficiency can be observed (Figure 15) suggests the aquifer freshening process. Few samples from CLU 1 show very high Na^+ and Cl^- values as well as Na/Cl ratio close to 1. Those samples could be the result of anthropogenic influence and halite dissolution delivered by road de-icing (Cloutier et al., 2008). As a result, CLU 1 shows two potential origins: (1) anthropogenic influence in urban areas and (2) freshwater mixing with more saline water or aquifer freshening.

3.2.2. Evaluation of Quaternary groundwater vulnerability

This study particularly addresses shallow groundwater from Quaternary sediments as they are the most vulnerable to pollution (Kalvāns et al., 2021; Kitterød et al., 2022). In addition to major ions, nitrogen compounds ($N\text{-}NO_3^-$, $N\text{-}NO_2^-$, $N\text{-}NH_4^+$) were included in multivariate statistical analysis (PCA and HCA) performed on 650 samples as they were essential to reach the aim of the study – to identify patterns in Quaternary groundwater composition that could be associated with vulnerability to land use. In this case, the reduction of the spatial coverage of the dataset could be justified. Information about *pH* is essential when analysing unconfined groundwater therefore was analysed within clusters but not added to the multivariate analysis due to too many missing values. TDS values were calculated from major ions and thus were not included in the analysis but were analysed within the delineated clusters.

Table 8. Principal component loadings and explained variance for three major Quaternary groundwater geochemical characteristics (components) in Latvia (variables with PC loadings greater than 0.5 are considered to be significant and are marked in bold).

Parameter	PC 1	PC 2	PC 3
Ca^{2+}	**0.89**	0.19	0.07
Mg^{2+}	**0.88**	0.28	0.08
Na^+	0.40	**0.74**	–0.08
K^+	0.20	**0.68**	0.22
HCO_3^-	**0.89**	0.09	0.07
Cl^-	0.40	0.69	0.11
SO_4^{2-}	0.32	0.49	0.23
$N\text{-}NH_4^+$	–0.19	**0.70**	–0.11
$N\text{-}NO_2^-$	–0.12	0.19	**0.82**
$N\text{-}NO_3^-$	0.29	–0.08	**0.82**
Eigenvalue	4.03	1.46	1.34
Explained variance (%)	40.32	14.63	13.36
Cumulative % of the variance	40.32	54.95	68.30

Based on the Kaiser criterion (Kaiser, 1958), three principal components (PCs) having eigenvalues greater than 1 were retained explaining 68% of the total variance in the data set. Principal component loadings (Table 8) suggest that PC 1 reflects the most common Ca–Mg–HCO_3 water type in Quaternary sediments of Latvia (Dēliņa, 2006) and accounts for nearly 40% of the explained variance. The highest positive loadings of parameters Na^+, K^+, Cl^-, and N-NH_4^+ suggest that PC 2 outlines groundwater samples having slightly highlighted salinity (Retike et al., 2016b). PC 3 groups the highest positive loadings for N-NO_2^- and N-NO_3^- probably indicating an active nitrification process (Valle Junior et al., 2014).

All samples were divided into four groups based on their geochemical similarities and dissimilarities using hierarchical cluster analysis (HCA) and by moving the Phenon line (Figure 16). The major results from PCA and HCA in form of median values are summarized in Table 9 together with TDS and *pH* values. It can be observed that all groups belong to a commonly found groundwater type in Latvia – bicarbonate water type (Figure 17).

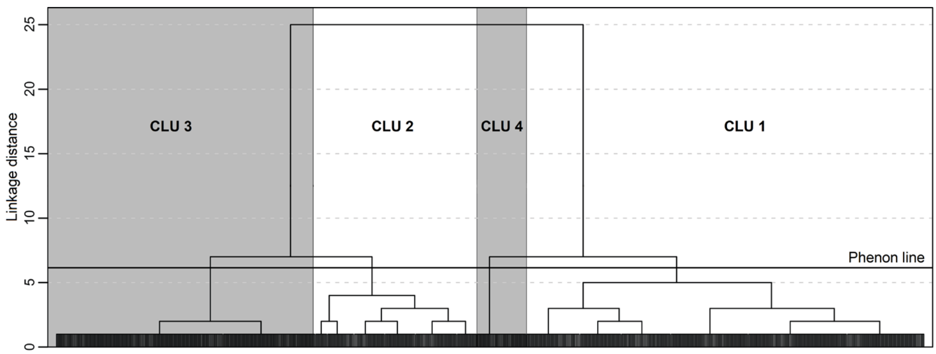

Figure 16. Dendrogram from hierarchical cluster analysis showing the division of Quaternary groundwater samples into four clusters based on the major ion and N-NO_3^-, N-NO_2^-, and N-NH_4^+ composition. The black line reflects four retained clusters for further analysis and the location of the Phenon line.

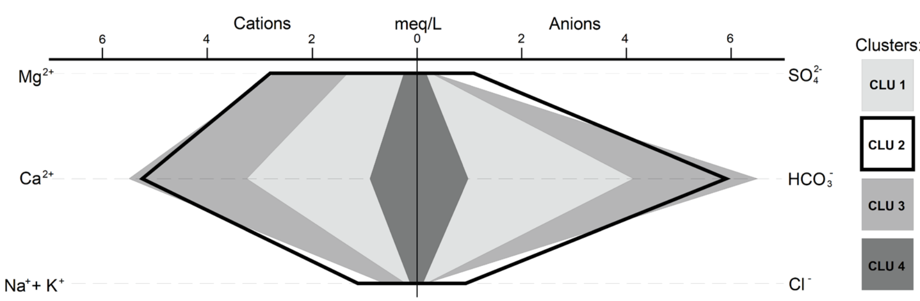

Figure 17. Stiff diagrams showing the median major ion composition of four delineated clusters by hierarchical cluster analysis.

It can be observed that the highest median values for major ions (except HCO_3^-) can be associated with samples grouped into CLU 2. The highest median positive loading of PC 2 coupled with the highest median TDS confirm the hypothesis of groundwater mixing with higher salinity water dominated by Na^+ and Cl^-. In some samples, Na/Cl ratio was close to 1 indicating the potential halite contribution from road de-icing (Cloutier et al., 2008). According to Dēliņa (2006), higher Na^+, Cl^- and K^+ values in Quaternary groundwater were found only in sandy deposits near the coastline while the distribution of sampling sites for CLU 2 cover much wider territories (Figure 18). However, most of the samples are in the Nitrate vulnerable zones set by the EU Nitrates Directive (Directive 91/676/EEC).

Table 9. The median chemical composition of Quaternary groundwater in Latvia for the four delineated groups (clusters) and the whole data set (highest values are marked in bold and the lowest are underlined; TDS values are calculated based on major ions and $N\text{-}NO_3^-$; PC – principal component, N – sample size).

Parameter	CLU 1 (N = 298)	CLU 2 (N = 121)	CLU 3 (N = 194)	CLU 4 (N = 37)	All samples (N = 650)
Ca^{2+} (mg/L)	65.5	**105.0**	**105.0**	<u>18.0</u>	81.0
Mg^{2+} (mg/L)	16.0	**34.0**	30.0	<u>3.1</u>	22.6
Na^+ (mg/L)	4.1	**20.0**	7.2	<u>2.2</u>	5.7
K^+ (mg/L)	1.5	**9.9**	2.5	<u>1.4</u>	2.2
HCO_3^- (mg/L)	252.5	360.0	**412.5**	<u>60.0</u>	315.0
Cl^- (mg/L)	6.0	**33.0**	15.0	<u>4.0</u>	11.0
SO_4^{2-} (mg/L)	13.0	**52.0**	26.5	<u>8.2</u>	20.0
$N\text{-}NH_4^+$ (mg/L)	0.18	**0.48**	<u>0.14</u>	0.19	0.18
$N\text{-}NO_2^-$ (mg/L)	0.01	0.01	0.01	0.01	0.01
$N\text{-}NO_3^-$ (mg/L)	<u>1.20</u>	10.23	**11.60**	1.68	3.19
pH	**7.4**	7.3	**7.4**	<u>6.5</u>	**7.4**
TDS (mg/L)	383.8	**776.1**	630.5	<u>100.9</u>	495.7
PC 1	−0.29	0.37	**0.78**	<u>−2.27</u>	0.10
PC 2	<u>−0.50</u>	**1.46**	−0.16	−0.33	−0.16
PC 3	<u>−0.41</u>	**0.57**	0.34	0.38	0.02

CLU 4 shows the lowest median concentrations of all major ions, TDS and *pH*, as well as the lowest median PC 1 loading compared with the other three clusters. All listed parameters in CLU 4 have concentrations much lower than in slightly altered precipitation water found in the earliest study (Retike et al., 2016b). The CLU 4 reflects $Ca–HCO_3$ water type and there are relatively low Mg^{2+} concentrations compared to Ca^{2+} concentrations. Thus, the groundwater samples from CLU 4 can be interpreted as very young groundwater formed in sandy deposits and representing local recharge areas. The CLU 1 groups $Ca–Mg–HCO_3$ type groundwater with the most typical chemical characteristics for Quaternary sediments in Latvia (Dēliņa, 2006), and sampling sites are distributed across the whole country with no spatial pattern (Figure 18).

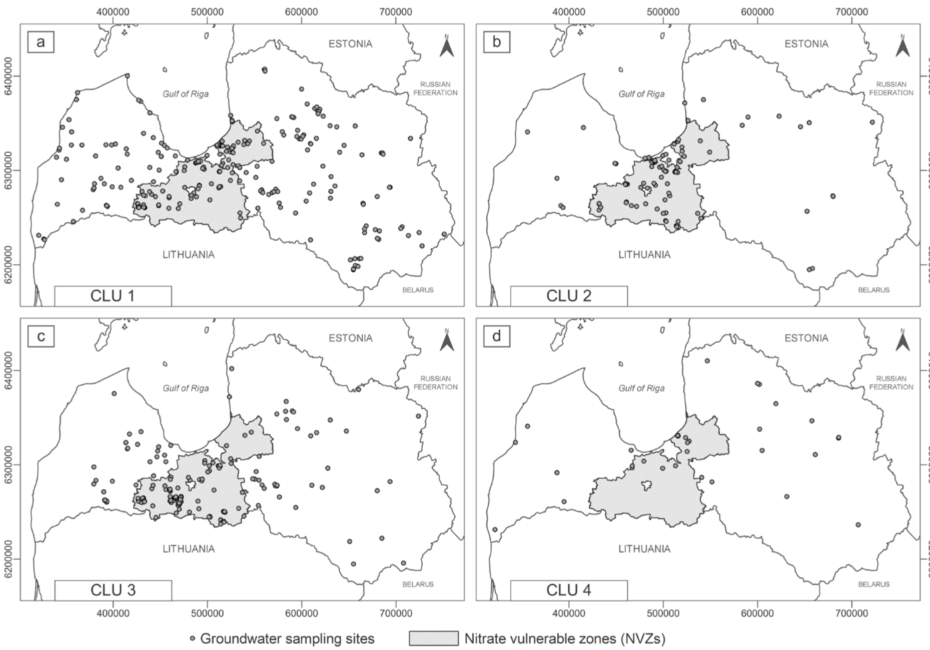

Figure 18. Spatial distribution of Quaternary groundwater sampling sites (springs and wells) divided into clusters using hierarchical cluster analysis: a) Cluster 1, b) Cluster 2, c) Cluster 3, d) Cluster 4.

Groundwater samples from CLU 3 also belong to $Ca–Mg–HCO_3$ water type and have the highest median Ca^{2+}, HCO_3^- and NO_3^- values, highest positive PC 1, and positive PC3 loadings. Similar results were obtained in a previous study (Retike et al., 2016) indicating diffuse agricultural influence. For example, Valle Junior et al. (2014) suggest that ploughing may promote the dissolution of carbonate and gypsum in the soils and increase the value of TDS in groundwater. Likewise, the location of sampling points from CLU 3 (Figure 18) in the most intensively used areas for agricultural needs (in the Lielupe and Gauja river basins) supports the hypothesis.

As can be observed from Table 9, the highest NO_3^- concentrations can be found in CLU 2 and CLU 3. According to CORINE Land Cover data (Figure 19, a), CLU 3 mostly represents agricultural areas and then artificial surfaces, but CLU 2 – artificial surfaces and then agricultural areas. Consequently, this explains the highest Na^+ and Cl^- concentrations in CLU 2 and supports the theory of possible road de-icing influence. Likewise, CLU 3 shows the highest $N\text{-}NO_3^-$ concentrations most likely produced via the nitrification of N-fertilizers (Valle Junior et al., 2014), while the lowest median $N\text{-}NO_3^-$ concentrations are found in CLU 1 and CLU 4. In both clusters, dominant land covers are forests and semi-natural areas or wetlands.

The fertility of the soil depends on the amount of clay minerals in it, therefore, areas with the highest clay content are mainly used in agriculture. Likewise, areas with more clay in the soil are considered to be of lower vulnerability to pollution. As a result, areas with the lowest groundwater vulnerability are mostly used in agriculture and have the highest anthropogenic pressure on groundwater. At first, it might seem that the results are contradicting – the most naturally protected areas are also the most polluted according to the nitrogen compound concentrations found in shallow groundwater from Quaternary aquifers. On the contrary, the results should be interpreted as that all Quaternary groundwater in Latvia becomes vulnerable to nitrogen pollution (and probably also to other pollutants) at a certain level of pressure, and that natural groundwater vulnerability should not be solely considered as a protection measure (being the case now) but rather should be assessed in a combination with other factors such as pressure loads or geological peculiarities.

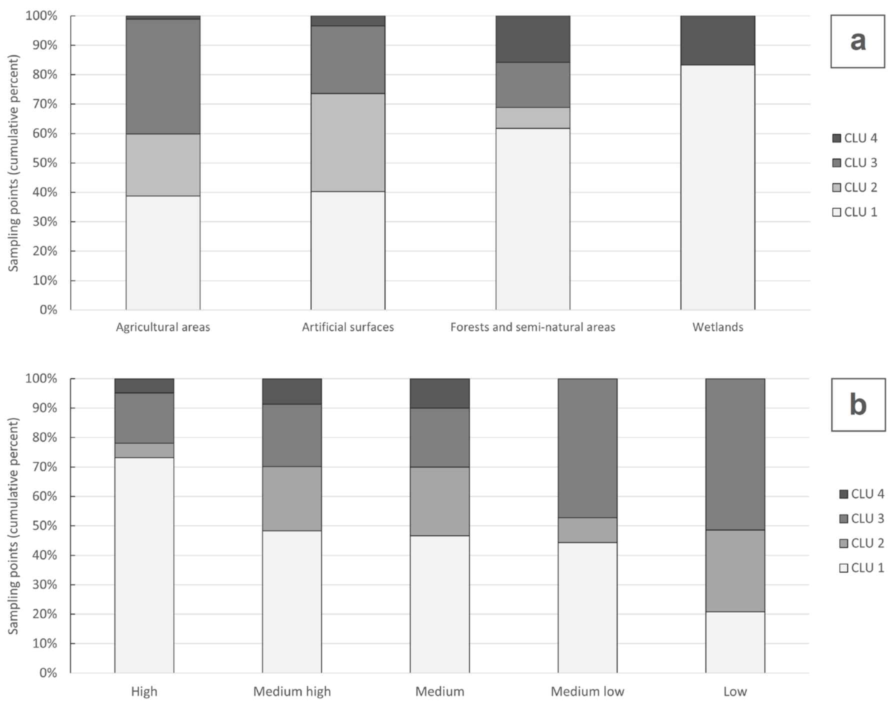

Figure 19. Variation of a) CORINE Land Cover 2012 (CLC, 2012) level 1 classes and b) natural Quaternary groundwater vulnerability classes (Dēliņa and Prols, 2008) within four delineated geochemically distinct Quaternary groundwater groups.

For instance, Kalvāns et al. (2021) propose a groundwater vulnerability to NO_3^- map for the Upper Devonian Plavinas aquifer (D_3*pl*) developed considering specific geological conditions – a thin layer of Quaternary sediments covering the karstic aquifer that is favourable to NO_3^- migration. In other words, such conditions are not favourable for the natural denitrification process typically responsible for the rapid reduction of nitrogen loads and low NO_3^- values in Latvian groundwater deeper than 5 meters (Kitterød et al., 2022). Here, future research is encouraged to identify responsible factors putting certain areas at risk to land use activities or their changes. Furthermore, the areas at risk should be delineated based on a conceptual understanding of groundwater system functioning (Koit et al., 2023) and considered when planning and revising the national groundwater quality monitoring networks.

3.2.3. Assessment and management of seawater intrusion into the freshwater aquifer

Seawater intrusion into the freshwater aquifer at the Baltic Sea coast can be observed in the vicinity of Liepaja – the third most populated city in Latvia. It is an Upper Devonian Mūru-Žagares (D_3*mr–žg*) partly confined aquifer that is formed of weakly cemented sandstones, siltstones, and dolomites in a total thickness of 44–47 m and a depth of 38–43 m. D_3*mr–žg* is covered by the Upper Devonian clayey formations and Quaternary till and sand (Figure 20). Deposits of D_3*mr–žg* aquifer outcrops at the bottom of the Baltic Sea, approximately 5 km from the coast. The cause is the dipping of Devonian deposits towards the southeast (and outcropping at north-northwest) and the lack of Quaternary sediments in some areas at the sea bottom. The underlying formation consists of dolomitic marls, clays, dolomite, and sandstones forming several aquitards and minor aquifers. At the depth of 230–241 m lies the upper Devonian Gaujas and the Middle Devonian Burtnieku formation (D_2*br*+D_3*gj*) – a significant hydraulically connected aquifer with a total thickness of more than 100 m consisting of sandstones and clays. The D_2*br*+D_3*gj* aquifer has no direct connection to the uppermost aquifers and the Baltic Sea, however, the aquifer is mainly used for industrial water supply due to elevated SO_4^{2-} content and TDS from gypsum dissolution. Consequently, for decades the most important aquifer for water supply needs in the Liepaja vicinity has been the D_3*mr–žg* freshwater aquifer (Bikše & Retike, 2018; Kitterød et al., 2022).

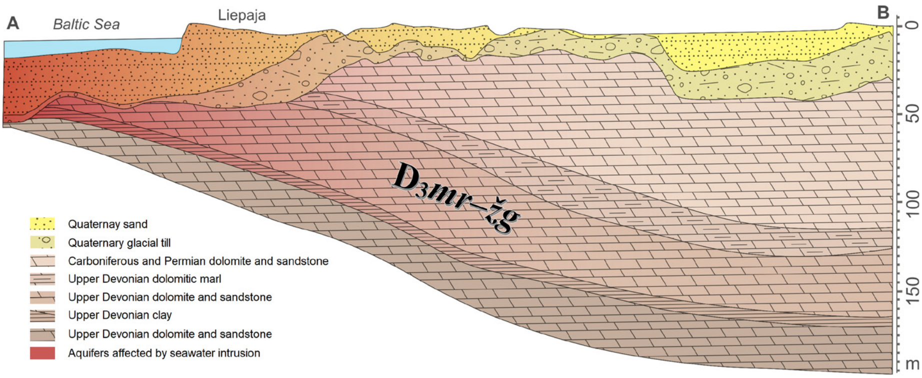

Figure 20. Simplified geological cross-section of the main geological units at Liepāja vicinity (modified after Pulido-Velazquez et al., 2022). A location of cross-section indicated by A-B through the area is given in Figure 22.

Consequences of the intensive groundwater abstraction from D_3*mr–žg* aquifer in the form of an increased salinity have been observed already since the 1930s. However, regular groundwater monitoring started only in 1961 (Figure 21, a) when an already formed depression cone was identified. Switching to a centralized water supply with new wellfield "Otaņķi" (start in 1961) exploiting the same D_3*mr–žg* freshwater aquifer and additionally using deeper situated Middle to Upper Devonian Arukila-Amata (D_2*ar*–D_3*am*) aquifer complex (start in 1967 and 1973) did not reduce the negative pressure on groundwater resources. As a result, the depression cone expanded southeast and in 1986 reached the "Otaņķi" wellfield. In 1986 groundwater levels in the exploited aquifer were reported as 14 m below sea level (Figure 21, a). The depression cone started to decline only at the beginning of the 1990s when groundwater demand significantly dropped due to the collapse of the Soviet Union (Figure 21, b). The groundwater level in the D_3*mr–žg* aquifer has significantly increased since then and currently is above the Baltic Sea level. Consequently, the Cl^- concentrations have decreased in the marginal zone of the affected area, yet the central part of the area still contains high Cl^- concentrations (~2000 mg/L) (Figure 20 and 22a).

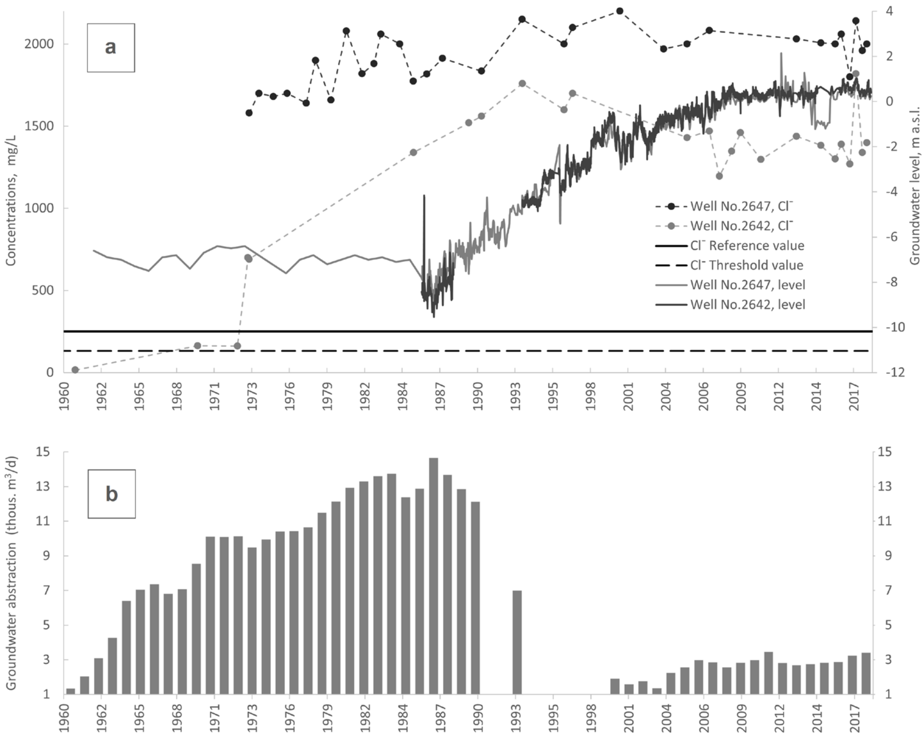

Figure 21. Evolution of seawater intrusion and depression cone formation in D_3mr–žg freshwater aquifer at Liepaja vicinity: a) variation of groundwater levels and chloride concentrations in the groundwater monitoring wells and b) changes in groundwater abstraction from centralized wellfield "Otaņķi" (TV – established threshold value 131.6 mg/L; REF – reference value 250 mg/L).

Yet, any intensification of groundwater abstraction from D_3*mr–žg* freshwater aquifer poses a risk for the activation of seawater intrusion that will take decades to recover. For instance, Spalvins et al. (2004) developed a 3D hydrogeological model to simulate aquifer response on several groundwater abstraction scenarios. It was concluded that groundwater abstraction up to 4.8 thousand m^3/d does not pose a risk for aquifer salinization. This amount is close to the current groundwater abstraction from the centralized wellfield "Otaņķi" supplying part of the Liepaja vicinity (Figure 21, b). Yet, the permissible amount of groundwater abstraction in the "Otaņķi" wellfield is 14 thousand m^3/d and, according to Spalvins et al. (2004) study, that amount can be abstracted only in combination with abstracting groundwater also from specially installed discharge wells to stop saline water migration and reduce the risk to aquifer salinization.

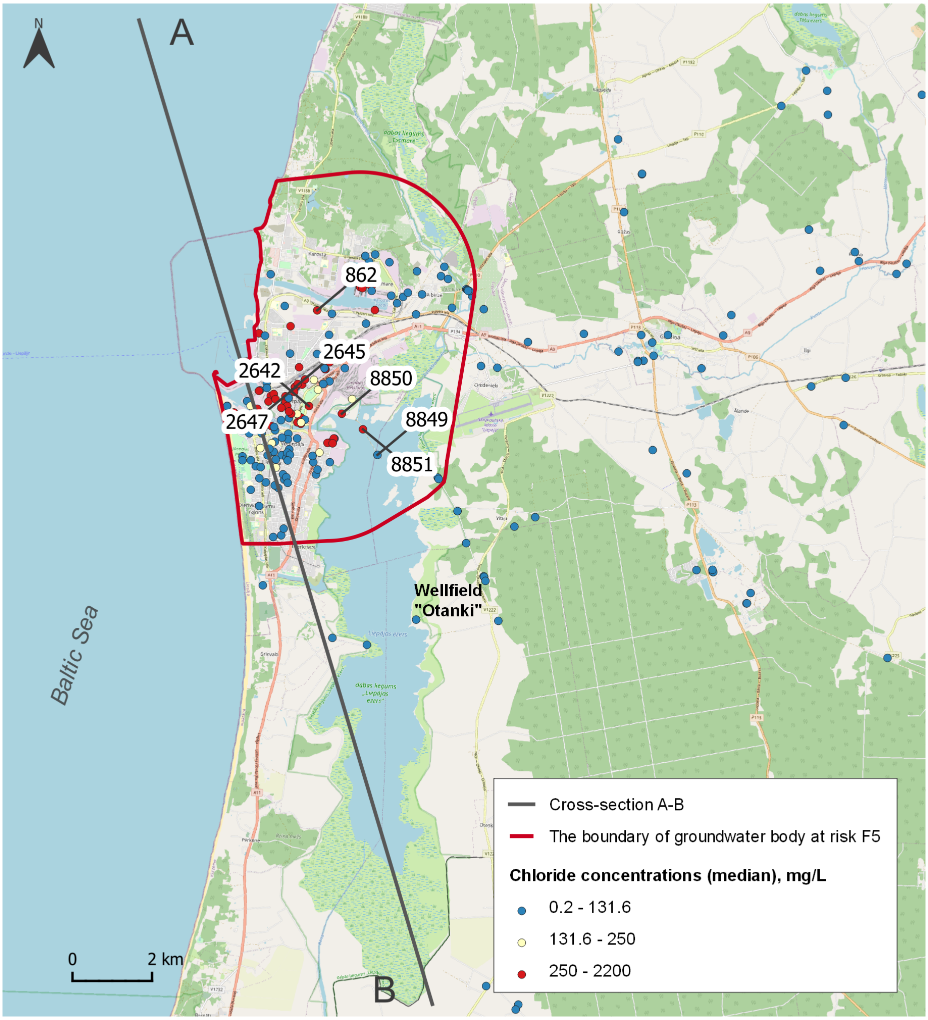

Figure 22. Location of groundwater body F5 affected by seawater intrusion into freshwater aquifer and median Cl^- concentration (mg/L) in the studied period. A vertical cross-section through the area indicated by A–B is given in Figure 20. Categories for Cl^- concentrations are set according to established threshold values (131.6 mg/L) by Retike and Bikše (2018) where groundwater is considered as being at pollution risk, and reference value (250 mg/L) indicating the water is not suitable for drinking. Numbers indicate well numbers being sampled during the water campaign by Retike and Bikše (2018).

The area affected by seawater intrusion in Liepaja is a relatively small part of larger GWB (the total area of GWB F1 is 2974 km^2), therefore the usage of the proposed procedure by the European Commission (2009) with 20% criterion was not applicable. On the one hand, it was nearly impossible to exceed the 20% criterion considering the size of GWB versus the affected area, and that would hide the presence of negative pressures. On the other hand, it would be inappropriate to set the whole GWB in poor status considering the much smaller size of the affected area by seawater intrusion. Yet, the GWB having any saltwater intrusion is automatically set as being in poor chemical status considering the guidelines (European Commission, 2009). Thus, a political decision was made in 2016 to delineate the area affected by seawater intrusion as new GWB F5 (size 46 km^2) and set it as being at risk (Bikše & Retike, 2018), and therefore ease and foster the management process of the area. Consequently, the status of risk makes it mandatory to derive NBLs and establish TVs for the GWB F5 (Retike & Bikše, 2018).

To deliver new data for the establishment of NBLs and derivation of TVs, as well as for status assessment needs of GWB at risk F5, a sampling campaign was carried out in 2017. Wells from the Upper Devonian D_3*mr–žg* aquifer were sampled and their respective database number is indicated in Figure 22. Additionally, two wells from inland background monitoring stations from D_3*mr–žg* aquifer were sampled and a water sample was taken from the Baltic Sea aquatory – all to deliver data for setting endmembers. Dataset and details are provided in Retike and Bikše (2018) paper.

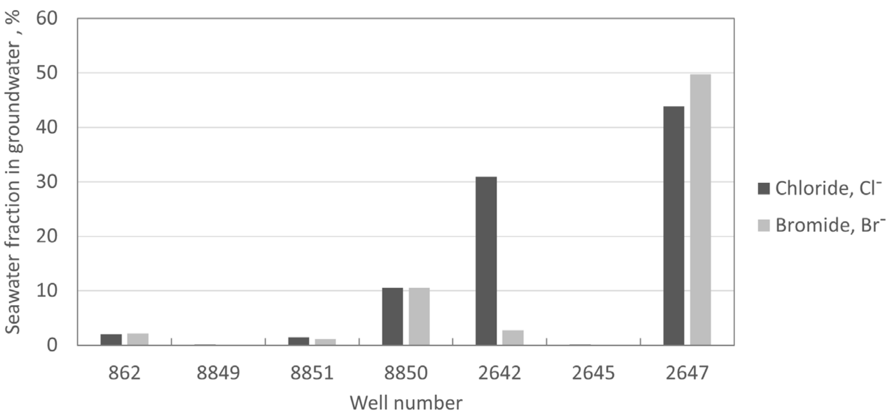

Figure 23. Seawater fractions in groundwater samples from representative monitoring wells of D3mr–žg aquifer calculated by Cl^- or Br^- ions (mg/L).

Seawater fraction in groundwater samples from D_3*mr–žg* aquifer was calculated based on chloride and bromide ions as conservative tracers. Calculation by both tracers yields comparable results for less mineralized groundwater, however, more saline groundwater samples from wells No. 2647 and No. 2642 yield different results (Figure 23). Seawater fraction reaches 50% in the groundwater sample at the central part of the seawater affected zone (distance from coastline about 1.3 km). The seawater fraction significantly decreases with increasing distance from the coastline – at 3.4 km from the coastline the fraction is negligible (1%) in well No. 8851. Wells No. 2647 and No. 2645 are both represent the same aquifer and located in the same area (one monitoring station about 1.3 km from the coastline) but they have different screen intervals, namely No. 2647 has 45–58 m, and well No. 2645 has 72–77 m (for more information see Table 1 and 2 in Retike and Bikše (2018)). Well No. 2647 with a shallower screen interval shows a seawater fraction of up to 50% while well No. 2645 having a deeper screen interval reflects no seawater presence. The cause for such difference is more than 6 m thick clay layer separating the D_3*mr–žg* upper part from the lower part of the aquifer.

Up to 50% of groundwater in the study area consists of seawater. Such high seawater fraction was promoted by continuous groundwater abstraction from the D_3*mr-žg* aquifer. Seawater fraction decreases with increasing distance from the coastline as well as with increasing depth. To assess the extent of seawater intrusion more accurately it is recommended to install new monitoring well in the southern part of the GWB F5 and include in regular quality monitoring private wells No. 8849, 8845, and 8851 located on the mole.

Data provided by groundwater monitoring networks are the basis for the estimation of NBLs (Lions et al., 2021; Menafoglio et al., 2021; Wendland et al., 2005). It is expected that NBLs are based on the long-term and continuous monitoring data collected from representative observation networks, while often limited and poor-quality groundwater chemical composition data require the application of simplified approaches (Bulut et al., 2020). Currently, each member state is free to choose the technique to identify NBLs, while the majority follow the BRIDGE methodology (Müller et al., 2006). BRIDGE is a pre-selection methodology combined with statistical NBL determination. The BRIDGE approach has been widely used and modified in the EU studies: the northwestern part of Estonia (Marandi & Karro, 2008), the southern (Sellerino et al., 2019) and northern Italy (De Caro et al., 2017), the whole Czech Republic (Vencelides et al., 2010), and the transboundary Upper Rhine basin (France, Germany, Switzerland) (Wendland et al., 2008). Often reported disadvantage of the BRIDGE methodology is that by eliminating potentially contaminated samples the final datasets drastically reduce (Bulut et al., 2020; Lions et al., 2021).

In GWB F5 the final NBL for chloride (Cl^-) was set as 13.2 mg/L, for sulfate (SO_4^{2-}) 42.5 mg/L, and for sodium (Na^+) as 22.3 mg/l. Calculated TV for Cl^-, SO_4^{2-} and Na^+ was respectively 131.6, 146.3 and 111.2 mg/L. TV values are officially introduced at the national level by 3rd October 2016 order No. 257 "On the threshold values of polluting substances and their groups in groundwater bodies at risk" on the basis of the Republic of Latvia Cabinet Regulation No. 42 "Regulations Regarding Procedures for Ascertaining of Groundwater Resources and Quality Criteria". Background levels established by the two-step approach are strict and account for the worst-case scenario. Such an approach yields lower TVs therefore it is more sensitive to water quality changes, and it takes more time to reach good chemical status. However, this leads to more sustainable water management in coastal areas where groundwater resources are limited and recovery takes decades.

Urresti-Estala et al. (2013) grouped the NBL identification approaches into two major categories: geochemical methods and hydrochemical modelling techniques. Geochemical methods are based on expert judgment examining individual samples or sets of samples, and the final results are highly subjective. While hydrochemical modelling techniques are technically complex (require a large number of parameters and detailed knowledge of the study area) and are suitable only for small study areas. Meanwhile, Biddau et al. (2017) differentiate between direct methods that use historical data and groundwater dating, and indirect methods which are based on multivariate statistics (especially hierarchical cluster analysis). Several statistical approaches to derive NBLs for Cl^- were tested in different hydrogeological settings across Europe in five case studies representing coastal aquifers of the Atlantic Sea, the Mediterranean Sea, The North Sea, and the Baltic Sea (Liepaja pilot) (Pulido-Velazquez et al., 2022). A detailed sensitivity analysis of the results to different Cl^- constraints (1000, 750, 500, 250 and 125 mg/L) was applied to remove samples affected by anthropogenic impacts. Based on the sensitivity analysis a novel approach that combined results from different statistical methods to identify consistently a feasible range of values for the Cl^- NBL establishment was proposed. For the Liepaja pilot most tested methods and constraints gave similar Cl^- values to the ones obtained before – 13.2 mg/L (Retike & Bikše, 2018) now being the nationally set NBL and a national wide geochemical classification suggesting that in typical carbonate freshwater (similar to the pilot area) Cl^- concentrations for 25^{th} and 75^{th} percentiles are 5 and 12 mg/L respectively. The only difference was the modified BRIDGE method that showed two to five times higher NBLs for all pilots depending on the applied constraint.

Conclusions

Eight geochemically distinct groundwater groups were identified in the active water exchange zone in Latvia using a combination of multivariate statistical analyses. They are characterized by particularly elevated or depressed concentrations of major ions, trace elements, and nitrogen compounds (namely NO_3^- and NH_4^+).

- The evolution of the groundwater composition is traced from recharge water not yet equilibrated with most of the sediment-forming minerals (CLU 6) to typical bicarbonate groundwater resulting from calcite and dolomite weathering (CLU 2 and 7). A group of bicarbonate groundwater with depleted Cl^- and SO_4^{2-} concentrations was interpreted as preindustrial time water (CLU 8).
- Three of the identified groundwater groups revealed the impacts of human activities and indicated groundwater vulnerability to pollution such as diffuse agricultural pollution in the water table aquifers (CLU 3) and aquifer salinization due to urban activities like roads de-icing (CLU 1) or water mixing with seawater or saltwater containing aquifers induced by groundwater over-abstraction (CLU 4 and 1).
- The salinization of freshwater aquifers due to the natural gypsum dissolution process was observed in aquifers incorporating gypsum as a mineral or due to water mixing (CLU 5).

Multivariate analyses performed on the Quaternary groundwater data set allowed to distinguish four geochemically different groups. All four groups belonged to the bicarbonate water type and could be characterized by differences in major ion and nitrogen compounds (namely NO_3^- and NH_4^+) composition as well as with differences in total dissolved solids and *pH*.

- The groups represent Ca–Mg–HCO_3 type groundwater commonly found in shallow aquifers across Latvia (CLU 1) as well as Ca–HCO_3 groundwater being characterized as very young groundwater located mostly in sandy deposits (CLU 4). The composition of the two other groups reflects pollution impacts and groundwater vulnerability to land use activities: diffuse agricultural contamination with NO_3^- (CLU 3) and the mixture of point source pollution derived from artificial surfaces and agricultural areas characterized as elevated NO_3^-, NH_4^+, Cl^- and SO_4^{2-} (CLU 2).
- The highest NO_3^- and NH_4^+ values were found in groundwater samples taken from Quaternary aquifers that have medium to low natural groundwater vulnerability. These areas are dominated by clayey sediments that hold fertile soils used in agriculture. Results show that all Quaternary groundwater in Latvia becomes vulnerable at a certain level of pressure and that the risk assessment of shallow groundwater and their protection should be elaborated using modified groundwater vulnerability map that includes dominant pressures.

Natural baseline levels (NBLs) and threshold (TVs) values were derived for Cl^-, SO_4^- and Na^+ for groundwater body at risk due to historical seawater intrusion into the freshwater aquifer in the Liepaja vicinity. Even though groundwater levels have been restored and currently exceed the Baltic Sea level, the improvements of groundwater quality are slower and in the central part of the groundwater body seawater fraction in groundwater samples still reaches 50%. Increased groundwater consumption from the Upper Devonian Mūru-Žagares aquifer in the future poses a risk for seawater intrusion and aquifer salinization. Derived NBLs and TVs allow evaluation of seawater intrusion and timely identification of any negative trends in the groundwater body at risk.

Data obtained during the systematic groundwater monitoring are fundamental for assessing and managing groundwater resources in Latvia. This study is the first attempt to provide the missing guidance on how to use and navigate historical to modern systematic groundwater monitoring data in Latvia.

- The main objective of systematic groundwater monitoring in Latvia has not changed over the past sixty years. It is to ensure good quality and sufficient quantity of groundwater resources. However, the specific objectives of groundwater monitoring have changed multiple times mainly due to available funding, existing regulations, and political framework at that time. Consequently, systematic groundwater monitoring in the territory of Latvia has undergone several optimizations that affected monitoring networks, the frequency of observations, the list of analysed chemical parameters and applied sampling and analytical methods. As a rule, the revisions driven by political reorganizations and/or lack of funding deteriorated the data quality. For instance, the collapse of the Soviet Union and the global financial crisis of 2007–2008 left a negative footprint on the amount of data gathered especially in groundwater chemical monitoring. In contrast, notable improvement can be observed since Latvia joined the European Union and had to comply with EU water policy requirements and could apply for financial grants. All in all, the changes have influenced the data in one or another way, and further usage of such data strongly depends on how well the changes were documented.
- Evolved understanding of groundwater importance (e.g., GDEs) and variability (seasonal fluctuations) in the water cycle in combination with climate change and emerging pollutants require rapid expansion of groundwater monitoring networks and increased sampling and observation frequency and type. These are challenging tasks for water managers operating with historical groundwater monitoring networks that already cannot fulfil the requirements of EU water policies. Following discrepancies between EU water policy requirements and the current groundwater monitoring were identified. Firstly, the monitoring network is outdated. The majority of currently active monitoring wells have been installed 40–50 years ago, thus replacement of old wells with new ones is a prerequisite to not interrupt valuable time series. Secondly, the specific aims of groundwater monitoring have changed over time. The current network density is unsatisfactory and has a lack of monitoring points in shallow (unconfined) aquifers that are most vulnerable to pollution as well as sustain GDEs. Thirdly, the network should be expanded in transboundary areas with neighbouring countries, for instance, Estonia and Lithuania. At the time of groundwater network installation, the political situation was different, thus monitoring density in cross border areas is too low and does not allow sustainable management of transboundary aquifers.
- The gaps in the groundwater monitoring network could be filled cost-efficiently by including more springs in the groundwater monitoring network as well as using already existing wells from more than 200 active groundwater well fields in Latvia. New springs must be selected based on a developed conceptual

understanding of the spring watershed such as by delineation of the catchment area, screening of groundwater seasonality (variation in groundwater chemical composition and discharge), and identification of major impacts and pressures such as dominant land use. On the one hand, the well fields already represent the most used aquifers and would allow better monitoring of groundwater systems providing water supply. On the other hand, installation of new monitoring wells could be prioritized in problematic areas (e.g. intensive land use, aquifer salinization, control of GDEs) where otherwise drilling new wells could not be economically justified.

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APPENDICES – ARTICLE DEPOSITORY

PAPER I

Invisible groundwater between Estonia and Latvia – an analysis of gaps and perspectives for better transboundary aquifer management.

Marandi, A., Demidko, J., Borozdins, D., Valters, K., **Retike, I.**, Bikše, J. & Männik, M.
Submitted to the *Journal of Hydrology: Regional Studies.*

Abstract

Groundwater resources play a crucial role in sustaining the global water supply and ensuring water security. Effective groundwater management requires a coordinated effort at multiple levels, particularly in transboundary management. It is important to identify common transboundary groundwater bodies, establish common principles, and enhance cooperation to effectively manage groundwater. In 2003, an inter-institutional cooperation agreement was signed between Estonia and Latvia to coordinate joint activities in managing the transboundary water courses. Despite the agreement being in place, most of the activities have been initiated by researchers rather than government institutions. Additionally, surface water has received more attention than groundwater. This article discusses the lack of political attention and funding for transboundary water management between Estonia and Latvia. One reason for the low cooperation is the absence of problems in the transboundary area due to its low population, almost no industry, and natural conditions. As a result, managing authorities and the public tend to neglect the importance of groundwater resources. To make groundwater more visible, springs and the effect of groundwater on groundwater-dependent terrestrial ecosystems can be effective tools. In conclusion, hydrogeology research conducted in the area since 2018 has provided valuable data and filled knowledge gaps but has also highlighted the need for governments and management authorities to review and improve their policies and institutional capacity for future development.

Keywords: Water Convention, Water Framework Directive, Transboundary cooperation, Transboundary Aquifer, Groundwater, Groundwater Body, Estonia, Latvia

PAPER II

Hydrochemical signatures of springs for conceptual model development to support monitoring of transboundary aquifers.

Koit, O., **Retiķe, I.**, Bikše, J., Terasmaa, J., Tarros, S., Abreldaal, P., Babre, A., Hunt, M., Pärn, J., Vainu, M., Marandi, A., Sisask, K., Lode, E. & Männik, M. (2023).

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PAPER III

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PAPER IV

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PAPER V

Rescue of groundwater level time series: how to visually identify and treat errors.
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PAPER VI

Assessment of chloride natural background levels by applying statistical approaches. Analyses of European coastal aquifers in different environments.

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PAPER VII

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PAPER VIII

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PAPER IX

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PAPER X

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Inga Retiķe

LATVIJAS PAZEMES ŪDEŅU ĢEOĶĪMISKĀ SASTĀVA UN PIESĀRŅOJUMA LĪMEŅU RAKSTUROJUMS MONITORINGA UN AIZSARDZĪBAS NODROŠINĀŠANAI

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Anotācija

Ilgtspējīga pazemes ūdeņu apsaimniekošana ir priekšnoteikums cilvēku un dabas labklājībai. Pazemes ūdeņi ne vien nodrošina gandrīz pusi no pasaules dzeramā ūdens apgādes, bet arī uztur no pazemes ūdeņiem atkarīgas ekosistēmas, piemēram, upes, ezerus un mitrājus, kas tālāk sniedz būtiskus ekosistēmu pakalpojumus. Paredzams, ka slodzes uz pazemes ūdeņiem un atkarība no pazemes ūdeņu resursiem palielināsies visā pasaulē, jo urbanizācija un klimata pārmaiņas veicina virszemes ūdeņu trūkumu un piesārņojumu. Neraugoties uz pazemes ūdeņu ievērojamo nozīmi sociālajos, ekonomiskajos un vides procesos, pazemes ūdeņi joprojām ir vāji izprasti un pārvaldīti, un regulāri atstāti novārtā, kā rezultātā tiek pieņemti neatbilstoši apsaimniekošanas lēmumi. Padziļināta izpratne par pazemes ūdeņu ģeoķīmiskajām īpašībām ir būtiska, lai apzinātu saldūdens nesējslāņu veidošanās ceļus un noteiktu pazemes ūdeņu aizsargātību pret piesārņojumu. Konceptuāla izpratne par pazemes ūdeņu sistēmām ir nepieciešama, lai veiktu reprezentatīvu pazemes ūdeņu monitoringu, kas savukārt apkopo nepieciešamos datus pazemes ūdeņu resursu novērtēšanai un tendenču analīzei. Šī pētījuma mērķis bija izvērtēt ģeoķīmisko procesu un piesārņojuma ietekmi uz pazemes ūdeņu ķīmiskā sastāva mainību Latvijā, lai uzlabotu pazemes ūdeņu monitoringa un pārvaldības sistēmas atbilstīgi ES ūdens politikas prasībām.

Balstoties uz daudzfaktoru statistiskās analīzes metodēm un pazemes ūdeņu ģeoķīmisko sastāvu, pētījumā raksturoti izplatītākie pazemes ūdeņu tipi aktīvajā ūdens apmaiņas zonā, kas atspoguļo dažādu hidroģeoloģisko apstākļu un piesārņojuma ietekmi. Rezultāti atklāja, ka saldūdens nesējslāņi Latvijā ir neaizsargāti pret dažādām cilvēku saimnieciskajām darbībām, piemēram, lauksaimniecības rādīto nitrātu piesārņojumu vai piesārņojuma noteci no pilsētvides. Turklāt vēl joprojām var novērot vēsturiskā piesārņojuma klātbūtni, piemēram, ūdens nesējslāņu sasāļošanos ko radīja pazemes ūdeņu pārmērīga ieguve, un sākotnējā stāvokļa atjaunošanās var prasīt desmitgades. Tomēr pazemes ūdeņu kvalitāte var būt pazemināta arī dabisku procesu rezultātā. Stipri reducējoši apstākļi veicina augstu dzelzs, amonija jonu vai pat arsēna koncentrāciju veidošanos pazemes ūdeņos, kamēr ģipšu šķīšanas rezultātā pazemes ūdeņos ir paaugstinātas fluora koncentrācijas. Tika izstrādāti dabiskie fona līmeņi un robežvērtības, lai nodrošinātu atbilstošu un savlaicīgu saldūdens nesējslāņu sasāļošanās uzraudzību un novērtējumu Liepājas apkārtnē, riska pazemes ūdensobjektā. Padziļināta analīze par ES ūdens politikas prasībām salīdzinājumā ar sistemātisko pazemes ūdeņu monitoringu atklāja galvenos trūkumus Latvijas pazemes ūdeņu monitoringa sistēmā: maz pārstāvēti seklie un vāji aizsargātie ūdens nesējslāņi, kā arī ir nepietiekams monitoringa punktu pārklājums, īpaši pārrobežu teritorijās. Trūkumus iespējams ātri un rentabli aizpildīt, ņemot paraugus jau esošajos urbumos no galvenajām pazemes ūdeņu ieguves vietām (atradnēm) un apzinot reprezentatīvākos ūdens avotus un iekļaujot tos valsts pazemes ūdeņu monitoringa tīklā.

Atslēgvārdi: pazemes ūdeņi, hidroģeoķīmija, pazemes ūdeņu monitorings, ES ūdens politikas, pazemes ūdeņu apsaimniekošana, pazemes ūdeņu aizsargātība, pazemes ūdeņu piesārņojums, jūras ūdeņu intrūzija, dabiskie fona līmeņi, robežvērtības.

Saturs

Saīsinājumi

CLU	Klāsteri
DFL	Dabiskais fona līmenis
DPSIR	metodika (angļu val.: *drivers, pressures, state, impact, and response methodology*)
ES	Eiropas Savienība
Fe_{kop}	Kopējā dzelzs saturs
GKA	Galveno komponentu analīze
HKA	Hierarhiskā klāsteranalīze
LVĢMC	Latvijas Vides, ģeoloģijas un meteoroloģijas centrs
Mineralizācija	Kopējais izšķīdušo vielu saturs
NR	Noteikšanas robeža
Pamatjoni	Katjoni Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} un anjoni HCO_3^{-}, Cl^{-}, SO_4^{2-}
PC	Galvenais komponents
PŪAE	No pazemes ūdeņiem atkarīgās ekosistēmas
PŪO	Pazemes ūdensobjekti
RV	Robežvērtības
UBA	Upju baseinu apgabali
UBAP	Upju baseinu apgabalu apsaimniekošanas plāni
ŪSD	Ūdens struktūrdirektīva (2000/60/EK)

Ievads

Pazemes ūdeņi visā pasaulē nodrošina ūdens apgādi, ekosistēmu funkcionēšanu un cilvēku labklājību, un sagaidāms, ka kopējā pazemes ūdeņu nozīme pieaugs, jo tie ir mazāk pakļauti sezonālajai un daudzgadu klimata mainībai salīdzinājumā ar virszemes ūdeņiem (UNESCO, 2015, 2020). Latvijā aptuveni 80% ūdens apgādes nodrošina pazemes ūdeņu resursi (UBAP, 2022). Neskatoties uz ievērojamo nozīmi, pazemes ūdens bieži tiek saukts par neredzamo resursu, jo dabiski tie kļūst redzami tikai alās, geizeros un izplūstot avotu veidā (Koit et al., 2023). Pazemes ūdeņu pētījumi bieži saskaras ar dažādām problēmām, piemēram, trūkstošiem datiem, zemu datu kvalitāti un konceptuālas izpratnes trūkumu par pazemes ūdeņu sistēmu darbību (Terasmaa et al., 2020). Tomēr pieaugošais pazemes ūdeņu pieprasījums dzeramā ūdens, lauksaimniecības un rūpniecības procesu nodrošināšanai kopā ar klimata pārmaiņām aktualizē pazemes ūdeņu pārvaldības un aizsardzības nozīmi (EEA, 2018; Naranjo-Fernandez et al., 2020; Obergfell et al., 2019; Witte et al., 2019).

Pazemes ūdeņu resursu neatbilstoša apsaimniekošana var negatīvi ietekmēt valstu attīstību, tostarp nodrošinātību ar ūdeni un pārtiku, kā arī negatīvi ietekmēt no pazemes ūdeņiem atkarīgas ekosistēmas ar bagātīgu bioloģisko daudzveidību, un pat ierobežot iespējas mazināt klimata pārmaiņas (Lapworth et al., 2022; Scheihing et al., 2022). Turklāt pazemes ūdeņi neseko cilvēku novilktām robežām, piemēram, tādām kā valstu robežas, un tādas neilgtspējīgas darbības kā pazemes ūdeņu pārmērīga ieguve un piesārņojums vienā valstī var novest pie slikta pazemes ūdeņu stāvokļa citā valstī (Terasmaa et al., 2020) vai pat saasināt konfliktus (Klare, 2020; Rigi un Warner 2020).

Kā norāda Appelo un Postma (2005), pazemes ūdeņu ķīmiskais sastāvs ir visu procesu rezultāts starp ūdeni, minerāliem un gāzēm, ar kuriem tas ir bijis saskarē no barošanās līdz atslodzes vietām. Papildus dabiskajiem faktoriem arī cilvēka darbība var ietekmēt pazemes ūdeņu kvalitāti. Piemēram, intensīva pazemes ūdeņu ieguve var mainīt ūdens līmeņu sadalījumu un ierosināt ūdens sajaukšanos (Pulido-Velazquez et al., 2022), t.i., jūras ūdens intrūziju saldūdens nesējslāņos (Bikše un Retike, 2018). Dažu vielu, piemēram, pesticīdu, klātbūtne pazemes ūdeņos ir tiešs cilvēka darbības ietekmes rādītājs, savukārt neorganisko izcelsmes vielu (tajā skaitā mikroelementu) avots var būt gan dabisku procesi, gan cilvēku darbību rezultāts (Biddau et al., 2017).

Padziļināta izpratne par pazemes ūdeņu ģeoķīmiskajām īpašībām ir būtiska, lai izprastu pazemes ūdeņu veidošanās mehānismus un atšķirtu dabiskos un cilvēka ietekmētos pazemes ūdeņu paraugus. Urresti-Estala et al. (2013) uzsver, ka ir liels skaits faktoru, kas ir atbildīgi par gala pazemes ūdeņu ķīmisko sastāvu, tādēļ nodalīt dabisko faktoru ietekmi uz pazemes ūdeņu sastāvu no cilvēka darbības izraisītajām ietekmēm ir ļoti sarežģīts uzdevums, ko pavada daudz nezināmo un nenoteiktības. Daudzfaktoru statistiskās analīzes metodes var izcelt pazemes ūdeņu ģeoķīmiskā sastāva raksturu, un metodes ir veiksmīgi pielietotas sākot uz lokāla (Koit et al., 2021, 2023; Slama et al., 2022) līdz reģionāla mēroga (Biddau et al., 2017; Bondu et al. al., 2020; Busico et al., 2018; Cloutier et al., 2008) hidroģeoķīmiskajām datu kopām.

ES ūdens politika ir tiesību aktu kopums, kuru mērķis ir ar dažādu pasākumu palīdzību pārvaldīt un aizsargāt pazemes ūdeņu resursus. Latvija ir Eiropas Savienības (ES) dalībvalsts kopš 2004. gada un līdz ar to tai ir jāīsteno ES ūdens politika. ES Ūdens struktūrdirektīva (ŪSD) (Direktīva 2000/60/EK) nosaka, ka ES dalībvalstīm ir jānodrošina labs kvantitatīvais un ķīmiskais stāvoklis visos pazemes ūdensobjektos, savlaicīgi identificējot negatīvās tendences, kas rada resursu izsīkšanas risku un no pazemes ūdeņiem atkarīgo ekosistēmu kvalitātes pasliktināšanos. ŪSD un tās "meitas" direktīvā Gruntsūdeņu direktīvā (Direktīva 2006/118/EK) ir noteikts, ka pazemes ūdens objektu ķīmiskais stāvoklis ir jānovērtē attiecībā pret robežvērtībām (RV), kas lokāli noteiktas piesārņotājiem, kas ir atbildīgi par pazemes ūdensobjekta riska stāvokli. Dabiskie fona līmeņi (DFL) ir jānosaka tiem parametriem, kuru koncentrācijas pazemes ūdeņos var mainīties plašā diapazonā dabisku procesu rezultātā atkarībā no hidroģeoloģiskajiem apstākļiem (piemēram, Cl^{-}, SO_4^{2-}) (Voutchkova et al., 2021). ES Nitrātu direktīvas (Direktīva 91/676/EEK) mērķis ir samazināt ūdens piesārņojumu, ko izraisa lauksaimniecībā izmantojamie slāpekli saturošie mēslošanas līdzekļi, nosakot īpaši jutīgās (nitrātu) teritorijas, kur mēslošanas līdzekļu izmantošana ir ierobežota. ŪSD un tā sauktā Ūdens konvencija (UNECE, 1992) ir vieni no galvenajiem normatīviem, kas nodrošina sadarbību kopīgo (pārrobežu) pazemes ūdeņu resursu ilgtspējības jomā.

Labas kvalitātes dati, kas iegūti regulāri un no reprezentatīviem pazemes ūdeņu monitoringa tīkliem, ir priekšnoteikums jebkurai hidroģeoloģiskai izpētei vai vietēja līdz nacionāla mēroga pazemes ūdeņu resursu novērtējumam. Sistemātiskais pazemes ūdeņu monitorings Latvijā tika uzsākts pirms vairāk nekā 60 gadiem. Valsts monitoringa ietvaros iegūtajai datu kopai ir liela vērtība, jo ir pieejami ilgtermiņa novērojumi ar labu telpisko pārklājumu un dažādu ūdens nesējslāņu reprezentāciju. Tomēr šādas unikālas datu kopas esamība ir tikusi nepietiekoši novērtēta, kaut arī apjoma ziņā šī datu kopa pārspēj jebkuru iepriekš Latvijā veikto hidroģeoloģisko pētījumu. Šādu datu izmantošana ir bijusi ilgstoši apgrūtināta, jo ir ierobežota piekļuve datu bāzēm un trūkst pavadošā informācija. Turklāt dažādas politiskās un ekonomiskās reformas ietekmē sistemātiskās pazemes ūdeņu monitoringa programmas valsts mērogā. Reformas rada ierobežojumus datu turpmākajai izmantošanai, ko var pārvarēt, ja izmaiņas ir labi dokumentētas un ietekmes ir izprastas.

Promocijas darba mērķis

Promocijas **darba mērķis** ir izvērtēt ģeoķīmisko procesu un piesārņojuma ietekmi uz pazemes ūdeņu ķīmiskā sastāva mainību Latvijā, lai uzlabotu pazemes ūdeņu monitoringa un pārvaldības sistēmas atbilstīgi ES ūdens politikas prasībām. No mērķa izriet šādi uzdevumi:

1. Raksturot pazemes ūdeņu ģeoķīmisko sastāvu un identificēt piesārņojuma klātbūtni.
2. Novērtēt sistemātiskā pazemes ūdeņu kvalitātes (ķīmiskā) un kvantitātes monitoringa Latvijā veiktspēju un ierosināt virzienus monitoringa uzlabošanai balstoties uz identificētajiem trūkumiem un nākotnes vajadzībām atbilstīgi ES ūdens politikas prasībām.
3. Sniegt ieguldījumu pazemes ūdeņu uzraudzības un aizsardzības metodoloģiju izstrādē.

Promocijas darba novitāte

- Pirmo reizi veikta visaptveroša Latvijas aktīvās ūdens apmaiņas zonas pazemes ūdeņu ķīmiskā sastāva analīze izmantojot daudzfaktoru statistiskās analīzes metodes un apskatot plašu parametru sarakstu (pamatjoni, mikrolementi, slāpekļa savienojumi).

- Izdalītās grupas ar atšķirīgu ķīmisko sastāvu sniedz jaunu ieskatu Latvijas pazemes ūdeņu izmantošanas potenciālā.
- Izstrādāta metodiskā pieeja jūras ūdeņu intrūzijas saldūdens nesējslāņos attīstības uzraudzībai Liepājas riska pazemes ūdensobjektam.
- Rezultāti atbalsta ES ūdens politikas prasību ieviešanu Latvijā un ļauj uzlabot nacionālo un pārrobežu ūdens nesējslāņu monitoringu, apsaimniekošanu un ilgtspējīgas izmantošanas plānošanu.

Promocijas darba zinātniskā un praktiskā nozīme

- Balstoties uz pētījuma rekomendācijām notiek Latvijas pazemes ūdeņu monitoringa tīkla pilnveide gan ierīkojot jaunus monitoringa urbumus, gan slēdzot vienošanos ar pazemes ūdeņu atradņu operatoriem.
- Pamatojoties uz rekomendācijām ūdens avotus plānots izmantot pazemes ūdeņu monitoringa tīkla paplašināšanai un pārrobežu pazemes ūdeņu monitoringa programmu sagatavošanai.
- Sistemātiskā pazemes ūdeņu monitoringa tīkla analīze kopā ar rekomendācijām pazemes ūdeņu monitoringa un pazemes ūdeņu novērtējuma uzlabošanai atbilstīgi ES Ūdens struktūrdirektīvas un Gruntsūdeņu direktīvas prasībām iekļautas ir iekļautas 2021.–2027. gada Upju baseinu apgabalu apsaimniekošanas plānos, nacionālajā Nitrātu direktīvas ziņojumā 2016.–2019. gadam un Vides politikas pamatnostādnēs 2021–2027. gadam.
- Izstrādātās fona un robežvērtības riska pazemes ūdensobjektam "Liepāja un teritorija uz dienvidaustrumiem no tās līdz ūdensgūtnei Otaņķi" ir iekļautas nacionālajos normatīvajos aktos (2016. gada 3. oktobra rīkojums Nr. 257 "Par piesārņojošos vielu un to grupu robežvērtībām riska pazemes ūdensobjektos" uz Ministru kabineta noteikumu Nr. 42 22.3 apakšpunkta pamata).
- Padziļināta sistemātiskā pazemes ūdeņu kvalitātes (ķīmiskā) un kvantitātes monitoringa analīze turpmāk atvieglos vēsturisko līdz mūsdienu hidroģeoķīmisko datu kopu izmantošanu, kā arī veicinās pētījumus hidroģeoloģijā un pazemes ūdens apsaimniekošanā.

Promocijas darba rezultātu aprobācija

Pētījuma rezultāti aprakstīti 10 publikācijās (9 zinātniskie raksti un 1 grāmatas nodaļa), kas iekļautas *Scopus* un/vai *Web of Science* datubāzes. Publikācija I atrodas recenzēšanas procesā. Kopumā autorei ir 17 publikācijas un visas iekļautas *Scopus* un/vai *Web of Science* datubāzes. Pētījuma rezultāti tika prezentēti 24 ziņojumos starptautiskās un 10 ziņojumos vietējas nozīmes konferencēs.

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3. Kitterød, N.-O., Kværner, J., Aagaard, P., Arustienė, J., Bikše, J., Dagestad, A., Gundersen, P., Hansen, B., Hjartarson, Á., Karro, E., Klavins, M., Marandi, A., Radienė, R., **Retike, I.**, Rossi, P. M. & Thorling, L. (2022). Hydrogeology and groundwater quality in the Nordic and Baltic countries. *Hydrology Research,* 53(7), 958–982. https://doi.org/10.2166/nh.2022.018 (Web of Science/Scopus, Q3, IF_{2022} = 2,752) (turpmāk tiek apzīmēta kā **Publikācija III**).
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6. Pulido-Velazquez, D., Baena-Ruiz, L., Fernandes, J., Arnó, G., Hinsby, K., Voutchkova, D. D., Hansen, B., **Retike, I.**, … Luque-Espina, J. A. (2022). Assessment of chloride natural background levels by applying statistical approaches. Analyses of European coastal aquifers in different environments. *Marine Pollution Bulletin*, 174, 113303. https://doi.org/10.1016/j.marpolbul.2021.113303 (Web of Science/Scopus, Q1, IF_{2022} = 7,001) (turpmāk tiek apzīmēta kā **Publikācija VI**).
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9. Bikse, J., **Retike, I.** & Kalvans, A. (2016). Historical evolution of seawater intrusion into groundwater at city Liepaja, Latvia. *XXIX Nordic Hydrological Conference.* Kauņa, Lietuva, 8–10. augusts.
10. **Retike, I.**, Delina, A., Bikse, J. & Kalvans, A. (2016). Quaternary Groundwater Vulnerability Assessment in Latvia Using Multivariate Statistical Analysis. *22nd Annual International Scientific Conference "Research for Rural Development 2016".* Latvijas Lauksaimniecības universitāte, Jelgava, Latvija, 18–20. maijs.
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Promocijas darba struktūra

Promocijas darba rezultāti aprakstīti 10 recenzētās zinātniskajās publikācijās turpmāk apzīmētas kā Publikācija I–X. Pētnieciskā darba galvenie rezultāti ir izklāstīti visās promocijas darba sadaļās. Promocijas darba kopsavilkums sastāv no 43 lapaspusēm, kas papildinātas ar 9 attēliem un 7 tabulām.

1. TEORĒTISKAIS PAMATOJUMS

1.1. Tiesiskais regulējums pazemes ūdeņu aizsardzībai Eiropas Savienības līmenī

Ūdens struktūrdirektīva stājās spēkā 2000. gada 22. decembrī un izveidoja sistēmu Kopienas rīcībai ūdens resursu politikas jomā visām ES dalībvalstīm, aizstājot iepriekš sadrumstalotos ūdens tiesību aktus (vairāk nekā divpadsmit 1970. un 1980. gadu direktīvas). Pazemes ūdeņu jēdziens, kas iepriekš tika risināts dažādos tiesību aktos, tika pilnībā integrēts ŪSD pamatpasākumos. Pirmo reizi pazemes ūdeņi kļuva par daļu no integrētas ūdens apsaimniekošanas sistēmas (European Commission, 2007, 2008; Quevauviller et al., 2011; Rejman, 2007).

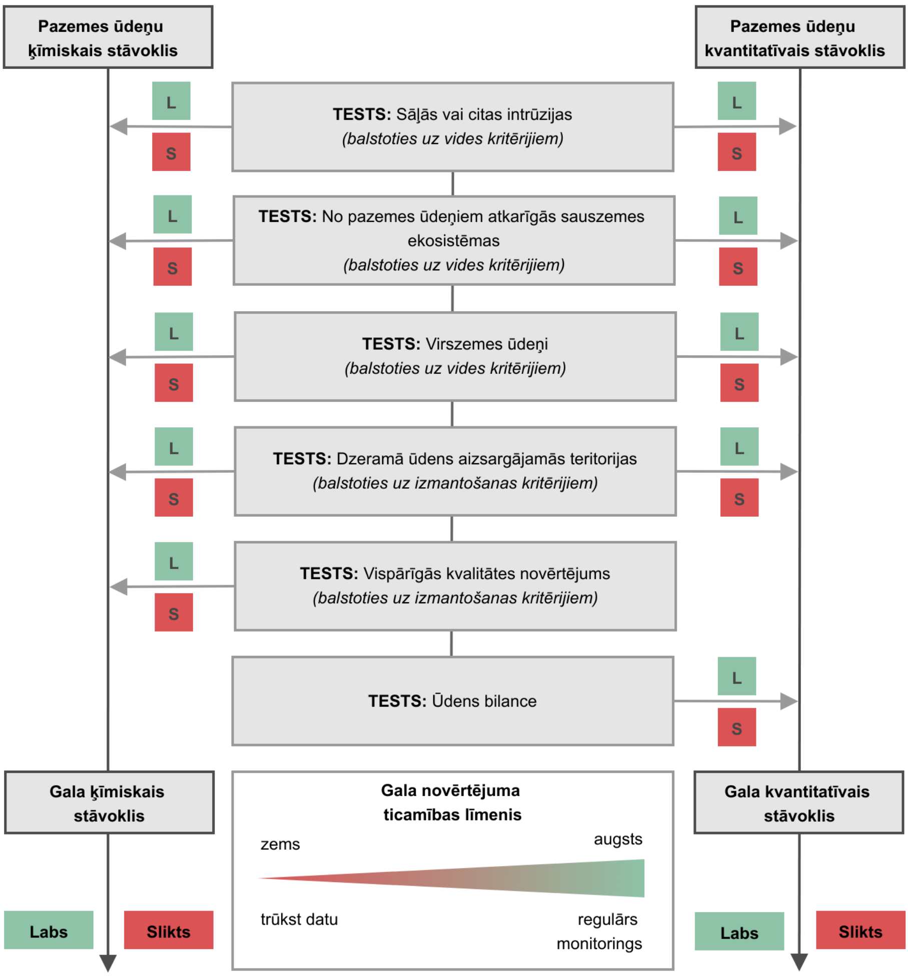
ŪSD galvenie mērķi ir izklāstīti direktīvas 4. pantā. ES dalībvalstīm ir jāaizsargā labas kvalitātes ūdensobjekti un, ja nepieciešams, jāveic ūdensobjektu uzlabošanas pasākumi, lai sasniegtu labu stāvokli un novērstu atkarīgo ekosistēmu pasliktināšanos. Upju baseinu apgabalu apsaimniekošanas plāni (UBAP) un pasākumu programma ir galvenie ŪSD ieviešanas instrumenti, un tie tiek izstrādāti pēc plašas sabiedriskās apspriešanas un ir spēkā sešus gadus. Holistiskā pieeja paplašina ūdens aizsardzības jomu iekļaujot visus ūdeņus (pazemes ūdeņus, upes, ezerus un piekrastes ūdeņus) un veicina pārrobežu sadarbību, nosakot to par obligātu (vismaz ES dalībvalstīm). Sabiedrības līdzdalība tiek stiprināta ar obligātu sabiedriskās apspriešanas procesu (vismaz 6 mēnešus garu). Visbeidzot, ŪSD ir skaidri mērķi, kas jāsasniedz ierobežotā termiņā – sasniegt labu stāvokli visiem ūdeņiem līdz noteiktajam 15 gadu termiņam (ar iespējamu pagarinājumu līdz 2027. gadam), vienlaikus atstājot dalībvalstīm elastību attiecībā uz to, kā rentabli sasniegt šos mērķus (European Commission, 2007; Quevauviller et al., 2011).

Pēc upju baseinu apgabalu (UBA) izveidošanas (Latvijā – Gaujas, Daugavas, Lielupes un Ventas) dalībvalstīm bija jāveic ietekmju un slodžu analīze, lai identificētu galvenos riskus laba stāvokļa mērķu nesasniegšanai. Ietekmju un slodžu analīze uz pazemes ūdeņiem sākas ar sākotnējā raksturojuma veikšanu, kas balstās uz ieteikto virzītājspēka–slodžu–stāvokļa–ietekmes–atbildes metodoloģiju/principu (angļu val. *Driver–Pressure–State–Impact–Response, DPSIR*), kam jāizveido konceptuāla izpratne par hidroloģisko sistēmu un ko plaši izmanto ES (Bagordo et al., 2016; Mattas et al., 2014). Lai veiktu sākotnējo raksturojumu, vispirms dalībvalstīm bija jāizdala pazemes ūdensobjekti (PŪO), kuru robežās jāīsteno efektīva un ilgtspējīga pazemes ūdeņu pārvaldība un jāziņo par progresu (European Commission, 2003b). Kopš 2018. gada Latvijā ir 25 PŪO (Bikše un Retike, 2018). Papildus raksturojums bija jāveic PUO, kam ir pārrobežu raksturs vai kuri tika identificēti kā tādi, kuriem pastāv risks, ka tie nesasniegs ŪSD mērķus. Raksturošanas un riska novērtēšanas process nodrošina pamatu reprezentatīva pazemes ūdeņu monitoringa tīkla izveidei, kas savukārt apkopo informāciju, lai sniegtu visaptverošu pārskatu par PŪO stāvokli. Visbeidzot, dalībvalstīm ir jāizstrādā un jāpieņem pasākumu programma, lai sasniegtu ŪSD vides mērķus.

Visiem pazemes ūdensobjektiem jāsasniedz labs kvantitatīvais un ķīmiskais stāvoklis. Lai gan pazemes ūdeņu kvantitatīvā stāvokļa mērķi ir viegli definējami, proti, nodrošināt līdzsvaru starp pazemes ūdeņu ieguvi un dabisko atjaunošanos, ķīmiskā stāvokļa kritēriju definēšana ir sarežģītāka. Tādējādi Gruntsūdeņu direktīva (2006/118/EK), saukta arī par "meitas" direktīvu, precizē laba ķīmiskā stāvokļa kritērijus un nosaka papildu tehniskās specifikācijas nacionālo kvalitātes standartu, ko sauc par robežvērtībām (RV), noteikšanai (Hinsby et al., 2008; Quevauviller et al., 2011). Saskaņā ar Gruntsūdeņu direktīvu dalībvalstīm ir jānosaka RV, jāizpēta piesārņojuma tendences un jāievieš pasākumi, lai novērstu un ierobežotu piesārņojošo vielu nokļūšanu pazemes ūdeņos.

1.1.1. Pazemes ūdeņu stāvokļa novērtējums

Lai novērtētu riskam pakļautā PŪO kopējo stāvokli jāpielieto noteiktu klasifikācijas testu kopums (1. attēls). Ir deviņi klasifikācijas testi (pieci ķīmiskie un četri kvantitatīvie), katrs izstrādāts, lai risinātu konkrētus ar pazemes ūdeņu aizsardzību saistītus aspektus un izpildītu ŪSD vides mērķus.



1. attēls. Pārskats par pazemes ūdensobjektu ķīmiskā un kvantitatīvā stāvokļa novērtēšanas procesu un klasifikācijas testiem (modificēts pēc European Commission, 2009).

Sliktākais scenārijs no jebkura klasifikācijas testa tiek ziņots kā kopējais stāvoklis. Turklāt galīgajam novērtējumam ir jānosaka ticamības svars augsta vai zema ticamības līmeņa veidā. Stāvokļa novērtējums tiek veikts UBAP perioda beigās, lai atspoguļotu pasākumu programmas efektivitāti, un tiek veikts balstoties uz monitoringa datiem, kas ievākti UBAP periodā (European Commission, 2009).

1.1.2. Pazemes ūdeņu kvalitātes standarti

ŪSD (Direktīva 2000/60/EK) un Gruntsūdeņu direktīva (Direktīva 2006/118/EK) pieprasa dalībvalstīm novērtēt PŪO ķīmisko stāvokli pret ES mērogā noteiktajiem kvalitātes standartiem tādiem parametriem kā nitrāti (NO_3^-, 50 mg/L) un individuāliem pesticīdiem un to summai (0,1 µg/L un 0,5 µg/L). Dalībvalstīm ir pienākums noteikt stingrākus kvalitātes standartus nitrātiem un pesticīdiem vai noteikt standartus papildu piesārņotājiem, ja pastāv risks, ka PŪO nesasniegs labu ķīmisko stāvokli. Robežvērtības (RV) ir pazemes ūdeņu kvalitātes standarti piesārņotājiem, ko nosaka atsevišķas dalībvalstis, lai nodrošinātu atbilstību laba ķīmiskā stāvokļa definīcijai un no pazemes ūdeņiem atkarīgo ekosistēmu (gan sauszemes, gan saldūdens) aizsardzību. RV ir jānosaka visiem piesārņotājiem un piesārņojuma rādītājiem, kas raksturojuši PŪO kā tādu, kam ir risks nesasniegt labu pazemes ūdeņu ķīmisko stāvokli. Valsts iestādes parasti izmanto RV kā kritērijus, lai pārbaudītu, vai PŪO ir labā ķīmiskajā stāvoklī (Bulut et al., 2020; De Caro et al., 2017; Voutchkova et al., 2021).

Gruntsūdeņu direktīvas noteikumi par PŪO ķīmisko stāvokli attiecas tikai uz cilvēka darbības ietekmētiem apstākļiem, tāpēc pirmais solis RV noteikšanā ir dabiskā fona līmeņu (DBL) noteikšana. DFL ir jānosaka tikai tiem parametriem, kuri pazemes ūdeņos var būt sastopami plašā koncentrāciju diapazonā arī dabiski atkarībā no hidroģeoloģiskajiem apstākļiem (Voutchkova et al., 2021).

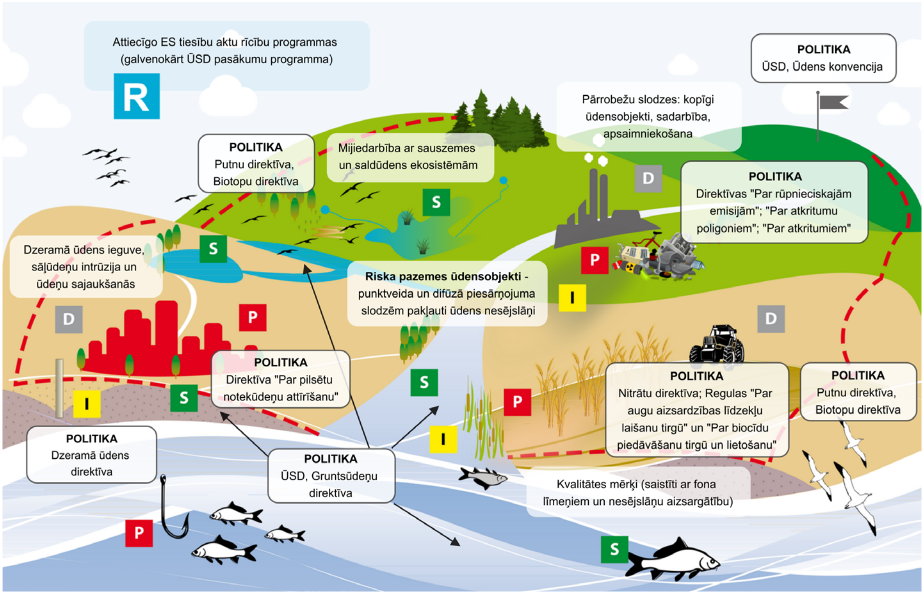
Katra dalībvalsts var brīvi izvēlēties pieeju, kā noteikt DBL, tomēr lielākā daļa (piemēram, De Caro et al., 2017; Marandi un Karro, 2008; Pulido-Velazquez et al., 2022; Retike un Bikše, 2018; Sellerino et al., 2019; Vencelides et al., 2010; Wendland et al., 2008) pielieto BRIDGE metodoloģiju (Müller et al., 2006).

1.1.3. Sasaiste ar citām direktīvām un Ūdeņu konvenciju

Pazemes ūdeņu aizsardzību nodrošina arī virkne citu direktīvu, no kurām lielākā daļa (vismaz sākotnējā formā) tika pieņemtas pirms ŪSD (Direktīva 2000/60/EK) un Gruntsūdeņu direktīvas (Direktīva 2006/118/EK) stājās spēkā. Visas direktīvas ietver dažādus instrumentus, kuru mērķis ir novērst vai ierobežot piesārņojošo vielu nokļūšanu arī pazemes ūdeņos, un tās ir tieši vai netieši saistītas ar ŪSD vai Gruntsūdeņu direktīvu (European Commission, 2008).

Galvenie juridiskie instrumenti un nozares ir apkopotas 2. attēlā (proti, Nitrātu direktīva (Direktīva 91/676/EEK), Direktīva "Par komunālo notekūdeņu attīrīšanu" (91/271/EEK), pārstrādātā Dzeramā ūdens direktīva (2020/2184), Regula 1107/2009 par augu aizsardzības līdzekļu laišanu tirgū un Regula 528/2012 par biocīdu piedāvāšanu tirgū un lietošanu, Direktīva "Par rūpnieciskajām emisijām (2010/75/ES), Direktīva "Par atkritumu poligoniem" (1999/31/EK), Direktīva "Par atkritumiem" (2008/98/ EK), Putnu direktīva (2009/147/EK) un Biotopu direktīva (92/43/EEK) un Ūdens konvencija

(UNECE, 1992, 2013), kā arī attēloti DPSIR metodoloģijas elementi, kas veido integrētu pazemes ūdeņu apsaimniekošanas ietvaru.



2. attēls. Juridiskie instrumenti un nozares, kas ir tieši vai netieši saistītas ar pazemes ūdeņu aizsardzību (saraksts nav izsmeļošs). “DPSIR” metodoloģijas princips norādīts kā D – virzītājspēks, P – slodzes, S – stāvoklis, I – ietekmes un R – atbilde. ŪSD – Ūdens struktūrdirektīva (modificēts pēc European Commission, 2009).

1.2. Sistemātiskā pazemes ūdeņu monitoringa attīstība Latvijā

Sistemātiska pazemes ūdeņu monitoringa tīkla izveide sākās 1953. gadā ar pirmajiem regulārajiem novērojumiem kopš 1959. gada. Sākumā monitoringa tīkls sastāvēja no dažiem desmitiem urbumu, no kuriem lielākā daļa tika ierīkota bezspiediena ūdens nesējslāņos (Juodkazis, 1994). Drīzumā tīkls paplašinājās strauji pieaugot jaunu pazemes ūdens atradņu skaitam ap lielākajām pilsētām, kā arī ierīkojot jaunus urbumus, lai uzraudzītu ūdens līmeņa paaugstināšanos jaunuzcelto hidroelektrostaciju tuvumā (Jankins et al., 1993; Juodkazis, 1994; Levina un Levins, 1994). Vēlākajos gados pieaugošās zināšanas par pazemes ūdeņu veidošanos veicināja pazemes ūdeņu monitoringa tīkla paplašināšanos visā valsts teritorijā (Levins et al., 1998).

Pirmā Latvijas valsts pazemes ūdeņu monitoringa tīkla optimizācija notika laikā no 1992. līdz 1993. gadam pēc Padomju Savienības sabrukuma un tam sekojošā finansējuma samazinājuma (Jankins et al., 1993). Otrās inventarizācijas laikā (1997.–1999. gads) aptuveni vienai trešdaļai pārbaudīto urbumu tika konstatēts slikts tehniskais stāvoklis urbumu aizsērējuma, konstrukcijas vai fizisku bojājumu dēļ. Daudzi monitoringa urbumi bija ierīkoti privātās zemēs, kas izraisīja konfliktus ar zemes īpašniekiem nesakārtoto īpašumtiesību dēļ (Levina un Levins, 2000).

Pirmā valsts pazemes ūdeņu monitoringa programma tika sagatavota 1999. gadā. Līdz tam monitorings tika turpināts, balstoties uz Padomju Savienības laikā izveidoto praksi un bez skaidriem mērķiem un pietiekama finansējuma (Levina un Levins, 2000, 2001). Pēc Latvijas iestāšanās ES 2004. gadā pazemes ūdeņu monitoringa programmu plānošana kļuva periodiska. Pirmā monitoringa programma aptvēra trīs gadus (2006.–2008. gads), jo tai bija jāsniedz nepieciešamie dati Upju baseinu apgabalu apsaimniekošanas plānu (UBAP) sagatavošanai 2009. gadā. Tāpat 2008. gadā Latvijai bija jāsagatavo pirmais četru gadu ziņojums par Nitrātu direktīvas ieviešanas progresu. Lielākie šķēršļi, kas aizkavēja ES prasību ieviešanu un bija drīzumā jānovērš, bija tehniska rakstura (piemēram, slikts urbumu stāvoklis) un likumdošanas jautājumi (pazemes ūdeņu monitoringa stacijas un aizsargjoslas ap tām nebija aizsargātas ar normatīviem). Trīsdesmit ūdens avoti tika iekļauti valsts pazemes ūdeņu kvalitātes monitoringa tīklā 2004. gadā, lai novērtētu zemes seguma un izkliedētā piesārņojuma ietekmi (Levina un Levins, 2005; Terasmaa et al., 2020). Veicot pazemes ūdeņu monitoringa tīkla modernizāciju no 2010. līdz 2012.gadam, tika ierīkoti 24 jauni monitoringa urbumi, bet 87 esošie tika aprīkoti ar automātiskajiem līmeņa mērītājiem (LVĢMC, 2013).

1.3. Latvijas hidroģeoloģiski apstākļi un pazemes ūdeņu kvalitāte

Latvijas teritorija atrodas Baltijas Artēziskā baseina centrālajā daļā, kas ir daudzslāņains sedimentācijas baseins (Lukševičs et al., 2012; Virbulis et al., 2013). Virs kristāliskā pamatklintāja (kas Latvijas teritorijā neatsedzas zemes virspusē) atrodas nogulumu sega ar biezumu no ~400 m ziemeļaustrumu daļā līdz virs 2000 m Latvijas dienvidrietumu daļā (Lukševičs et al., 2012). Pēc hidroģeoloģiskajiem apstākļiem pazemes ūdeņus Latvijā var iedalīt trīs lielās zonās, kas atšķiras pēc ūdens apmaiņas intensitātes un ūdens nesējslāņu sasaistes, ūdens ķīmiskā sastāva un ūdens izmantošanas potenciāla. Visas trīs zonas ir atdalītas ar reģionālajiem sprostslāņiem (Kitterød et al., 2022; Retike et al., 2016b).

Stagnantā (pasīvā) ūdens apmaiņas zona jeb kembrija–venda (Cm–V) nesējslāņu komplekss atrodas virs kristāliskā pamatklintāja un sastāv no smilšakmeņiem, aleirolīta un māliem, kas satur Na–Cl vai Na–Ca–Cl sālsūdeņus ar mineralizāciju ap 100–140 g/l (Levins et al., 1998; Raidla et al., 2009). Apakšdevona līdz vidusdevona Pērnavas ūdens nesējslāņi veido pasīvo ūdens apmaiņas zonu un sastāv no smilšakmeņiem, ar aleirolītu, merģeļu un mālu starpslāņiem, un Latvijas rietumu daļā sasniedz maksimālo biezumu 200 m. Pasīvajā ūdens apmaiņas zonā dominē Na–Cl (dažreiz Na–Cl–SO_4) tipa sāļūdeņi ar mineralizāciju robežās no 3 līdz 10 g/L (Levins un Gosk, 2008; Levins et al., 1998), izņemot Latvijas ziemeļu daļā, kur nesējslāņi satur labas kvalitātes Ca–Mg–HCO_3 saldūdeņus (mineralizācijai nepārsniedzot 600 mg/L) (Retiķe un Dēliņa, 2018).

Vidējā līdz augšdevona un kvartāra nogulumi veido aktīvās ūdens apmaiņas zonu, savukārt Latvijas dienvidrietumu daļā ir sastopami arī plāni karbona, perma, triasa un juras nogulumieži (Lukševičs et al., 2012). Kopējais aktīvās ūdens apmaiņas zonas biezums svārstās no dažiem metriem Latvijas ziemeļrietumu malā līdz 650 m Latvijas dienvidu daļā (Retiķe un Dēliņa, 2018). Lielākajā daļā Latvijas pazemes ūdens atradņu tiek izmantoti vidusdevona Arukilas, Burtnieku un augšdevona Gaujas un Amatas ūdens nesējslāņi (Klints un Dēliņa, 2012). Aktīvajā ūdens apmaiņas zonā dominē Ca–Mg–HCO_3 ūdens tipa saldūdeņi ar mineralizāciju līdz 500 mg/L un bieži paaugstinātu kopējā dzelzs saturu (līdz 1,5–1,7 mg/L). Ģipša šķīšanas un ūdens sajaukšanās dēļ aktīvās ūdens apmaiņas zonas centrālajā un rietumu daļā var novērot arī Ca–Mg–SO_4 tipa saldūdeņus un Ca–SO_4 iesāļūdeņus ar mineralizāciju līdz 2 g/L (Kitterød et al., 2022; Levins un Gosk, 2008; Retike et al., 2016b).

Visu Latvijas teritoriju pārsedz kvartāra, pārsvarā ledāju un jūras nogulumi, un virsma ir ļoti neviendabīga (Popovs et al., 2015). Kvartāra nogulumu biezums svārstās no dažiem metriem līdz pat 200 m aprakto ieleju apkārtnē. Sekla ieguluma dziļuma dēļ kvartārsegas pazemes ūdeņus bieži izmanto lauku apvidos, kur iedzīvotāji ūdensapgādē lieto privātas akas vai spices (Klavins et al., 1996; Retike et al., 2016a). Augstākās nitrātu koncentrācijas Latvijas pazemes ūdeņos konstatētas seklos urbumos līdz 5 metru dziļumam un avotos, dažkārt pārsniedzot robežvērtību 50 mg/L un pat sasniedzot ~100–200 mg/L (Nitrates report, 2020). Jaunākie pētījumi uzrāda ļoti mainīgas NO_3^- koncentrācijas Latvijas avotos, sākot no dažiem miligramiem litrā (Koit et al., 2023) līdz 50 mg/L augstām koncentrācijām (Kalvāns et al., 2021).

Pazemes ūdeņu intensīva ieguve iepriekšējās desmitgadēs ir izraisījusi ievērojamu jūras ūdens intrūziju augšdevona Mūru-Žagares (D_3*mr-žg*) nesējslānī Liepājā, izraisot plašas piekrastes teritorijas stāvokļa pasliktināšanos. Jūras ūdens intrūzijas ietekmētā teritorija ir izdalīta kā atsevišķs pazemes ūdensobjekts un tam piešķirts riska stāvoklis (Bikše un Retike, 2018). Saldūdens nesējslāņu sasāļošanas ir novērota arī Rīgas apkārtnē, kur 70. gados intensīvas pazemes ūdeņu ieguves dēļ izveidojās liela depresijas piltuve (Klints un Dēliņa, 2012). Tomēr sasāļošanās avots, visticamāk, nav saistīts ar jūras ūdeņu intrūziju, bet gan ar dziļākieguļošo sālsūdeņu augšupejošu migrāciju caur tektoniskajiem lūzumiem no pasīvās jeb stagnantās ūdens apmaiņas zonas (Kalvāns, 2012).

2. MATERIĀLI UN METODES

2.1. Hidroģeoloģiskie dati

Šajā pētījumā datu kopas tika iegūtas no dažādiem avotiem, lielā daļa pēc pieprasījuma no datu īpašniekiem un uzturētājiem, piemēram, Latvijas Vides, ģeoloģijas un meteoroloģijas centra (LVĢMC) (https://videscentrs.lvgmc.lv/). Katram paraugam papildus tika apkopota pavadošā informācija par vietas raksturlielumiem (piemēram, urbuma numurs, stacija, koordinātes), hidroģeoloģiskajiem un ģeoloģiskajiem apstākļiem (piemēram, ūdens nesējslānis un tā materiāls, paraugu ņemšanas dziļums) un analītiskajiem ierakstiem (piemēram, paraugu ņemšanas/analīzes datums, analītiskās metodes noteikšanas robežas, atzīmes par iespējamām kļūdām), ja šāda informācija bija pieejama. Promocijas darba izstrādei izmantoto datu avotu kopsavilkums ir parādīts 1. tabulā. Detalizēti katram konkrētajam pētījumam izmantoto vai apkopoto datu kopu apraksti ir atrodami publikācijās (Publikācija I–X).

1. tabula. Šajā darbā izmantoto hidroģeoloģisko datu kopu kopsavilkums ar atsauci uz publikācijām

Datu avots	Izgūtie parametri	Datu veids	Laika periods	Zinātniskie raksti, kuros izmantots datu avots
Latvijas pazemes ūdeņu novērojumu datubāze (Observation database, n.d.)	Lauka parametri, pamatjoni, slāpekļa savienojumi, smagie metāli, pazemes ūdens līmeņi	MU, MA	1960–2018	**Publikācija II–X**
Pazemes ūdeņu reģistrs "Urbumi" (Urbumi, n.d.)	Lauka parametri, pamatjoni, slāpekļa savienojumi, smagie metāli, mikroelementi ([1])	ŪU	1994–2018	**Publikācija II–X**
Retike et al., 2016b; Levins and Gosk, 2007	Lauka parametri, pamatjoni, smagie metāli, mikroelementi ([1,2])	ŪU, MA, A, PU, DR	1997–2013	**Publikācija II, IX–X**
Baltijas jūras ūdens paraugs (Retike un Bikše, 2018)	Lauka parametri, pamatjoni, Br, As, P_{kop}, NH_4^+	J	2017	**Publikācija VIII**

Saīsinājumi:
MU, monitoringa urbums; MA, monitoringa avots; ŪU, ūdensapgādes urbums; A, avots; PU, projekta urbums; DR, drena; J, jūras ūdens.
Lauka parametri (*pH*, temperatūra, elektrovadītspēja, oksidēšanās-reducēšanas potenciāls, Fe_{kop}); pamatjoni (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-)
Slāpekļa savienojumi (NO_3^-, NO_2^-, NH_4^+, N_{kop}); smagie metāli (Cd, Pb, Ni, Hg)
Mikroelementi[1] (F, B, Cr, Cu, Sb, Se), [2] (Al, Ba, Br, Co, Rb, Si, Sr, U, V, Zn, Zr, As)

Datiem tika veikta pamata kvalitātes kontrole un viendabīguma novērtējums, tādējādi nodrošinot uzticamas un reprezentatīvas informācijas izmantošanu turpmākai analīzei. Galvenie datu pirmapstrādes posmi ir aprakstīti turpmākajās sadaļās.

Dēliņa (2006) ir veikusi līdz šim plašāko pētījumu par pazemes ūdeņu izpētes vēsturi no 19. gadsimta līdz 2006. gadam Latvijā, savukārt šajā pētījumā uzsvars tiek likts uz sistemātiskā pazemes ūdeņu monitoringa novērtējumu Latvijā, tā raksturojumu un ES ŪSD prasību ieviešanas radītajām izmaiņām. Pārskati par monitoringa programmu īstenošanu līdz 2005. gadam tika apkopoti no Valsts ģeoloģijas fonda (Latvija) arhīva, kur oriģināleksemplāri pieejami tikai drukātā veidā.

2.2. Daudzfaktoru statistikas analīzes

Daudzfaktoru statistikas izmantošana ir pierādījusi savu efektīvi, analizējot hidroģeoķīmiskās datu kopas, kas iegūtas dažādos mērogos, sākot no lokāla līdz reģionālam (Biddau et al., 2017; Bondu et al., 2020; Busico et al., 2018; Cloutier et al., 2008; Koit et al., 2021, 2023; Slama et al., 2022). Lai identificētu procesus, kas kontrolē pazemes ūdeņu ķīmiskā sastāva attīstību, tika izmantotas divas biežāk lietotās daudzfaktoru statistiskās metodes – galveno komponentu analīze (GKA) un hierarhiskā klāsteranalīze (HKA). Datu pirmapstrāde un analīze tika veikta, izmantojot SPSS *Statistics 22* un *26* programmatūru. Galveno darbību kopsavilkums, kas veikts, lai sagatavotu hidroģeoķīmisko datu kopas daudzfaktoru statistiskai analīzei, ir parādīts 2. tabulā.

2. tabula. Datu apstrādes darbplūsma daudzfaktoru statistiskajām analīzēm Publikācijai IX un X (NR — analītiskās metodes noteikšanas robeža)

Datu apstrādes solis	Veiktās darbības	Atsauces uz līdzīgām datu apstrādes pieejām
Kvalitātes un precizitātes kontrole	Dublikātu, izlecošos vērtību un paraugu ar iztrūkstošām vērtībām izņemšana	Cloutier et al. (2008)
	Paraugu ar jonu bilances novirzi > ± 10% izņemšana	Güler et al. (2002)
Priekšapstrāde	NR vērtību aizvietošana ar pusi no NV	Bondu et al. (2020) Farnham et al. (2002) Walter et al. (2019)
	Parametru ar nelielām vērtību variācijām datu kopā izslēgšana no turpmākās analīzes	Bondu et al. (2020) Farnham et al. (2002, 2003) Cloutier et al. (2008)
Transformācija	Logaritmiskā transformācija, lai tuvotos datu normālsadalījumam	Cloutier et al. (2008) Güler et al. (2002)
	Standartizācija (z vērtības)	

Šajā pētījumā mikroelementi netika iekļauti daudzfaktoru statistikas analīzēs daudzu iztrūkstošo mērījumu dēļ, kas krasi samazinātu sākotnēji apjomīgo datu kopu telpisko pārklājumu. Bet papildus parametri, piemēram, slāpekļa savienojumi un mikroelementi, tika tālāk analizēti izdalīto grupu ietvaros.

2.3. Piesātinājuma indeksu un jūras ūdens proporcijas aprēķini

Kalcīta, dolomīta, ģipša un halīta minerālu piesātinājuma indeksi Publikācijai X tika aprēķināti, izmantojot programmatūras PHREEQC 3. versiju (Parkhurst un Appelo, 2013). Aprēķins tika veikts izmantojot pamatjonu koncentrācijas, temperatūru un *pH* vērtības.

Publikācijā VIII (Retike un Bikše, 2018) jūras ūdens proporcijas $f_{\text{jūra}}$ pazemes ūdeņu paraugos tika aprēķinātas gan uz hlorīda (Cl^-), gan bromīda (Br^-) joniem, kurus var uzskatīt par konservatīviem marķieriem Baltijas valstu reģionam saskaņā ar šādu vienādojumu (Appelo un Postma, 2005):

$$\frac{m_{x(paraugs)} - m_{x(saldūdens)}}{m_{x(jūras\ ūdens)} - m_{x(saldūdens)}} \times 100\% \qquad (1)$$

kur m_X – Cl^- vai Br^- koncentrācija saldūdens, jūras ūdens vai pazemes ūdens paraugā. Hlorīdjonu koncentrācija saldūdens paraugam tika aprēķināta kā vidējais Cl^- saturs no urbumiem Nr. 9322 un Nr. 2254 (Urbumi, n.d.). Šie urbumi ir iekšzemes fona monitoringa stacijas, kas ierīkotas augšdevona Mūru-Žagares (D_3*mr-žg*) ūdens nesējslāņos un tika uzskatītas par tādām, kuras nav jūras ūdeņu intrūzijas ietekmētas. No Baltijas jūras ņemtais paraugs aprēķinos izmantots kā jūras ūdens gala sastāvs. Jūras ūdens paraugu ņemšanas zonas un dziļums (9 metri) tika izvēlēts pamatojoties uz hipotētisku jūras ūdens intrūzijas saldūdens nesējslāņos atrašanās vietu.

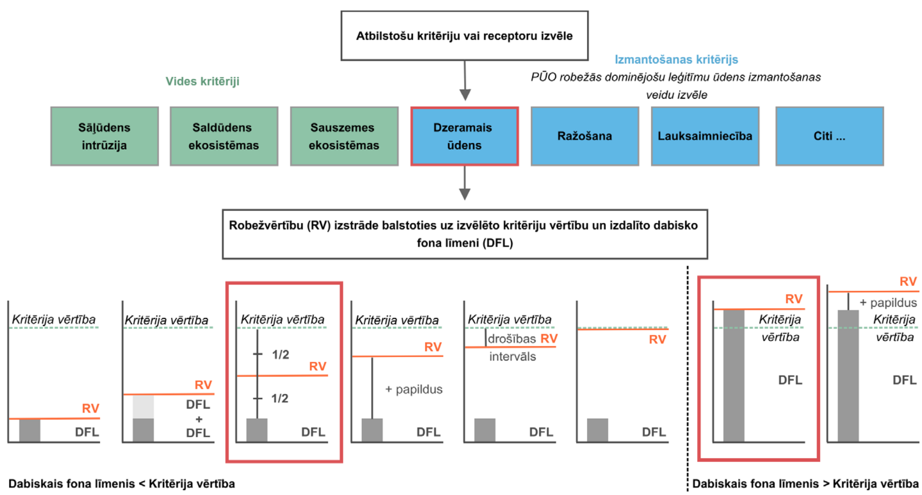
2.4. Dabīgo fona līmeņu un robežvērtību noteikšana

Šajā pētījumā (Publikācija VIII) tika adaptēta un izmantota plaši pielietotā BRIDGE metodoloģija (Müller et al., 2006), lai noteiktu dabisko fona līmeņus (DFL) un robežvērtības (RV) riska PŪO "Liepāja un teritorija uz dienvidaustrumiem no tās līdz ūdensgūtnei Otaņķi". Pamatojoties uz pētījuma vietas hidroģeoloģiskajiem apstākļiem, tika nolemts noteikt DFL un RV nātrija, hlorīda un sulfātjoniem, kas ir reprezentatīvākie parametri, lai identificētu jūras ūdeņu intrūziju Liepājas apkārtnes saldūdens nesējslāņos. Turklāt šie parametri vienmēr ir bijuši iekļauti pazemes ūdeņu kvalitātes jeb ķīmiskā sastāva monitoringā Latvijā. Galvenie soļi, lai aprēķinātu dabiskos fona līmeņus ir apkopoti 3. tabulā.

3. tabula. Darbplūsma dabiskā fona līmeņu noteikšanai

Datu apstrādes solis	Veiktās darbības
Kvalitātes un precizitātes kontrole	Paraugu ar nezināmu dziļumu un ģeogrāfiskajām koordinātām izņemšana no datu kopas
	Paraugu izņemšana, kuriem iztrūkst kāda no pamatjonu vērtībām
	Paraugu ar jonu bilances novirzi > ± 10% izņemšana
Piesārņotu paraugu izņemšana	Paraugu ar Cl^- > 18 mg/L un NO_3^- > 4 mg/L izņemšana atbilstīgi Retike et al. (2016a, b) pētījumam
Dabisko fona līmeņu (DFL) noteikšana	Monitoringa punktiem aprēķinātas mediānās vērtības
	Sliekšņa vērtības noteikšana pazemes ūdeņu paraugiem atbilstīgi Panno et al. (2006) pieejai un 90. procentiles noteikšana saldūdens paraugos zem sliekšņa vērtības

Ņemot vērā šobrīd ierobežoto zināšanu bāzi par citu receptoru ūdens kvalitātes vajadzībām, šajā pētījumā, tāpat kā lielākajā daļā dalībvalstu (Scheidleder, 2012), tika izmantoti nacionālie dzeramā ūdens kvalitātes standarti (Ministru kabineta 2017. gada 14. novembra noteikumi Nr. 671 “Dzeramā ūdens obligātās nekaitīguma un kvalitātes prasības, monitoringa un kontroles kārtība”) kā kritēriju vērtības (3. attēls).



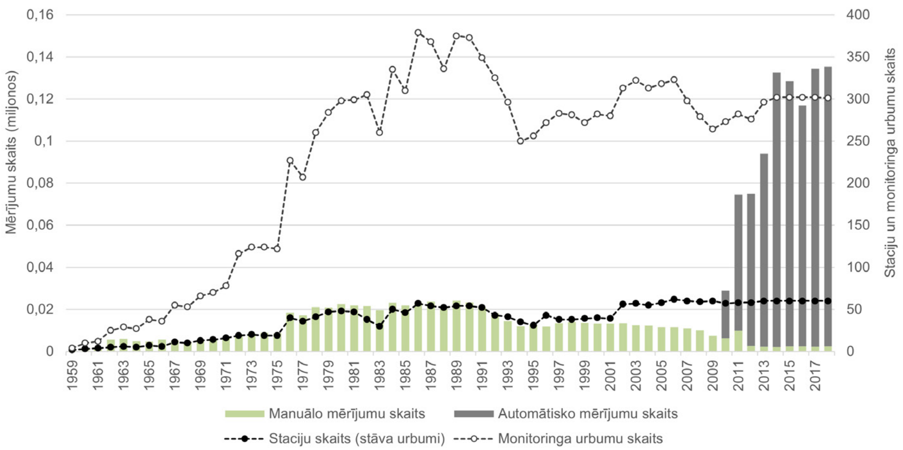
3. attēls. ES dalībvalstīs robežvērtību iegūšanai izmantoto metodoloģiju shematisks attēlojums. Ar sarkanu norādīta izvēlētā pieeja Latvijai un šim pētījumam (pielāgots no European Commission and Scheidleder, 2012).

3. REZULTĀTI UN DISKUSIJA

3.1. Pazemes ūdeņu monitoringa raksturojums un perspektīvas Latvijā

3.1.1. Sistemātiskais pazemes ūdeņu līmeņu monitorings

Pirmie sistemātiskie pazemes ūdeņu līmeņu mērījumi Latvijā tika veikti sākot ar 1959. gadu (4 urbumos) un ir vērojama monitoringa urbumu skaita pieauguma tendence līdz 1990. gadam (375 urbumi) 4. attēls). Pazemes ūdeņu līmeņa monitorings Latvijā piedzīvoja krasas izmaiņas kopš tika ieviesti automātiskie ūdens līmeņa mērītāji – 2010. gadā ar tiem tika aprīkoti pirmie urbumi un jau tajā pašā gadā kopējais līmeņa mērījumu skaits, salīdzinot ar 2009. gadu, pieauga gandrīz četras reizes. Kopš tā laika automātiskie mērījumi veido lielāko daļu pazemes ūdeņu līmeņu datu kopā. Pazemes ūdeņu līmeņu monitoringa urbumu telpiskais pārklājums ir palielinājies visā monitoringa periodā, savukārt kopš 90. gadiem izmaiņas ir bijušas nelielas.



4. attēls. Izmaiņas sistemātiskajā pazemes ūdeņu līmeņu monitoringā no 1959. līdz 2018. gadam Latvijas teritorijā (modificēts pēc Retike et al., 2022).

Automātiski pazemes ūdeņu līmeņu novērojumi tiek veikti lielākajā daļā Eiropas valstu, piemēram, Igaunijā, Lietuvā, Austrijā, Dānijā, Vācijā un citās (IGRAC, 2020). No vienas puses, automātisko līmeņu mērītāju ieviešana ir devusi jaunu ieskatu pazemes ūdeņu dinamiku ietekmējošajos faktoros Latvijā, piemēram, devusi iespēju pētīt pazemes ūdeņu sausuma epizodes (Bikše et al., 2023; Babre et al., 2022). No otras puses, ja automātiskie līmeņu mērītāji ir nepareizi ievietoti vai nedarbojas, laika rindās rodas jauna veida kļūdas. Visbiežāk konstatētās kļūdas pazemes ūdeņu līmeņu laikrindās ir apkopotas 4. tabulā un tās ir ietekmējušas 88% no Latvijas pazemes ūdeņu līmeņu laikrindām (Retiķe et al., 2022). Patlaban automātisko līmeņu mērītāju datu lejupielāde Latvijā tiek veikta līdz divām reizēm gadā un bieži vien tiek apvienota ar ūdens paraugu ņemšanu, lai ietaupītu izmaksas. Līdz ar to jebkādas problēmas ar līmeņa mērītājiem tiek atklātas tikai pēc pusgada vai vēlāk. Telemetrija (datu nosūtīšana tiešsaistē) ļautu attālināti un savlaicīgi atklāt jebkādas novirzes un palielināt mērījumu skaitu (pašreiz 2 reizes diennaktī), kas pašlaik neļauj fiksēt ļoti īslaicīgas izmaiņas, kā uzsver Rau et al. (2019).

4. tabula. Latvijas pazemes ūdeņu līmeņa laikrindās konstatēto raksturīgāko kļūdu apkopojums un to apstrādes iespējas (modificēts pēc Retike et al., 2022 – Publikācija V).

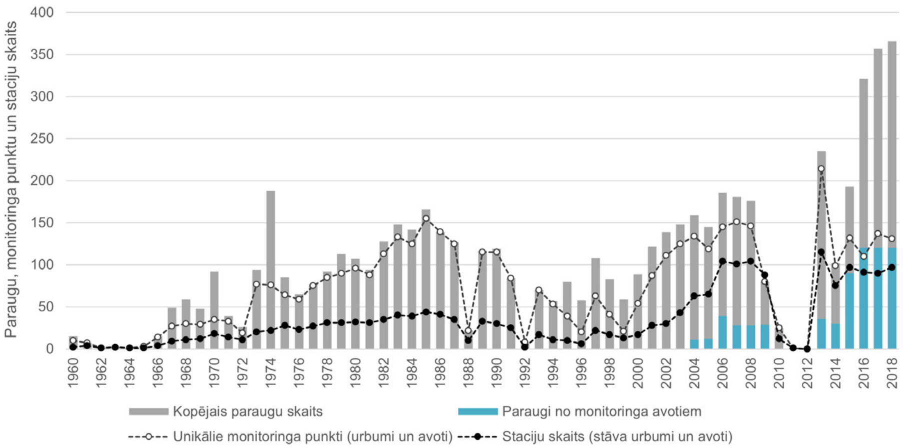
Problēmas	Iespējamie rašanās iemesli	Raksturīgi automātiskajiem/ manuālajiem mērījumiem	Problēmas identificēšanas/ apstrādes sarežģītība
Izlecoša vērtība	Mērījums vai datu apstrāde	Nē/Jā	Zema/Zema
Līmeņa nobīde	Automātiskā līmeņu mērītāja nepareiza ievietošana vai datu apstrāde	Jā/Reizēm (vēsturiskie dati)	Zema/Zema
Līmeņu nobīde ar sekojošu līmeņu atjaunošanos	Urbuma īpatnības vai tuvumā notiekoša atsūknēšana/ papildināšanās	Jā/Nē	Zema/Vidēja
Datu novirze	Automātiskā līmeņu mērītāja darbības traucējums	Jā/Nē	Zema/Vidēja
Izmaiņas laikrindas raksturā	Datu apstrāde vai cilvēka darbības ietekme	Jā/Jā	Augsta/Augsta
Robains/ zobains līmeņa raksturs (lielas novirzes)	Mērījums	Nē/Jā	Zema/Augsta
Troksnis līmeņa novērojumos (daži cm)	Barometriskā līmeņa mērītāja darbības traucējumi pie sasalšanas vai dabiskas svārstības	Jā/Nē	Augsta/Augsta
Plato līmeņa novērojumos	Urbuma komplektācijas/ līmeņa mērītāja ievietošanas problēmas	Jā/Nē	Zema/Augsta

Lielākā daļa pazemes ūdens līmeņu Latvijā un Igaunijā tiek mērīti spiedienūdeņos un dziļi iegulošos ūdens nesējslāņos, savukārt Arustiene (2011) norādīja, ka Lietuvā pazemes ūdeņu līmeņu monitorings ir vērsts uz seklajiem ūdens nesējslāņiem, lai novērtētu klimata pārmaiņu ietekmi uz pazemes ūdeņu atjaunošanos. Gruntsūdeņu un seklāko ūdens nesējslāņu zemā reprezentācija ir viens no lielākajiem Latvijas pazemes ūdens līmeņu datu kopas trūkumiem. Vistuvāk virsmai esošie ūdens nesējslāņi visvairāk reaģē uz sezonālām un starpgadu līmeņa svārstībām un tādējādi ir pirmais klimata pārmaiņu rādītājs (Babre et al., 2022). Turklāt daudzu no pazemes ūdeņiem atkarīgo ekosistēmu (PŪAE) (piemēram, mitrāju, upju un ezeru) pastāvēšana ir atkarīga no pazemes ūdeņu pieplūdes, īpaši no zemes virsai tuvākajiem ūdens nesējslāņiem (Kalvāns et al., 2021; Koit et al., 2023).

Latvijā avoti šobrīd nav iekļauti pazemes ūdeņu kvantitatīvajā monitoringa tīklā. Monitoringa tīklā iekļauto avotu skaita palielināšana, sākot no apgabaliem, kuros trūkst datu (piemēram, pārrobežu ūdens nesējslāņi (Koit et al., 2023)) un avotu aprīkošana ar automātiskiem debita mērītājiem, varētu aizpildīt vairākas konstatētās nepilnības Latvijas pazemes ūdeņu līmeņu monitoringā, piemēram, novērojumu trūkumu PŪAE tuvumā (Terasmaa et al., 2020) un virszemes un pazemes ūdeņu mijiedarbības (Delina et al., 2012; Kalvāns et al., 2020) identificēšanai.

3.1.2. Sistemātiskais pazemes ūdeņu ķīmiskā sastāva monitorings

Sistemātisks pazemes ūdeņu kvalitātes monitorings Latvijā tika uzsākts 1960. gadā (5. attēls) un tas sakrīt ar pazemes ūdens līmeņu monitoringa sākumu (skatīt 4. attēlu). Bet pirmais ievērojamais pazemes ūdeņu paraugu daudzums tika ievākts 1967. gadā. Laika posms no 1973. līdz 1986. gadam ilustrē stāva staciju ierīkošanu – tie ir vairāki blakus esoši monitoringa urbumi vienas stacijas ietvaros, kas ierīkoti dažādos dziļumos, un pieeja ir bijusi Latvijas pazemes ūdeņu monitoringa neatņemama sastāvdaļa. Šī pieeja, kaut arī nav plaši izplatīta, tiek izmantota arī citās valstīs, piemēram, Dānijā (Jørgensen un Stockmarr, 2009) un Lietuvā (Arustiene, 2011), kurās ir līdzīgi hidroģeoloģiskie apstākļi, proti, daudzslāņu sistēmas vai pastāv jūras ūdens/ sālsūdens intrūziju riski (Kitterød et al., 2022). Pēc Padomju Savienības sabrukuma (Jankins et al., 1993) paraugoto urbumu skaits un paraugu ņemšanas biežums samazinājās. Līdz 1999. gadam monitorings turpinājās, balstoties uz padomju laikā izveidoto praksi un ar nepietiekamu finansējumu, tāpēc monitorings bija sadrumstalots un aptvēra tikai daļu Latvijas.



5. attēls. Izmaiņas sistemātiskajā pazemes ūdeņu kvalitātes monitoringā no 1960. līdz 2018. gadam Latvijas teritorijā.

Kopš Latvija kļuva par ES kandidātvalsti 1999. gadā un iestājās ES 2004. gadā, bija vērojams pakāpenisks visu pazemes ūdeņu kvalitātes monitoringu raksturojošo skaitļu pieaugums. Līdzīgas izmaiņas tika novērotas lielākajā daļā ES dalībvalstu, cenšoties strauji uzlabot nacionālos monitoringa tīklus un izpildīt ES ŪSD prasības (Jørgensen un Stockmarr, 2009; Onorati et al., 2006; Quevauviller, 2005). Kopš 2009. gada var novērot būtisku paņemto paraugu un paraugu ņemšanas vietu skaita samazinājumu (5. attēls) globālās ekonomiskās krīzes negatīvās ietekmes un līdz ar to saistītā finansējuma samazinājuma dēļ. Pazemes ūdeņu kvalitātes monitorings Latvijā tika pārtraukts no 2009. gada vidus līdz 2012. gadam un tika atsākts tikai 2013. gadā (VMP, 2010). Ekonomiskās krīzes ietekme uz pazemes ūdens līmeņu monitoringu bija mazāk pamanāma (4. attēls), kas saistāms ar tajā laikā uzstādītajiem automātiskiem līmeņa mērītājiem un kopumā mazākām monitoringa ekspluatācijas izmaksām. Apturētais pazemes ūdeņu kvalitātes monitorings radīja būtiskas nepilnības datu kopās un ievērojami pasliktināja turpmāko 2. un 3. cikla UBAP ziņojumu kvalitāti, jo novērojumu biežums nebija pietiekošs, lai aprēķinātu ilgtermiņa tendences lielākajai daļai monitoringa punktu (Frollini et al., 2021). Līdzīgi arī Jørgensen un Stockmarr (2009) ziņoja par samazinātu Dānijas pazemes ūdeņu monitoringa programmas budžetu jau 2007. gadā, kas negatīvi ietekmēja savākto datu un analizēto parametru skaitu un apdraudēja turpmākās ziņošanas iespējas Eiropas Komisijai.

Pazemes ūdeņu kvalitātes monitorings 2013. gadā tika atsākts mēģinot aizpildīt 3,5 gadu laikā radušos caurumus datu kopā ievērojami samazināta novērojumu skaita dēļ. Kā redzams 5. attēlā, 2013. gadā bija vēsturiski lielākais monitoringā iekļauto novērojuma punktu (214) un staciju (115) skaits. Ziņots, ka no 2015. gada atsevišķos avotos ūdens paraugi tika ievākti sezonāli – līdz 4 reizēm gadā (VMP, 2015).

Lielākā daļa monitoringa urbumu, kas pašlaik darbojas, ir ierīkoti 1970. un 1980. gados pazemes ūdeņu ieguves kontrolei, tādējādi tie ir ierīkoti dziļos ūdens nesējslāņus, kas tiek izmantoti ūdens apgādei (Gosk et al., 2007). Līdz ar to daudzām vērtīgām datu kopām ir risks tikt pārtrauktām urbumu nolietojuma dēļ, tādēļ būtu jāpārbauda vecāko urbumu tehniskais stāvoklis un jāierīko jauni urbumi. Seklo ūdens nesējslāņu reprezentācijas nepietiekamība un ilgtermiņa koncentrēšanās tikai uz dziļajiem ūdens nesējslāņiem ir viens no lielākajiem Latvijas pazemes ūdeņu kvalitātes monitoringa tīkla trūkumiem. Piesārņojums ar nitrātiem un pesticīdiem seklos ūdens nesējslāņos ir labi dokumentēts Baltijas valstīs un ārpus tām (Kalvāns et al., 2021; Kitterød et al., 2022; Retike et al., 2016a, b; Levins un Gosk, 2008). Kā norādījuši Jørgensen un Stockmarr (2009), jaunāku un pret piesārņojumu vāji aizsargātu pazemes ūdeņu monitorings ļauj laikus identificēt piesārņojuma pārvietošanos un novērtēt ilgtermiņa draudus uz ūdens apgādē plaši izmantotajiem spiedienūdens nesējslāņiem īstenojot piesardzības principu.

Jāņem vērā, ka Latvijā ir vairāk nekā 200 pazemes ūdeņu atradņu (iegūst vairāk nekā 100 m^3/d) ar labu spiedienūdeņu nesējslāņu telpisko reprezentāciju, kuriem katru gadu ir jāziņo pazemes ūdeņu kvalitāte (ap 15 dažādiem parametriem). Daudzas pasaules valstis izmanto esošās ūdensapgādes sistēmas valsts pazemes ūdeņu monitoringa ietvaros (IGRAC, 2020), tostarp kaimiņvalsts Lietuva (Arustiene, 2011). Jāpieliek pūles, lai kontrolētu un motivētu pazemes ūdeņu atradņu operatorus veikt valstī noteikto monitoringu, piemēram, sedzot daļu no monitoringa izdevumiem vai nodrošinot apmācību pareizai ūdens paraugu ņemšanai, kas ir viens no galvenajiem šādu datu izmantošanas ierobežojumiem.

Straujā pazemes ūdeņu kvalitātes monitoringa tīkla paplašināšana Latvijā ir nepieciešama, lai izpildītu dažādas ES ūdens politikas vajadzības, piemēram, pārrobežu pazemes ūdeņu monitoringa izveidi, virszemes un pazemes ūdeņu mijiedarbības novērtējumu, nitrātu piesārņojuma novērtējumu un daudzas citas (Quevauviller, 2005). Latvijas pazemes ūdeņu kvalitātes monitoringa tīkla paplašināšana ar ūdens avotiem varētu daļēji aizpildīt robus (Koit et al., 2023) un veicināt starptautisko tiesību aktu un līgumu ieviešanu Latvijā (piemēram, ŪSD, Nitrātu direktīva vai Ūdens konvencija) (Flem et al., 2022; Terasmaa et al., 2020). Avotu ieviešanai monitoringa tīklā ir vairākas būtiskas priekšrocības, piemēram, zemākas paraugu ņemšanas/ monitoringa izmaksas un lielāka sateces baseina raksturojums, kas arī ir iemesls, kāpēc avoti tiek izmantoti kā daļa no valsts pazemes ūdeņu monitoringa visā pasaulē (Bender et al., 2001; IGRAC, 2020; Terasmaa et al., 2020).

3.2. Par pazemes ūdeņu ķīmisko sastāvu atbildīgo galveno procesu raksturojums

3.2.1. Aktīvās ūdens apmaiņas zonas pazemes ūdeņu ģeoķīmiskā sastāva klasifikācija

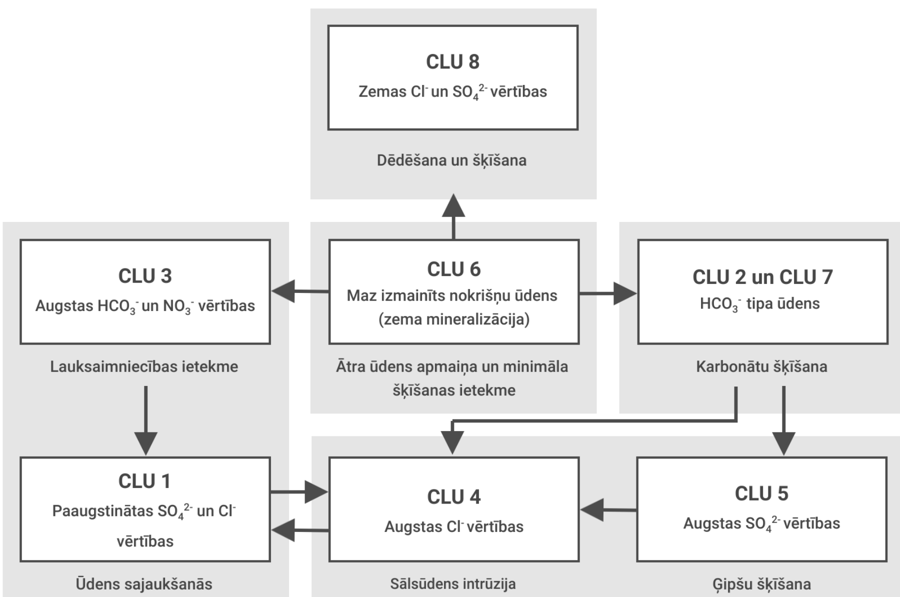
Galveno komponentu analīze ļāva izdalīt trīs galvenos ģeoķīmiskos procesus, kas ir atbildīgi par pazemes ūdeņu evolūciju Latvijas aktīvajā ūdens apmaiņas zonā un izskaidro 84% no kopējās datu kopas variācijas (5. tabula).

5. tabula. Galveno komponentu svars un izskaidrotā dispersija trīs galvenajiem ģeoķīmiskajiem procesiem (galvenajiem komponentiem) Latvijas aktīvās ūdens apmaiņas zonā (mainīgie ar galveno komponentu (PC) svaru lielāku par 0,6 tika uzskatīti par būtiskiem un iezīmēti ar treknrakstu).

Parametrs	PC 1	PC 2	PC 3
Ca^{2+}	0,168	**0,652**	**0,667**
Mg^{2+}	0,524	**0,625**	0,428
Na^{+}	**0,916**	0,104	0,182
K^{+}	**0,824**	0,139	0,123
HCO_3^{-}	0,007	**0,933**	–0,139
Cl^{-}	**0,783**	–0,001	0,381
SO_4^{2-}	0,331	–0,099	**0,878**
Īpašvērtība	3,69	1,40	0,79
Izskaidrotā dispersija (%)	52,67	20,10	11,30
Kumulatīvā dispersija %	52,67	72,72	83,98

Rezultāti atspoguļo jau labi zināmos pazemes ūdeņu tipus, kas novēroti aktīvajā ūdens apmaiņas zonā (Levins et al., 1998). PC 1 atspoguļo palielinātu sāļumu un pāreju uz Na–Cl ūdens tipu un izskaidro vairāk nekā 50% no dispersijas. Šis ūdens tips parasti sastopams sākot no vidus- un apakšdevona līdz kembrija ūdens nesējslāņiem, bet tas nav dominējošais ūdens tips aktīvajā ūdens apmaiņas zonā. Ir vērts pieminēt, ka aptuveni 16% no GKA iekļautajiem paraugiem bija laikrindas, proti, paraugi no tām pašām vietām, kas bieži ierīkoti apgabalos, kuros pastāv riski ūdens kvalitātei (piemēram, depresijas piltuves, lūzumi), un daļēji varētu būt kā izskaidrojums šādiem rezultātiem. Visbeidzot, PC 3 atspoguļo ģipšu šķīšanas ietekmi un Ca–SO_4 ūdens tipu, kas raksturīgs apgabaliem, kur ģipsis ir sastopams augšējā un apakšējā devona ūdens nesējslāņos (galvenokārt augšdevona Salaspils svītā), bet to var atrast arī citās aktīvās ūdens apmaiņas zonas daļās ūdens sajaukšanās dēļ (Levins et al., 1998).

Izmantojot iteratīvu pieeju un pārvietojot Fenona līniju dendrogrammā, tika nolemts izdalīt astoņas ģeoķīmiski atšķirīgas pazemes ūdeņu grupas jeb klāsterus (CLU). Daudzfaktoru statistiskā analīze (GKA un HKA) un astoņu pazemes ūdeņu grupu izdalīšana tika veikta izmantojot tikai pamatjonu datus. Viens no galvenajiem šīs pieejas trūkumiem ir tas, ka cilvēka veselībai kaitīgi elementi, (piemēram, As, F), lielā koncentrācijās bieži sastopami tikai lokāli (Walter et al., 2019). Tāpēc analīzē tieši neiekļautie parametri (mikroelementi, slāpekļa savienojumi) vēlāk tika novērtēti katra klastera ietvaros, balstoties uz daudz mazākām datu kopām. Izvēlētā pieeja labi izskaidroja izdalīto klasteru skaitu un sniedza jaunu ieskatu par iespējamajiem pazemes ūdeņu veidošanās ceļiem aktīvajā ūdens apmaiņas zonā (6. attēls). Galvenie rezultāti ir apkopoti 6. tabulā, savukārt informācija par pazemes ūdeņu ķīmiskā sastāva atšķirībām katrā klasterī (CLU) ir sniegta Publikācijā X.



6. attēls. Pazemes ūdeņu ķīmiskā sastāva evolūcijas ceļi aktīvajā ūdens apmaiņas zonā Latvijā. Pelēkās zonas atspoguļo ciešu savienojuma attālumu, kas novērots hierarhiskajā klasteru analīzē.

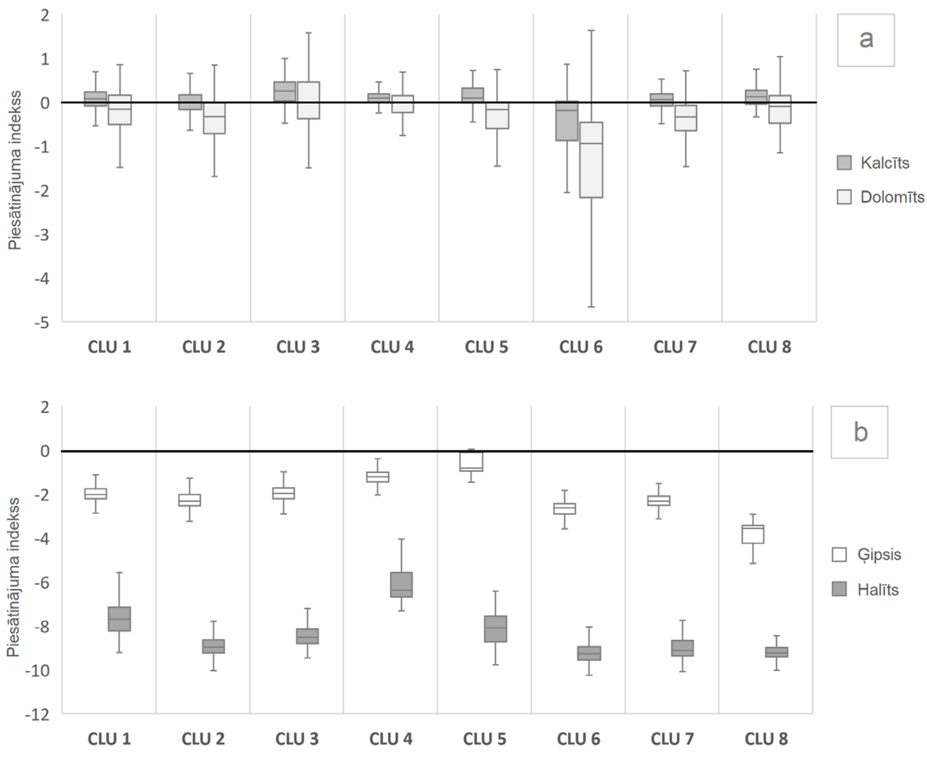
6. tabula. Astoņu atšķirīgu aktīvās ūdens apmaiņas zonas pazemes ūdeņu tipu (klāsteru), kas iegūti no hierarhiskās klastera analīzes, galvenie ģeoķīmiskie un hidroģeoloģiskie raksturlielumi (vidējais dziļums norādīts kā 25. un 75. procentiles; MU – monitoringa urbums, ŪU – ūdensapgādes urbums, A – avots, PU – projekta urbums, DR – drena).

Klāsteris (N, paraugu skaits)	Dominējošais paraugu veids	Vidējais dziļums, (m)	Nesējslāņa materiāls	Dominējošais nesējslānis	Vidējā mineralizācija, (mg/L)	Mediānais ūdens tips	Raksturlielumi (mediānās vērtības)
CLU 1 (*N* = 218)	MU, ŪU, A, PU	4–100	Smilšakmens, smilts, dolomīts, morēna	Q, D_3*gj*, vidusdevons	520–700	Ca–Mg–HCO_3	–
CLU 2 (*N*=213)	MU, ŪU, PU	4–90	Smilšakmens, smilts, dolomīts	Q, D_3*gj*, vidusdevons	400–500	Ca–Mg–HCO_3	Augstākās Al
CLU 3 (*N* = 223)	PU, A, DR	2–7	Morēna, smilts, dolomīts	Q, D_3*pl-slp*	570–750	Ca–Mg–HCO_3	Augstākās Cd, Mn, Ni, Pb, U, Zn, NO_3^-
CLU 4 (*N* = 115)	ŪU, MU	65–170	Smilšakmens	Vidus- un apakšdevons	780–1520	Ca–Mg–Na–Cl–HCO_3	Augstākās B, Br, Rb, Sb, Se, V
CLU 5 (*N* = 98)	MU, ŪU, A	15–100	Smilšakmens, dolomīts, ģipsis	D_3*pl-slp,* D_3*gj*	800–2050	Ca–Mg–SO_4	Augstākās Cu, F, Li, Sr
CLU 6 (*N* = 242)	PU, A, MU	3–15	Smilts, smilšakmens	Q, D_3*gj*, D_2*br*	170–300	Ca–Mg–HCO_3	Zemākās mikro-elementu, slāpekļa savienojumu un mineralizācijas vērtības
CLU 7 (*N* = 240)	A, PU, ŪU	3–50	Smilts, smilšakmens, dolomīts	Q, Augš- un vidusdevons	410–490	Ca–Mg–HCO_3	–
CLU 8 (*N* = 93)	MU, ŪU	25–75	Smilšakmens, dolomīts	Augš- un vidusdevons	420–570	Ca–Mg–HCO_3	Augstākās As, Ba, Fe_{tot}, Si, NH_4^+ un zemas SO_4^{2-}, Cl^-, NO_3^-

Pazemes ūdeņiem no CLU 6 ir viszemākās mineralizācijas un pamatjonu vērtības, kā arī zemas teju visu mikroelementu koncentrācijas (6. tabula). Ņemot vērā salīdzinoši mazo dziļumu un to, ka šīs grupas pazemes ūdeņi ir nepiesātināti attiecībā pret kalcītu (7. attēls), CLU 6 var uzskatīt par sākumpunktu vai sākotnējo sastāvu jebkurai no turpmāk minētajām pazemes ūdeņu grupām.

Pazemes ūdeņu paraugi no CLU 2 un CLU 7 pieder pie Ca–Mg–HCO_3 ūdens tipa, kas bieži sastopams smilšainos kvartāra nogulumos un augšējā un vidējā devona smilšakmens un dolomīta ūdens nesējslāņos. Paraugi galvenokārt ņemti no ūdensapgādes urbumiem, kur ūdeņu kvalitāte kopumā vērtējama kā laba. Galvenā atšķirība starp CLU 2 un CLU 7 ir vidējais nesējslāņu ieguluma dziļums (lielāks dziļums CLU 2) un nedaudz augstākas pamatjonu Na^+, K^+, SO_4^{2-} un mikroelementu Sr, Rb, B koncentrācijas.

Pazemes ūdeņu paraugos no CLU 8 ir ļoti zemas SO_4^{2-} un Cl^- koncentrācijas, abiem anjoniem zem 3 mg/L. Augstas Fe_{kop}, NH_4^+ un zemas NO_3^- vērtības var uzskatīt par indikatoriem, kas liecina par stipri reducējošiem apstākļiem ūdens nesējslānī. Augsts Ba saturs var veidoties zemo SO_4^{2-} koncentrāciju dēļ, pretējā gadījumā Ba tiktu izgulsnēts kā barīts (Mokrik et al., 2009). Pazemes ūdeņu paraugu no CLU 8 izplatību Latvijas teritorijā var iedalīt trīs lielās grupās: (1) saldūdens paraugi no apakšdevona ūdens nesējslāņiem Latvijas ziemeļaustrumu daļā (citās Latvijas daļās ūdens nesējslāņi satur iesāļu vai sāļu ūdeni); (2) paraugu ņemšanas vietas netālu no Daugavpils pilsētas Latvijas dienvidaustrumu daļā, kur atrodas apraktas ielejas; un (3) paraugi no tipiskiem karbonātu nogulumiem augšdevona un Perma ūdens nesējslāņos bez ģipša klātbūtnes.



7. attēls. Piesātinājuma indeksi a) kalcītam un dolomītam un b) ģipsim un halītam, kas sagrupēti atbilstoši astoņām ģeoķīmiski atšķirīgām aktīvās ūdens apmaiņas zonas pazemes ūdeņu grupām (CLU) (izlecošās vērtības nav parādītas). Piesātinājuma slieksnis ir virs nulles, kas norādīts ar melnu līniju.

Pazemes ūdeņu paraugi no CLU 3 atspoguļo nepiesātinātus nesējslāņus vai atsevišķos gadījumos paraugus, kas ņemti no drenām. CLU 3 raksturīgas paaugstinātas NO_3^- un tādu mikroelementu vērtības, kas ir mobili aerobā vidē (skatīt 6. tabulu), un galvenokārt augstākas parametru vērtības tiek saistītas ar lauksaimniecības ietekmi (Helena, 2000; Levins un Gosk, 2008). Augstākas NO_3^- vērtības seklajos ūdens nesējslāņos atspoguļo izkliedēto piesārņojumu un ir nitrifikācijas procesa rezultāts (Valle Junior et al., 2014), un līdzīgus novērojumus veikuši arī citi pētījumi kā Levins un Gosk (2008). Drenāžas un apūdeņošanas procesi veicina pazemes ūdeņu aerāciju (Levins un Gosk, 2008), kā rezultātā var palielināties arī U vērtības, kas oksidējošos apstākļos ir mobilāks. Augsta mineralizācija seklos nesējslāņos un tas, ka pazemes ūdeņi ir piesātināti gan attiecībā uz kalcītu, gan dolomītu, liecina, ka zemes apstrāde (piemēram, aršana) ir veicinājusi karbonātu un ģipša šķīšanu augsnēs (Valle Junior et al., 2014). Iespējamais CLU 3 attīstības ceļš ir tieši no CLU 6 (6. attēls).

Paraugi no CLU 4 atspoguļo divas galvenās pazemes ūdeņu izcelsmes: (1) pazemes ūdeņi ar augstu mineralizāciju no pasīvās ūdens apmaiņas zonas vai saldūdeņu sajukšanās rezultāts ar pazemes ūdeņiem no pasīvās un stagnantās ūdens apmaiņas zonas ar lielāku ieguluma dziļumu (2) sāļūdens intrūzijas ietekmēti pazemes ūdeņi Rīgas un Liepājas apkārtnes augšējā un vidusdevona saldūdens nesējslāņos (Bikše un Retike, 2018; Kitterød et al., 2022; Pulido-Velazquez et al., 2022; Retike un Bikše, 2018). Abu izcelsmju pazemes ūdeņi ir piesātināti attiecībā pret kalcītu un dolomītu, tomēr tikai mineralizētākie jeb sālsūdens paraugi ir piesātināti vai tuvu piesātinājumam pret ģipsi un halītu. Daudzu mikroelementu augstākās vērtības, kas novērotas CLU 4 (6. tabula), ir raksturīgas ūdeņiem ar augstu mineralizāciju (Faye et al., 2005; Cloutier et al., 2008). Galvenie procesi, kas kontrolē CLU 4 ķīmiju, ir ģipšu šķīdināšana, ūdeņu ar dažādu mineralizāciju sajaukšanās un jonu apmaiņa starp Ca^{2+} un Na^+.

Paraugi no CLU 5 pieder vai tuvojas $Ca–SO_4$ ūdens tipam. Dominējošais ģeoķīmiskais process, kas veido CLU 5, ir ģipša šķīdināšana, ko var pamatot ar parauga piesātinājumu attiecībā pret kalcītu un ģipsi (7. attēls). Lielākā daļa paraugu atrodas apgabalos, kur nogulumos ir sastopams ģipsis vai ir zināms, ka nesējslāņi satur sulfātiem bagātus pazemes ūdeņus (iespējams, ūdens sajaukšanās rezultātā). Ir zināms, ka CLU 5 piederošajiem pazemes ūdeņiem raksturīgie mikroelementi (6. tabula) ir iekļauti karbonātos vai evaporītos kā sekundāri minerāli, piemēram, celestīns (Faye et al., 2005; Klimas un Mališauskas, 2008). $Ca–SO_4$ ūdens tipa pazemes ūdeņi parasti attīstās no $Ca–Mg–HCO_3$ pazemes ūdeņiem, tāpēc iespējamais evolūcijas ceļš ir no mazāk mineralizētiem hidrogēnkarbonātu ūdeņiem no CLU 2 vai CLU 7 (6. attēls).

CLU 1 paraugi raksturo dažādus ģeoķīmiskos procesus. Daļa paraugu pieder $Ca–Mg–HCO_3$ ūdens tipa spiedienūdeņiem ar nedaudz paaugstinātu līdz augstu Cl^- koncentrāciju. Dažas paraugu ņemšanas vietas atrodas Rīgas, Jūrmalas un Liepājas apkaimē, kur notiek sāļūdens intrūzijas (Bikše un Retike, 2018; Kitterød et al., 2022; Pulido-Velazquez et al., 2022; Retike un Bikše, 2018), tādējādi atspoguļojot iespējamo saikni starp CLU 1 un CLU 4 (6. attēls). Daži paraugi no CLU 1 uzrāda ļoti augstas Na^+ un Cl^- vērtības, kā arī Na/Cl attiecību, kas ir tuvu 1. Šie paraugi varētu būt cilvēku saimnieciskās darbības ietekmēti un halīta šķīšanas rezultāts no ceļu kaisīšanas (Cloutier et al., 2008). Rezultātā CLU 1 paraugiem ir divas iespējamās izcelsmes: (1) cilvēka saimnieciskās darbības ietekme pilsētvidē un (2) saldūdens sajaukšanās ar augstākas mineralizācijas ūdeni vai nesējslāņu atsāļošanās process.

3.2.2. Kvartāra pazemes ūdeņu aizsargātības novērtējums

Šī pētījuma daļa padziļināti analizēja kvartārsegas pazemes ūdeņus, jo tie ir mazāk aizsargāti pret virszemes piesārņojumu (Kalvāns et al., 2021; Kitterød et al., 2022). Papildus pamatjoniem daudzfaktoru statistiskajā analīzē (GKA un HKA), kas veikta 650 paraugiem, tika iekļauti tādi slāpekļa savienojumi kā N-NO_3^-, N-NO_2^-, N-NH_4^+, jo tie bija būtiski pētījuma mērķa sasniegšanai. Galvenie GKA un HKA rezultāti mediāno vērtību veidā ir apkopoti 7. tabulā kopā ar mineralizācijas un *pH* vērtībām.

Var novērot, ka augstākās mediānās pamatjonu vērtības (izņemot HCO_3^-) sastopamas paraugos, kas grupēti CLU 2. Augstākais mediānais pozitīvā galvenā komponenta PC 2 svars kopā ar augstāko mediāno mineralizāciju apstiprina hipotēzi par saldūdeņu sajaukšanos ar augstākas mineralizācijas ūdeņiem, kuros dominē Na^+ un Cl^-. Dažos paraugos Na/Cl attiecība bija tuvu 1, kas norāda uz iespējamo halīta šķīšanu, kura izcelsme ir ceļu kaisīšana ziemā (Cloutier et al., 2008). Kā norāda Dēliņa (2006), augstākas Na^+, Cl^- and K^+ vērtības kvartāra pazemes ūdeņos konstatētas tikai smilšainos nogulumos jūras piekrastē , tomēr CLU 2 paraugu ņemšanas vietu telpiskā izplatība aptver plašākas teritorijas un punkti pārsvarā koncentrējas īpaši jutīgajās teritorijās (8. attēls).

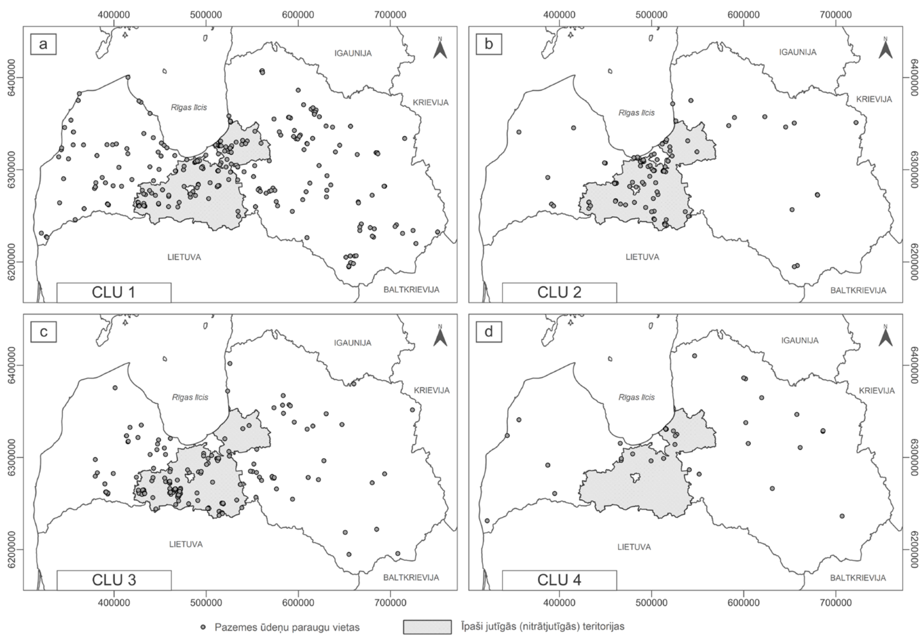
7. tabula. Latvijas kvartāra pazemes ūdeņu ķīmiskais sastāvs četrām izdalītajām grupām (klāsteri) un visai datu kopai (augstākās vērtības iezīmētas treknrakstā un zemākās pasvītrotas; mineralizācija aprēķināta no pamatjoniem un N-NO_3^-; PC – galvenais komponents, N – paraugu skaits, CLU – klāsteris).

Parametrs	CLU 1 (*N* = 298)	CLU 2 (*N* = 121)	CLU 3 (*N* = 194)	CLU 4 (*N* = 37)	Visi paraugi (*N* = 650)
Ca^{2+} (mg/L)	65,5	**105,0**	**105,0**	<u>18,0</u>	81,0
Mg^{2+} (mg/L)	16,0	**34,0**	30,0	<u>3,1</u>	22,6
Na^+ (mg/L)	4,1	**20,0**	7,2	<u>2,2</u>	5,7
K^+ (mg/L)	1,5	**9,9**	2,5	<u>1,4</u>	2,2
HCO_3^- (mg/L)	252,5	360,0	**412,5**	<u>60,0</u>	315,0
Cl^- (mg/L)	6,0	**33,0**	15,0	<u>4,0</u>	11,0
SO_4^{2-} (mg/L)	13,0	**52,0**	26,5	<u>8,2</u>	20,0
N-NH_4^+ (mg/L)	0,18	**0,48**	<u>0,14</u>	0,19	0,18
N-NO_2^- (mg/L)	0,01	0,01	0,01	0,01	0,01
N-NO_3^- (mg/L)	<u>1,20</u>	10,23	**11,60**	1,68	3,19
pH	**7,4**	7,3	**7,4**	<u>6,5</u>	**7,4**
Mineralizācija (mg/L)	383,8	**776,1**	630,5	<u>100,9</u>	495,7
PC 1	–0,29	0,37	**0,78**	<u>-2,27</u>	0,10
PC 2	<u>-0,50</u>	**1,46**	-0,16	-0,33	-0,16
PC 3	<u>-0,41</u>	**0,57**	0,34	0,38	0,02

CLU 4 paraugiem raksturīgas visu pamatjonu, mineralizācijas un *pH* zemākās mediānās vērtības, kā arī zemākais mediānais PC 1 galvenā komponenta svars, salīdzinot ar pārējām trim grupām. Visu CLU 4 parametru uzskaitītās koncentrācijas ir daudz zemākas nekā iepriekš veiktajā pētījumā konstatētajā grupā, kas tika raksturota kā maz mainīts nokrišņu ūdens sastāvs (Retike et al., 2016b). CLU 4 pieder Ca–HCO_3 ūdens tipam ar relatīvi zemākām Mg^{2+} koncentrācijām salīdzinājumā ar Ca^{2+} koncentrācijām. Tādējādi pazemes ūdeņu paraugus no CLU 4 var interpretēt kā ļoti jaunus pazemes ūdeņus (arī gruntsūdeņus), kas veidojušies smilšainos nogulumos un reprezentē lokālus barošanās apgabalus.

CLU 1 grupē Ca–Mg–HCO_3 tipa pazemes ūdeņus ar kvartāra nogulumiem raksturīgākajām ķīmiskajām īpašībām Latvijā (Dēliņa, 2006), un paraugu ņemšanas vietas ir izvietotas visā valstī bez īpaša telpiskā rakstura (9. attēls).

Pazemes ūdeņu paraugi no CLU 3 arī pieder pie Ca–Mg–HCO_3 ūdens tipam, un tiem ir augstākās vidējās Ca^{2+}, HCO_3^- and N-NO_3^- vērtības, visaugstākais pozitīvais PC 1 un pozitīvs PC3 komponenta svars. Līdzīgi rezultāti tika iegūti iepriekšējā pētījumā (Retike et al., 2016), kas liecina par izkliedētu lauksaimniecības slodzi. Tāpat hipotēzi apstiprina CLU 3 paraugu ņemšanas vietu novietojums (8. attēls) lauksaimniecības intensīvāk izmantotajās teritorijās Lielupes un Gaujas upju baseinos.



8. attēls. Kvartāra pazemes ūdeņu paraugu (avotu un urbumu) telpiskais novietojums atbilstīgi sadalījumam grupās (klāsteros) izmantojot hierarhisko klastera analīzi: a) CLU 1, b) CLU 2, c) CLU 3, d) CLU 4 (CLU – klāsteris).

Kā redzams 7. tabulā, lielākās N-NO_3^- koncentrācijas ir atrodamas CLU 2 un CLU 3 paraugos. Saskaņā ar CORINE Land Cover zemes seguma klašu datiem CLU 3 paraugi lielākoties atrodas lauksaimniecības platībās kam seko mākslīgās platības, bet CLU

2 paraugi – mākslīgās platībās un pēc tam seko lauksaimniecības platības. Zemākās mediānās N-NO_3^- koncentrācijas ir CLU 1 un CLU 4. Abos klāsteros dominējošais zemes segums ir meži un dabiskas platības vai mitrzemes. Teritorijas ar augstāku māla saturu nogulumos tiek uzskatītas par labāk aizsargātām no virszemes piesārņojuma. Tajā pašā laikā lauksaimniecībā šīs labāk pasargātās teritorijas tiek plaši izmantotas auglīgo augšņu dēļ, tādēļ uz tām pastāv lielāka cilvēku darbības radītā slodze. Rezultātu interpretācija norāda, ka visi Latvijas kvartāra pazemes ūdeņi pie noteiktām slodzēm var kļūt neaizsargāti pret piesārņojumu ar slāpekļa savienojumiem (un, iespējams, arī citiem piesārņotājiem). Tāpat pazemes ūdeņu dabiskā aizsargātība pati par sevi nav izmantojama kā pazemes ūdeņu aizsardzības rīks, bet drīzāk jāizmanto apvienojumā ar citiem faktoriem, piemēram, mēslošanas slodzēm vai ģeoloģiskajām īpašībām.

Piemēram, Kalvāns et al. (2021) piedāvā pazemes ūdeņu jutīguma pret nitrātiem karti augšdevona Pļaviņu ūdens nesējslānim (D_3*pl*), kas izstrādāta, ņemot vērā specifiskos ģeoloģiskos apstākļus – plānu kvartāra nogulumu slāni, kas pārsedz karsta procesu ietekmētu nesējslāni ar nitrātu migrācijai labvēlīgiem apstākļiem. Šādi apstākļi nav labvēlīgi dabiskajam denitrifikācijas procesam, kas parasti ir atbildīgs par strauju slāpekļa slodzes samazināšanos un zemām nitrātu koncentrācijām Latvijas pazemes ūdeņos, kas ieguļ dziļāk par 5 metriem (Kitterød et al., 2022). Šeit tiek rosināti turpmāki pētījumi, lai identificētu visus atbildīgos faktorus, kas pakļauj noteiktas teritorijas zemes izmantošanas veida vai to izmaiņu radītam riskam. Turklāt riskam pakļautās teritorijas būtu jādefinē, pamatojoties uz konceptuālu izpratni par pazemes ūdeņu sistēmas darbību (Koit et al., 2023), un tās jāņem vērā, plānojot un pārskatot valsts pazemes ūdeņu kvalitātes pārvaldības praksi, piemēram, nosakot vai pārskatot īpaši jutīgo teritoriju robežas.

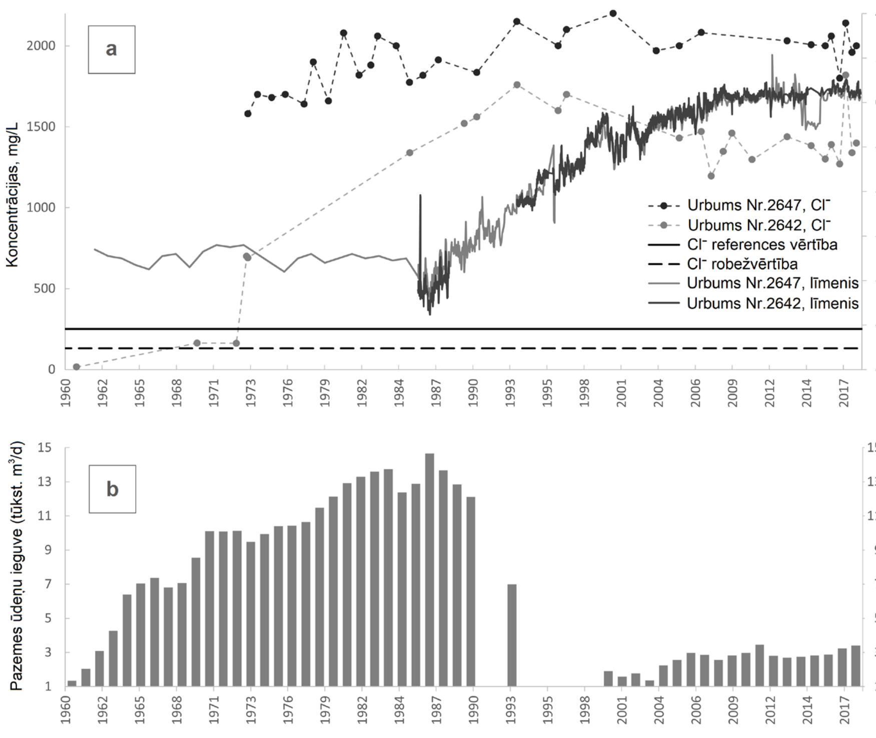
3.2.3. Jūras intrūzijas saldūdens nesējslānī novērtējums un pārvaldība

Intensīvas pazemes ūdeņu ieguves no augšdevona Mūru-Žagares (D_3*mr–žg*) ūdens nesējslāņa sekas paaugstināta mineralizācijas veidā novērotas jau kopš 20. gadsimta 30. gadiem. Taču regulāru pazemes ūdeņu monitoringu uzsāka tikai 1961. gadā (9. attēls, a), kad tika konstatēta jau izveidojusies depresijas piltuve. Pāreja uz centralizētu ūdensapgādi ar jaunu pazemes ūdeņu atradni "Otaņķi" (darbību uzsāka 1961. gadā), izmantojot to pašu D_3*mr–žg* saldūdens ūdens nesējslāni un papildus izmantojot dziļāk esošo vidus- un augšdevona Arukilas-Amatas (D_2*ar–D3am*) ūdens nesējslāņu kompleksu, nesamazināja negatīvās ietekmes uz pazemes ūdeņu resursiem. Rezultātā depresijas piltuve paplašinājās uz dienvidaustrumiem un 1986. gadā sasniedza "Otaņķu" pazemes ūdeņu atradni. 1986. gadā tika ziņots, ka gruntsūdens līmenis izmantotajā ūdens nesējslānī bija pazeminājies 14 metrus zem jūras līmeņa. Depresijas piltuve sāka samazināties tikai 20. gadsimta 90. gadu sākumā, kad Padomju Savienības sabrukuma dēļ būtiski samazinājās pieprasījums pēc pazemes ūdeņiem (9. attēls, b). Kopš tā laika pazemes ūdeņu līmenis D_3*mr–žg* ūdens nesējslānī ir ievērojami paaugstinājies un šobrīd ir virs Baltijas jūras līmeņa. Līdz ar to Cl^- koncentrācijas ir samazinājušās jūras ūdeņu intrūzijas skartās zonas marginālajā zonā, bet zonas centrālajā daļā joprojām ir augsta Cl^- koncentrācija (~2000 mg/L). 2016. gadā tika pieņemts politisks lēmums jūras intrūzijas skarto zonu izdalīt kā jaunu, atsevišķu PŪO (46 km^2) un noteikt tam riska stāvokli (Bikše un Retike, 2018), tādējādi atvieglojot un uzlabojot ietekmētās teritorijas apsaimniekošanas procesu.

Jūras ūdens daļa pazemes ūdeņu paraugos no D_3*mr–žg* ūdens nesējslāņa tika aprēķināta, pamatojoties uz hlorīda un bromīda joniem kā konservatīviem marķieriem. Jūras ūdens daļa sasniedz 50% pazemes ūdens paraugā jūras inrūzijas skartās zonas centrālajā daļā (attālums no krasta līnijas aptuveni 1,3 km). Jūras ūdens daļa pazemes ūdeņu paraugos būtiski samazinās, palielinoties attālumam no krasta līnijas – 3,4 km attālumā no krasta līnijas jūras ūdens daļa tikai 1%. Lai precīzāk novērtētu jūras ūdens intrūzijas apmēru, ieteicams ierīkot jaunu monitoringa urbumu PŪO dienvidu daļā un iekļaut regulārā kvalitātes monitoringā uz mola izvietotos privātos urbumus.

PŪO gala DFL hlorīdiem (Cl^-) tika noteikti kā 13,2 mg/L, sulfātiem (SO_4^{2-}) 42,5 mg/L un nātrijam (Na^+) kā 22,3 mg/L. Aprēķinātās RV Cl^-, SO_4^{2-} un Na^+ ir attiecīgi 131,6; 146,3 un 111,2 mg/L. RV ir apstiprinātas ar 2016.gada oktobra rīkojumu Nr. 257 “Par piesārņojošos vielu un to grupu robežvērtībām riska pazemes ūdensobjektos” uz Ministru kabineta noteikumu Nr. 42 22.3 apakšpunkta pamata.

Vairākas statistiskās pieejas hlorīdjonu DFL vērtību aprēķinam (Pulido-Velazquez et al., 2022) tika pārbaudītas dažādos hidroģeoloģiskos apstākļos visā Eiropā piecās pētījumu teritorijās, tostarp Liepājas pilotvietā (PŪO), kur lielākā daļa pārbaudīto metožu un testēto kritēriju deva līdzīgas Cl^- iepriekš iegūtajām – 13,2 mg/L (Retike un Bikše , 2018).



9. attēls. Jūras intrūzijas un depresijas piltuves veidošanās D_3mr–žg saldūdens nesējslānī izmaiņas Liepājas apkārtnē: a) pazemes ūdeņu līmeņu un hlorīdu koncentrāciju izmaiņas monitoringa urbumos un b) izmaiņas pazemes ūdeņu ieguvē no centralizētās pazemes ūdeņu atradnes “Otaņķi” (RV – noteiktā robežvērtība 131,6 mg/L; REF – dzeramā ūdens kvalitātes robežvērtība 250 mg/L).

Secinājumi

Latvijas aktīvajā ūdens apmaiņas zonā tika izdalītas astoņas ģeoķīmiski atšķirīgas pazemes ūdeņu grupas, izmantojot daudzfaktoru statistiskās analīzes metodes. Grupas savā starpā atšķir paaugstinātas vai pazeminātas pamatjonu, mikroelementu un slāpekļa savienojumu (NO_3^- un NH_4^+) koncentrācijas.

- Pazemes ūdeņu ķīmiskais sastāvs reprezentē ūdeņu veidošanās apstākļus sākot ar pazemes ūdeņiem, kas vēl nav nonākuši līdzsvarā ar nogulumus veidojošajiem minerāliem (nepiesātināti) (CLU 6), līdz tipiskiem hidrogēnkarbonātu tipa pazemes ūdeņiem, kas rodas kalcīta un dolomīta dēdēšanas ietekmē (CLU 2 un CLU 7). Hidrogēnkarbonātu tipa pazemes ūdeņu grupa ar pazeminātu Cl^- un SO_4^{2-} koncentrācijām tika interpretēta kā pirmsindustriālajā periodā infiltrējies ūdens (CLU 8).
- Trīs no identificētajām pazemes ūdeņu grupām uzrādīja cilvēka darbības ietekmi un norādīja uz pazemes ūdeņu neaizsargātību pret piesārņojumu, piemēram, izkliedēto lauksaimniecības piesārņojumu seklos ūdens nesējslāņos (CLU 3), ūdens nesējslāņa sasāļošanos pilsētvidē ceļu kaisīšanas rezultātā (CLU 1), vai ūdens ieguves ierosinātu ūdens sajaukšanos ar jūras ūdeni (intrūzija) vai dziļāko nesējslāņu ūdeņiem ar paaugstinātas mineralizāciju (CLU 4 un 1).
- Dabiska saldūdens nesējslāņu sasāļošanās ģipša šķīdināšanas rezultātā tika novērota ūdens nesējslāņos, kuros ģipsis atrodas kā minerāls vai ūdens sajaukšanās rezultātā (CLU 5).

Daudzfaktoru statistiskās analīzes, kas veiktas izmantojot kvartāra pazemes ūdeņu ķīmiskā sastāva datu kopu, ļāva izdalīt četras ģeoķīmiski atšķirīgas pazemes ūdeņu grupas. Visas četras grupas pieder pie hidrogēnkarbotnātu ūdens tipa, un tās savā starpā atšķiras pēc pamatjonu un slāpekļa savienojumu (NO_3^- un NH_4^+) koncentrācijām, kā arī mineralizācijas un *pH* vērtībām.

- Grupas pārstāv $Ca–Mg–HCO_3$ tipa pazemes ūdeņus, kas bieži sastopami seklos ūdens nesējslāņos visā Latvijā (CLU 1), kā arī $Ca–HCO_3$ tipa pazemes ūdeņus, kas interpretējami kā ļoti jauni pazemes ūdeņi, un kas galvenokārt atrodas smilšainos nogulumos (CLU 4). Divu pārējo grupu sastāvs uzrāda piesārņojuma ietekmi un pazemes ūdeņu neaizsargātību pret zemes lietojuma veidam raksturīgām slodzēm: izkliedēto lauksaimniecības piesārņojumu ar NO_3^- (CLU 3) un dažāda veida punktveida piesārņojumu, kas radies no mākslīgām platībām un lauksaimniecības platībām un izpaužas kā paaugstinātas NO_3^-, NH_4^+, Cl^- un SO_4^{2-} koncentrācijas (CLU 2).
- Augstākās NO_3^- un NH_4^+ vērtības konstatētas pazemes ūdeņu paraugos, kas ņemti no kvartāra ūdens nesējslāņiem, kuriem ir vidēja līdz augsta dabiskā pazemes ūdeņu aizsargātība. Šajos apgabalos dominējošie mālaini nogulumi ir par pamatu auglīgām, visbiežāk lauksaimniecībā izmantotajām augsnēm. Rezultāti liecina, ka visi kvartāra pazemes ūdeņi Latvijā var kļūt neaizsargāti pie noteikta slodžu apmēra un, ka seklo pazemes ūdeņu piesārņojuma riska novērtēšanai un aizsardzībai pašreizējā dabiskā aizsargātības karte jāpapildina ar dominējošām slodzēm.

Liepājas apkaimē esošajam pazemes ūdensobjektam, kas pakļauts riskam vēsturiski radušās jūras intrūzijas dēļ saldūdens nesējslānī, tika noteikti Cl^-, SO_4^- un Na^+ dabiskie fona līmeņi (DFL) un robežvērtības (RV). Kaut arī pazemes ūdeņu līmeņi atjaunojušies to sākotnējā stāvoklī un atrodas virs Baltijas jūras līmeņa, pazemes ūdeņu kvalitātes uzlabošanās ir lēnāka un pazemes ūdensobjekta centrālajā daļā jūras ūdeņu daļa pazemes ūdeņu paraugos joprojām sasniedz 50%. Palielinoties pazemes ūdeņu ieguvei no vidusdevona Mūru-Žagares ūdens nesējslāņa pastāv risks sasāļoties ūdens nesējslānim aktivizējoties jūras ūdeņu intrūzijai. Noteiktie DFL un RV ļauj novērtēt jūras intrūzijas attīstību un savlaicīgi identificēt negatīvās ūdens kvalitātes izmaiņu tendences riska pazemes ūdensobjektā.

Sistemātiskā pazemes ūdeņu monitoringa laikā iegūtie dati ir būtiski, lai novērtētu un apsaimniekotu pazemes ūdens resursus Latvijā. Šis pētījums ir pirmais mēģinājums sniegt trūkstošās vadlīnijas kā izmantot un orientēties vēsturiskajos līdz mūsdienu sistemātiskā pazemes ūdeņu monitoringa datos Latvijā.

- Galvenais sistemātiskā pazemes ūdeņu monitoringa mērķis Latvijā pēdējo sešdesmit gadu laikā nav mainījies. Tas ir nodrošināt kvalitatīvus un pietiekama apjoma pazemes ūdeņu resursus. Tomēr specifiskie pazemes ūdeņu monitoringa mērķi ir vairākkārt mainījušies galvenokārt pieejamā finansējuma, pastāvošo regulējumu un politiskā ietvara dēļ. Līdz ar to sistemātiskais pazemes ūdeņu monitorings Latvijas teritorijā ir vairākkārt pārskatīts, kas ietekmēja monitoringa tīklu, novērojumu biežumu, analizējamo ķīmisko parametru sarakstu un pielietotās paraugu ņemšanas un analīzes metodes. Politiskās reorganizācijas un/vai finansējuma trūkuma izraisītās optimizācijas ir pasliktinājušas datu kopas kvalitāti. Piemēram, Padomju Savienības sabrukums un globālā finanšu krīze 2007.–2008. gadā atstāja negatīvu ietekmi uz savākto datu apjomu, īpaši ietekmējot pazemes ūdeņu kvalitātes monitoringu. Turpretim ievērojams uzlabojums ir vērojams kopš Latvijas iestāšanās Eiropas Savienībā, jo bija pienākums ieviest ES ūdens politikas prasības un radās iespēja pretendēt uz ES fondu finansējumu. Kopumā izmaiņas ir vienā vai otrā veidā ietekmējušas datus, un šādu datu turpmākās izmantošanas iespējas nosaka tas vai un kā veikta izmaiņu dokumentācija.
- Attīstoties izpratnei par pazemes ūdeņu nozīmi (piemēram, PŪAE) un mainīgumu (sezonālas svārstības) ūdens aprites ciklā mijiedarbībā ar klimata pārmaiņām un jauniem piesārņotājiem prasa strauju pazemes ūdeņu monitoringa tīklu paplašināšanu, kā arī paraugu ņemšanas un novērojumu veikšanas biežuma un veida palielināšanu. Ūdens apsaimniekotājiem šie ir izaicinoši uzdevumi, jo apsaimniekošana balstās uz vēsturiski ierīkotiem pazemes ūdeņu monitoringa tīkliem, kuri nespēj izpildīt esošās ES ūdens politikas prasības. Tika konstatētas vairākas neatbilstības starp ES ūdens politikas prasībām un pašreizējo pazemes ūdeņu monitoringu. Pirmkārt, monitoringa tīkls ir novecojis. Lielākā daļa šobrīd aktīvo monitoringa urbumu ir ierīkoti pirms 40–50 gadiem, tāpēc veco urbumu nomaiņa pret jauniem ir priekšnoteikums, lai nepārtrūktu vērtīgās laikrindas. Otrkārt, laika gaitā ir mainījušies specifiskie pazemes ūdeņu monitoringa mērķi. Pašreizējais tīkla blīvums ir neapmierinošs, un tam trūkst monitoringa punktu seklos (arī bezspiediena) ūdens nesējslāņos, kas ir mazāk aizsargāti pret virszemes piesārņojumu, kā arī uztur PŪAE mazūdens periodos. Treškārt, tīkls jāpaplašina pārrobežu zonās ar kaimiņvalstīm, piemēram, Igauniju un Lietuvu. Pazemes ūdeņu tīkla ierīkošanas laikā politiskā situācija bija atšķirīga, tāpēc monitoringa blīvums pārrobežu teritorijās ir pārāk zems un neļauj ilgtspējīgi apsaimniekot pārrobežu ūdens nesējslāņus.

- Pazemes ūdeņu monitoringa tīkla trūkumus varētu efektīvi aizpildīt, iekļaujot pazemes ūdeņu monitoringa tīklā jaunus ūdens avotus, kā arī izmantojot jau esošos urbumus no vairāk nekā 200 aktīvajām pazemes ūdeņu atradnēm Latvijā. Jauni avoti ir jāizvēlas, pamatojoties uz izstrādātu konceptuālu izpratni par avota ūdensšķirtni, piemēram, sateces baseinu, pazemes ūdeņu sezonalitāti (ķīmiskā sastāva un debita izmaiņas) un dominējošo ietekmju un slodžu analīzi. No vienas puses, pazemes ūdeņu atradnes jau tagad reprezentē visvairāk izmantotos ūdens nesējslāņus un ļautu labāk uzraudzīt pazemes ūdeņu resursus, kas nodrošina ūdens apgādi. No otras puses, jaunu monitoringa urbumu ierīkošana varētu būt prioritāte tieši problemātiskajās zonās (piemēram, lauksaimniecības platībās, ūdens sasāļošanās zonas, PŪAE tuvumā), kur citādi jaunu urbumu ierīkošana privātajam sektoram nebūtu ekonomiski pamatota.

Atsauces

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